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Improving the catalytic nitrate reduction

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Abstract

Technologies for the nitrate removal from drinking water and waste water will be required in the near future and the catalytic nitrate reduction is one of the most promising ones. To establish a technical-scale nitrate reduction a further improvement of the catalyst is necessary and new concepts should be introduced in the process. It is shown, that palladium–tin and palladium–indium catalysts can be much more suited for an efficient nitrate reduction than palladium–copper catalysts. Furthermore, two new innovative concepts are presented — the use of in situ buffering formic acid as reductant instead of hydrogen and the application of PVAL-encapsulated catalysts with superior diffusional properties — which may contribute to solve selectivity problems. ©2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Nitrate is one of the most ubiquitous pollutants. Namely caused by over-manuring with natural and synthetic fertilizers the nitrate concentration in ground water has risen in recent years throughout the world [1]. As most of the drinking water is produced from ground water and nitrate is suspected to cause serious health risks (blue baby syndrome, cancer [2]) legislators have introduced maximum admissible concentrations for nitrates in drinking water, e.g. 50 mg/l in the European Drinking Water Directive or 25 mg/l as guide level given by the World Health Organization [3]. In several regions, the water works nowadays have to remove nitrate from water not to violate the permitted level.

Additionally, in order to reduce the pollution of natural aquifers legislators in the last years have lowered the permitted nitrate concentrations in waste water streams, thereby forcing the industry concerned, e.g. production of fertilizers and explosives, upgrading of uranium, chemical industry (nitrations, polyurethane production), power plants (desulphurization of smoke gases) to remove their excess nitrates.

The most common technologies for nitrate removal from water are divided into physico-chemical, biological and catalytical processes [4–5]. The main disadvantage of the physico-chemical processes ion exchange, reverse osmosis and electrodialysis is the fact, that the nitrate is not converted into harmless compounds but only removed from the water into brine which has to be treated afterwards or has to be disposed of. In addition, these processes do not selectively target nitrate so that the composition of the treated water changes. Although sometimes preferred for economical reasons, in the medium-term these processes should have to be avoided for ecological reasons. The most favorable way to remove nitrate from the ecological point of view is to convert it into harmless gaseous nitrogen as it can be achieved by biological denitrification (autotrophic or heterotrophic). Furthermore, biological denitrification is nitrate-selective so that the water composition does not change. Nevertheless, problems such as the release of NO_2^-, NO_x

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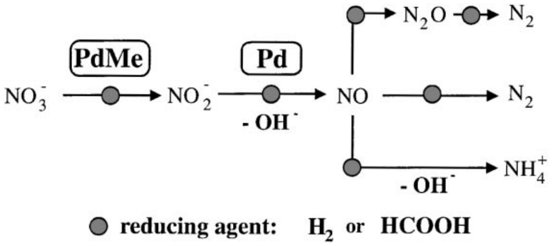

Fig. 1. Reaction scheme of the catalytic nitrate reduction.

and N_2O can arise by incomplete denitrification. In addition, biological denitrification processes are not at all easy to handle — extensive regulations of parameters like concentrations and pH value are necessary — and complex and cost-intensive post-treatment steps are needed to remove by-products such as biomass, turbidity, taste impairing substances and others.

An new economical as well as ecological technology for the removal of nitrates from water was first described in 1989 by Vorlop et al. [6,7], a technology which is based on the catalytic hydrogenation of nitrate to nitrogen. Nitrate was found to be hydrogenated only by bimetallic, preferably palladium–copper, catalysts, whereas nitrite and its intermediates can be reduced with a monometallic, preferably palladium, catalyst. With hydrogen as the reductant nitrate is converted to nitrogen as main product and ammonium as by-product. The reaction scheme is shown in Fig. 1.

The following investigations mainly dealt with the development of nitrite-reducing palladium catalysts and nitrate-reducing palladium–copper catalysts together with the influence of the reaction conditions on activity and selectivity [8–20].

New catalysts and concepts in the field of catalytic nitrate reduction were introduced by Prüsse et al. [21], who described new selective nitrate-reducing bimetallics (Pd–Sn, Pd–In) and Hähnlein et al. [22], who reported about extremely high selective nitrite-reducing Pd/PVP colloids and their immobilization in hollow fiber dialyser reactors. An effective immobilization of catalyst powders and colloids was also achieved by entrapment in macroporous gels of poly (vinyl alcohol), PVAL, with superior diffusional properties [23–24]. Furthermore, formic acid was introduced as an alternative reductant instead of hydrogen promising a higher selectivity due to an in situ buffering effect [25].

The objective of this work is to show possible ways to improve the catalytic nitrate reduction in activity and selectivity, an improvement that starts at the choice of the proper catalyst and the optimum reaction conditions. It will be shown in continuous nitrate reduction experiments that it is of major importance to circumvent the negative impact of the pH-gradient in macroscopic catalyst particles, which can be achieved by using formic acid as reductant. Problems in technical scale nitrate reduction and concepts to solve them will also be covered.

2. Experimental

2.1. Preparation of supported metal catalysts

2.1.1. Wet impregnation

A Pd(5%)/Al_2O_3 catalyst (Aldrich, Germany) served as a base for the preparation of the bimetallic impregnation catalyst. After suspension of the Pd catalyst in a solution of the second metal nitrate the water was evaporated under heating till dryness. Afterwards the catalyst was activated at 350°C in a H_2/N_2-stream for 6 h.

2.1.2. Deposition/precipitation

First, the support material, alumina type HL (Martinswerke, Bergheim, Erft, Germany) calcined for 24 h at 1000°C (BET surface = 36 m^2/g, main pore diameter = 70 Å, isoelectric point at pH 10.2, particle size = 2–3 μm) was suspended in a 2% Na_2CO_3-solution for 15 min. By dropping a 1.4% Na_2PdCl_4-solution slowly into the suspension, the Pd was let to precipitate and deposit onto the support under vigorous stirring. Then the second metal was introduced in the desired amount as a metal chloride solution in the same manner. The catalyst was finally reduced by adding sodium formate at about 80°C. After drying at 70°C over night, the catalyst is ready to use.

The nominal palladium content of the catalysts is 5%. Although the actual palladium content of the catalysts prepared by the deposition/precipitation method is slightly lower than 5%, the desired palladium/second metal ratio (Pd : Me ratio) was obtained (see Table 1 for representative data of different

Table 1
Representative nominal and actual metal contents of different bimetallic catalysts prepared by the deposition/precipitation method. Me = second metal (Cu, Sn or In). Analysis was made by atom absorption spectroscopy (AAS)

Catalyst	Nominal metal composition	Nominal metal ratio Pd : Me	Actual metal composition	Actual metal ratio Pd : Me
Pd–Cu	5% Pd, 1.25% Cu	4 : 1	4.74% Pd, 1.15% Cu	4.1 : 1
Pd–Sn	5% Pd, 1.25% Sn	4 : 1	4.26% Pd, 1.10% Sn	3.9 : 1
Pd–In	5% Pd, 1.25% In	4 : 1	4.43% Pd, 1.12% In	4.0 : 1

bimetallic catalysts). Catalysts with Pd : Me ratios other than 4 : 1 were randomly checked by AAS. Again, the desired Pd : Me was always achieved.

2.1.3. Controlled surface reaction with Sn(n-butyl)$_4$

The surface of a preformed Pd/Al_2O_3-catalyst prepared by deposition/precipitation according to the procedure given in Section 2.1.2 was saturated with hydrogen in the gas-phase [26]. By dropping a solution of Sn(*n*-butyl)$_4$ in *n*-hexane to the catalyst the Sn(*n*-butyl)$_4$ was led to react with the Pd–H groups at the catalyst surface. Afterwards the catalyst was reduced with hydrogen for 3 h at 300°C.

2.1.4. Controlled surface reaction with Sn(HCOO)$_2$

Two gram of a preformed Pd/Al_2O_3-catalyst prepared by deposition/precipitation according to the procedure given in Section 2.1.2 were suspended in 25 ml of 0.01 mol H_2SO_4 and 1 ml of 98% HCOOH. After introduction of the second metal as a metal sulfate dissolved in 0.05 mol H_2SO_4 at 80°C the in situ formed Sn(HCOO)$_2$ decomposes at the Pd surface thereby generating the bimetallic sites. Afterwards the catalyst was dried for 12 h at 80°C. As the metal formate decomposes only at the Pd surface, which is already known from relevant literature [27], this kind of preparation method can be regarded as a controlled surface reaction.

2.2. Preparation of PVAL-encapsulated catalysts

The preformed catalyst was suspended in a poly (vinyl alcohol) solution (PVAL solution) consisting of 10% w/w PVAL (Mowiol 10–98, Clariant, Germany), 9% polyethylenglycol (PEG 600, Clariant, Germany) and 81% w/w water in a way that the resulting suspension had a catalyst content of 2% w/w (equal to a palladium content of 0.1%). This suspension is able to form hydrogels by freezing–thawing [23,24,28]. The same suspension was used for the production of beads by applying the Jet Cutting Method described in detail elsewhere [29–31]. The beads were let to freeze in silicon oil (AK 10, Wacker, Germany) at −20°C and then thaw inside the oil up to room temperature. After washing the beads, measuring 0.5–0.6 mm in diameter, the PVAL-encapsulated catalysts were ready for use.

2.3. Batch experiments with hydrogen as reductant

Unless otherwise stated, a 500 ml glass vessel equipped with a magnetic stirrer (500 rpm) was used for the batch experiments. The pH value was adjusted by using an automatical pH control unit by adding 0.2M HCl. The experiments were carried out at 10°C, pH 5 and a total pressure of 1 bar which was equal to the hydrogen pressure. Hydrogen was fed by a frit into the solution using a flow rate of 50 ml/min to ensure the maximum possible hydrogen concentration in solution, which is equal to 0.85 mmol/l at 10°C. Before nitrate in the starting concentration of 100 mg/l was added, hydrogen was bubbled 15 min through the vessel with the suspended catalyst (1–2 g/l) to remove dissolved and adsorbed oxygen. Liquid phase samples were taken periodically and analyzed as described in Section 2.7. Unless explicitly mentioned, deionized water was used for all experiments.

2.4. Batch experiments with formic acid as reductant

Experiments were carried out according to the procedure given in Section 2.3 with the only difference that nitrogen was used as gas for oxygen stripping and formic acid was used to adjust the pH value. Thus, formic acid acts as reductant and neutralizing agent. To ensure a sufficient starting concentration of formic acid (approx. 5 mg/l) at the beginning of the reaction the pH value was first increased to pH 8 and then decreased by adding formic acid to the reaction pH of 5 before 100 mg/l nitrate were added. By this experimental setup the concentration of formic acid or formate, respectively, is increasing during the reaction course up to a concentration of about 70 mg/l towards its end, i.e. the complete conversion of the nitrate to the products.

2.5. Continuous flow experiments with catalyst powders

For continuous flow experiments the catalyst powders were filled in the hollow fibres of a hollow fibre dialyser. The nitrate solution was continuously pumped out of a vessel, where temperature and pH adjustment took place, through the extracapillary volume of the dialyser and back into the vessel, so that the dialyser acts as an outer loop of the vessel. The vessel itself was used as a continuous stirred tank reactor with an inlet and an outlet stream. This experimental setup is described in detail in [22].

For all continuous flow experiments the nitrate inlet concentration was equal to 100 mg/l, the outlet concentrations are given in the discussion. Since the activity of the bimetallic catalysts for the reductants differ, the residence times in the dialyser were adjusted to ensure comparable reaction conditions, i.e., nitrate and reductant concentrations.

2.6. Continuous flow experiments with PVAL-encapsulated catalysts

Experiments were carried out as described in Sections 2.3 and 2.4, respectively. The reaction vessel was additionally equipped with an inlet and an outlet stream, i.e., it was used as an continuous stirred tank reactor. The PVAL-encapsulated catalysts (100 g/l) were retained inside the reactor by a frit in the outlet stream. For all continuous flow experiments the nitrate inlet concentration was equal to 100 mg/l, the outlet concentrations are given in the Section 3.

2.7. Sample analysis

Periodically withdrawn liquid phase samples were analyzed for the reaction components nitrate, nitrite and formate by HPLC as described in [10]. Ammonium was analyzed in an automatical flow-injection-analysis system using a fluorescence detector according to [32]. For some experiments carried out in a special reactor to determine the reaction kinetics [33] also gas phase samples were taken to analyze the amount of nitrous oxide (N_2O) released as an intermediate product. The nitrous oxide was analyzed by means of gas chromatography as described in detail in [34].

2.8. Determination of activity and selectivity

For nitrate reduction in batch experiments the average activity is given for hydrogen as reductant and the maximum activity is given for formic acid as reductant, due to completely different temporal nitrate concentration courses during the experiments (Fig. 2). For nitrate reduction with hydrogen the average activity is determined by the time necessary to obtain a nitrate conversion >99%. When using formic acid as reductant, first an induction period is obtained, during which the oxygen dissolved and adsorbed onto the catalyst's surface is reduced (see also Section 2.4). After this period nitrate is reduced with a constant rate until complete conversion (Fig. 2). It is therefore allowed to directly compare the average activity for hydrogen as reductant with the maximum activity, given by the

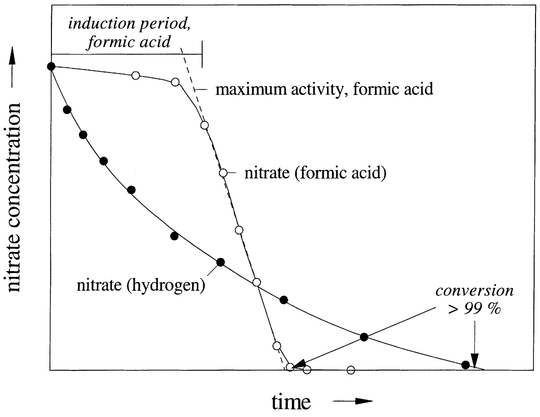

Fig. 2. Definition of the two different types of activity for hydrogen and formic acid as reductants by typical concentration-time-curves. Average activity for hydrogen as reductant is given by the time for >99% conversion. Maximum activity for formic acid is given by the slope of the linear concentration-time-curves.

slope of the linear concentration-time-curve, in case of formic acid as reductant.

For continuous flow experiments under steady-state conditions, of course, no average or maximum activity can be given. For both reductants it is just the same kind of activity.

In batch experiments with both reductants a kind of negative selectivity is given in terms of the formation of the undesired by-product ammonium, which means, that the more ammonium is formed, the less selective is the catalyst. As under the reaction conditions used, nitrogen and ammonium are the only two products, it is allowed to directly determine the selectivity from the amount of ammonium formed, which was done for the continuous flow experiments.

3. Results and discussion

3.1. Choice of the catalyst

As already stated, most of the work in the field of catalytic nitrate reduction was done using palladium–copper bimetallic catalysts, the first bimetallic catalyst known to reduce nitrate with a moderate ammonium formation, while many other bimetallic catalysts screened were less selective [6–11]. By different preparation methods Pd–Cu catalysts were optimized in their nitrate removal activity and selectivity [10–20]. So far, the nitrate removal activity seemed to be an appropriate parameter for the characterization of the catalyst's activity. It has to be considered, though, that the catalytic nitrate reduction to nitrogen, as shown in Fig. 1, is a consecutive reaction (with parts of parallel reactions) and that the desired 'product' is, of course, not the lack of nitrate but the formation of nitrogen. Therefore, the nitrogen formation activity is a better means for the characterization of a catalyst. If the nitrate reduction is the rate determining step in nitrate reduction to nitrogen, then certainly the nitrate removal activity is a sufficient parameter.

When palladium–copper catalysts were used for nitrate reduction significant amounts of nitrite were intermediately released during reaction course. The nitrite released is further converted to the next intermediates (NO, N_2O) not before nitrate is completely removed [10,12–13,16]. So far, nitrous oxide as intermediate during nitrate reduction was not determined, although its contribution to the greenhouse effect is known and a release should be strictly avoided.

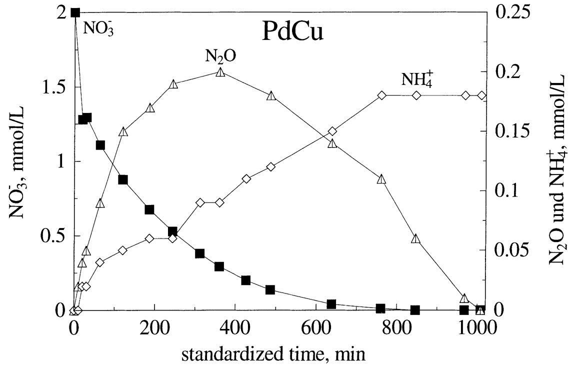

Fig. 3. Concentration-time-curves of nitrate, nitrous oxide and ammonium for the nitrate reduction with hydrogen using a Pd(5%)Cu(1.25%)/Al_2O_3 catalyst prepared by the deposition/precipitation method. The time axis is standardized for a catalyst amount of 1 g/l. Reaction conditions: $T = 10°C$, $c_0(NO_3^-) = 2$ mmol/l, pH 5, 1130 mbar hydrogen pressure. The reactions were carried out in the reactor described in [33].

As displayed in Fig. 3 large amounts of nitrous oxide are released in the gas phase above the reaction suspension when nitrate is reduced with a Pd–Cu catalyst. Since N_2O is dissolved to a large amount in water, the total amount of N_2O released is even higher. It is also shown in Fig. 3, that for the Pd–Cu catalyst the nitrate removal activity and the nitrogen formation activity differ considerably: The nitrogen formation activity, which is determined by the time when no more N_2O is present in the reactor, is about 25% lower than the nitrate removal activity. Lastly, Fig. 3 illustrates, that the intermediary-formed N_2O is only converted to nitrogen and is not transformed to ammonium.

In contrast, when using a Pd–Sn catalyst significantly smaller amounts of N_2O are released during reaction course (see Fig. 4). In addition, the N_2O released is converted to nitrogen with a much higher rate than with the Pd–Cu catalyst, so that the nitrate reduction to nitrogen can be regarded as complete — without making a significant mistake — when all nitrate has been removed. Therefore, the nitrogen formation activity of the Pd–Sn catalyst (Fig. 4) is about 10 times higher than for the Pd–Cu catalyst (Fig. 3).

It can thus be concluded, that if a Pd–Sn catalyst is used, it can be sufficiently characterized by the nitrate removal activity, whereas this is not allowed for

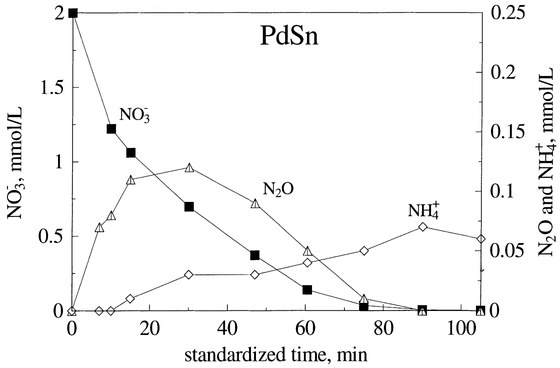

Fig. 4. Concentration-time-curves of nitrate, nitrous oxide and ammonium for the nitrate reduction with hydrogen using a Pd(5%)Sn(1.25%)/Al_2O_3 catalyst prepared by the deposition/precipitation method. The time axis is standardized for a catalyst amount of 1 g/l. Reaction conditions: $T = 10°C$, $c_0(NO_3^-) = 2$ mmol/l, pH 5, 1130 mbar hydrogen pressure. The reactions were carried out in the reactor described in [33].

the palladium–copper bimetallic system. This was also confirmed for other reaction conditions, such as other pH values, nitrate and reductant concentrations [35]. We also widely used another bimetallic system, which is Pd–In. Referring to the release of nitrite and N_2O the Pd–In catalysts show a behavior similar to the Pd–Sn catalysts [35]. Regarding Table 2, where the nitrogen formation activity and the ammonium formation for these three bimetallic catalysts are shown, it can be further concluded, that the Pd–Sn and Pd–In catalysts used in this study are much more suited for nitrate reduction than the Pd–Cu catalyst.

The ratio of the two metals in bimetallic catalysts can alter activity and selectivity to a large extent. In case of nitrate-reducing catalysts, it was already reported, that the ratio of palladium to the second metal (Pd : Me as weight ratio) should be equal to 4 : 1 for Pd–Cu catalysts prepared by impregnation [11] and 6 : 1 for Pd–In catalysts prepared by the deposition/precipitation method [22] to obtain the highest selectivity. As shown in Fig. 5, for Pd–Sn catalysts prepared by deposition/precipitation the highest selectivity for nitrate reduction with hydrogen can be obtained with a Pd : Sn ratio of 6 : 1. Still, Pd–Sn catalysts with a ratio of 4 : 1 and Pd–In catalysts with a ratio of 5 : 1 were chosen for the following experiments. Using these ratios a considerably higher activity can be achieved whereas the ammonium formation increases only to a small amount for both bimetallic catalysts. The optimum ratio to obtain the highest selectivity for nitrate-reducing catalysts for a given bimetallic system also depends on the catalyst preparation method. In case of the Pd–Sn bimetallic system this ratio can vary to a large extent as shown in Table 3. It is therefore necessary to determine this optimal metal ratio for each preparation method which is used.

Table 2
Nitrogen formation activity and ammonium formation for batch nitrate reduction with hydrogen using different bimetallic catalysts prepared by the deposition/precipitation method. $T = 10°C$, $c_0(NO_3^-) = 2$ mmol/l, pH 5, 1130 mbar hydrogen pressure. The reactions were carried out in the reactor described in [33]

Catalyst	Nitrogen formation activity, mmol N_2/(h·g cat.)	Ammonium formation (mmol/l)
Pd(5%)Cu(1.25%)	0.26	0.16
Pd(5%)Sn(1.25%)	2.6	0.07
Pd(5%)In(1%)	2.1	0.11

With increasing tin content of the catalyst (decreasing Pd : Sn ratio) the nitrate removal activity increases (Fig. 5). Physico-chemical characterization methods confirmed that with increasing total tin content of the catalyst the amount of surface tin rises in parallel [26]. It becomes obvious, that the nitrate reduction takes place at active sites containing tin, which are suspected to be real bimetallic sites [26]. On the other hand, the ammonium formation is increasing significantly with decreasing tin amount, i.e., increasing palladium con-

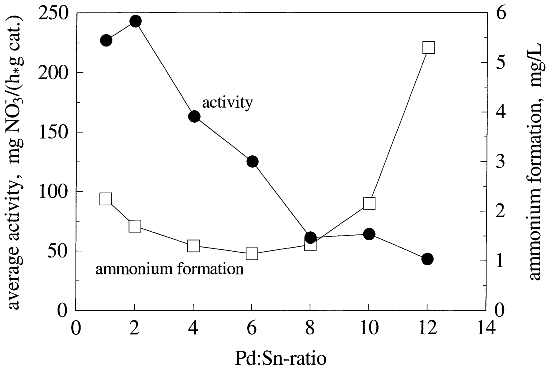

Fig. 5. Dependence of nitrate removal activity and ammonium formation on the catalyst's Pd : Sn ratio for hydrogen as reductant. Catalysts prepared by the deposition/precipitation method. Reaction conditions: $T = 10°C$, $c_0(NO_3^-) = 100$ mg/l, pH 5, 1 bar hydrogen pressure.

Table 3

Preparation method and corresponding optimal Pd : Sn ratio to achieve the lowest ammonium formation for the nitrate reduction with hydrogen. The palladium content of all catalysts is equal to 5%. Reaction conditions: $T = 10°\mathrm{C}$, $c_0(\mathrm{NO_3}^-) = 100\,\mathrm{mg/l}$, pH 5, 1 bar hydrogen pressure

Preparation method	Pd : Sn weight ratio	Activity, mg $\mathrm{NO_3}^-$/(h·g cat.)	Ammonium formation (mg/l)
Wet impregnation	4 : 1	70[a]	5.2[a]
Deposition/precipitation	6 : 1	125	1.2
CSR [Sn(*n*-butyl)$_4$]	6 : 1	350	2.2
CSR [Sn(HCOO)$_2$]	12 : 1	204	0.9

[a] pH 6.

tent of the crystals and also the surface. One can therefore suppose, that the selectivity is determined not by the tin-containing (bimetallic) sites but by monometallic palladium sites known to be also present at the catalyst's surface [26]. These mechanistic aspects will be discussed in detail in a subsequent paper [36].

3.2. *Influence of the pH value*

When nitrate is reduced to nitrogen hydroxide ions in stoichiometric amounts are formed according to Eq. (1). If ammonium is the product even double-stoichiometric amounts of hydroxide ions are formed (2).

$$2\mathrm{NO_3}^- + 5\mathrm{H_2} \rightarrow \mathrm{N_2} + 2\mathrm{OH}^- + 4\mathrm{H_2O} \qquad (1)$$

$$2\mathrm{NO_3}^- + 8\mathrm{H_2} \rightarrow 2\mathrm{NH_4}^+ + 4\mathrm{OH}^- + 2\mathrm{H_2O} \qquad (2)$$

Unfortunately, the activity and selectivity of the nitrate reduction strongly depends on the pH value. It was already reported, that for the catalytic nitrate reduction with Pd–Cu catalysts and also for the catalytic nitrite reduction with Pd catalysts the activity considerably decreases whereas the ammonium formation rises with increasing pH value [6,8,10,23].

As displayed in Fig. 6, the same activity and selectivity decrease can be noticed when a Pd–Sn catalyst is used for nitrate reduction. In addition, the amount of nitrite released intermediately during reaction course also rises with increasing pH value. Obviously, the rate for nitrite reduction decreases to a larger extent than the rate for nitrate reduction.

To conclude, the catalytic nitrate as well as nitrite reduction can be regarded as a self-inhibiting reaction concerning the product (inhibitor) hydroxide ions. This kind of pH dependence is not a problem if the reaction is performed under pH control and small catalyst particles are used as in most studies done in a laboratory scale. The pH dependence will cause problems, however, if pilot-scale or even technical-scale reactors should be used. Here the catalyst particles will be larger in size and mass transfer effects due to pore diffusion will no longer be negligible. Thus, a pH-gradient will be built up inside the catalyst particles, thereby decreasing both activity and selectivity, a phenomenon that was already confirmed for the catalytical nitrite reduction [8,37].

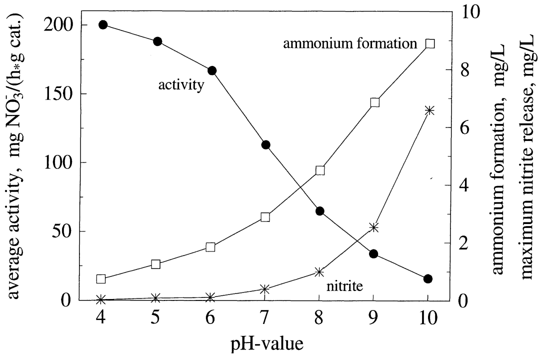

Fig. 6. Activity, maximum intermediary nitrite release and ammonium formation for the nitrate reduction with a Pd(5%) Sn(1.25%)/$\mathrm{Al_2O_3}$ catalyst prepared by the deposition/precipitation method in dependence on the pH value. Reaction conditions: $T = 10°\mathrm{C}$, $c_0(\mathrm{NO_3}^-) = 100\,\mathrm{mg/l}$, 1 bar hydrogen pressure.

There are different possibilities to reduce this negative impact of the pH-gradient:

1. buffering
2. use of egg-shell catalysts
3. improvement of diffusion

The first method — buffering — has led to the idea of using formic acid as reductant. It is widely known, that formic acid can be decomposed at metal catalysts according to Eq. (3) forming hydrogen and carbon dioxide as products [38–39]. Theoretically, hydrogen can 'as usual' act as reductant (1), whereas the simultaneously formed carbon dioxide serves as an 'in

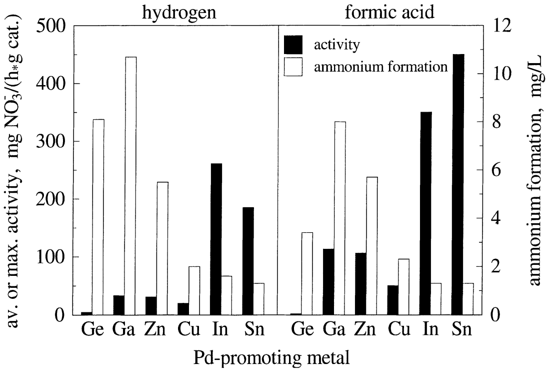

Fig. 7. Activity and ammonium formation for the nitrate reduction with different bimetallic catalysts in dependence of the reductant. The bimetallic catalysts consist of 5% w/w palladium and 1.25% w/w of the promoting metal and were prepared by the deposition/precipitation method. The average activity is given for hydrogen as reductant whereas for the use of formic acid as reductant the maximum activity is displayed. Reaction conditions: $T=10^\circ C$, $c_0(NO_3^-)=100\,mg/l$, pH 5.

situ' buffer for the inhibitor OH^- according to Eq. (4). Thereby, CO_2 is generated both at the right time and the right place — the catalyst's surface — exactly where and when it is needed to neutralize OH^-, so that no pH-gradient is built up inside the catalyst.

$$5HCOOH \xrightarrow{cat} 5H_2 + 5CO_2 \quad (3)$$

$$2NO_3^- + 5H_2 \xrightarrow{cat} N_2 + 2OH^- + 4H_2O \quad (1)$$

$$2CO_2 + 2OH^- \rightarrow 2HCO_3^- \quad (4)$$

$$\begin{aligned} 2NO_3^- + 5HCOOH &\xrightarrow{cat} N_2 + 3CO_2 \\ &+ 2HCO_3^- + 4H_2O \quad (5) \end{aligned}$$

Although nitrate reduction with formic acid can be described correctly by the overall reaction Eq. (5) it is still questionable whether hydrogen (H_2) really is the reductant. It is much more likely that formic acid itself — which is present as the formate in solution and at the catalyst surface — reduces adsorbed nitrate by transfer hydrogenation. However, the desired 'in situ' buffering effect is out of question.

As a proof, this new idea had to undergo some practical tests. Several bimetallic catalysts, both established and new ones, were used for the batch nitrate reduction with formic acid in correspondence to the conditions given in the Section 2. Fig. 7 displays the resulting activity and ammonium formation in comparison to the use of hydrogen as reductant. Surprisingly, the catalysts in general turn out to have a higher activity and a slightly lower ammonium formation when used with formic acid instead of hydrogen as reductant. Again, Pd–Sn and Pd–In catalysts perform much better than any other bimetallic system tested so far.

3.3. Continuous flow experiments using a hollow fibre dialyser reactor

To proof whether the theoretical 'in situ' buffering effect of formic acid really exists, nitrate reduction has to be carried out under conditions where diffusional limitations are present. This was achieved by using a hollow fibre dialyser reactor, where the catalyst powder is situated inside the hollow fibres. The inner diameter of the hollow fibres is about 200 μm surrounded by a membrane of a thickness of about 10–50 μm. The mean pore diameters in the membrane are smaller than 10 nm. Under the reaction conditions used, diffusion is the only form of mass transfer through the membrane.

To have meaningful results experiments were carried out under continuous flow and steady state conditions. Typical continuous flow experiments last from several days up to several weeks. Thereby, the excellent long-term stability of the catalysts was additionally proved. Furthermore, the high long-term stability of the catalysts clearly indicates that no CO is formed as decomposition product of formic acid which otherwise would lead to a poisoning of the catalyst.

An experimental setup was chosen where nitrate reduction was first performed with formic acid as reductant. After some days of steady state nitrate reduction, the reductant was switched to hydrogen followed by the necessary adjustments in resistance time to have comparable reaction conditions. After a few more days of steady state operation with hydrogen, the reductant was switched back to formic acid. The results obtained with the Pd–In catalyst together with the reaction conditions used are shown in Table 4. These results clearly demonstrate the higher selectivity with formic acid as reductant, which, of course, is due to the 'in situ' buffering effect. On the other hand, nitrate reduction with formic acid is poor in activity (about 7 times lower) compared to hydrogen. This poor activity is mainly due to the fact, that the dif-

Table 4
Activity and selectivity for continuous nitrate reduction at pH 6 in a hollow fibre dialyser reactor using hydrogen or formic acid as reductant. Catalyst: $Pd(5\%)In(1\%)/Al_2O_3$ prepared by the deposition/precipitation method. Hollow fibre dialyser: F5 HPS (Fresenius, Germany) filled with 6.3 g catalyst and 13 g of inert Al_2O_3 which also served as support material for the catalyst

Reductant	Reductant (mmol/l)	Nitrate (mg/l)	Activity, mg NO_3^-/(h·g cat.)	Selectivity (%)
HCOOH	0.84	55	2.4	91
H_2	0.85	54	16.4	50
HCOOH	1.44	59	2.3	87

fusion coefficients (D_0) of formic acid and hydrogen in water significantly differ. Compared to hydrogen, owing a diffusion coefficient of $4.34\times10^{-5}\,cm^2/s$ at 10°C, the diffusion coefficient of formate is more than 4 times lower ($D_0=0.96\times10^{-5}\,cm^2/s$ at 25°C) [40]. As the pores of the hollow fibre membranes are quite small ($<10\,nm$), the effective diffusion coefficient D_{eff} of formic acid in the membrane should be further lowered compared to hydrogen resulting in that considerable activity loss. Nevertheless, the high selectivity achieved with formic acid as reductant overcompensates the lower activity.

Another more classical than smart way to reduce the negative impact of the pH-gradient in larger catalyst particles is to use egg-shell catalysts. This was already done for nitrite-reducing Pd catalysts [41,42] and also for nitrate-reducing Pd–Cu catalysts [41,42]. Although for both catalysts an improvement in activity and selectivity was observed, two problems concerning classical egg-shell catalysts need to be taken into consideration.

The first problem to mention refers especially to nitrate-reducing bimetallic catalysts. There is no doubt, that activity and selectivity of nitrate-reducing bimetallics strongly depend on their preparation conditions (e.g. [21]). It has to be kept in mind, that the difficulties in generating active and selective bimetallic crystals on the support material, which are already present when microscopic (powdered) catalysts are prepared, will probably further increase when macroscopic egg-shell catalysts are to be prepared.

The second problem is a more general one referring to the support material. Mostly, inert metal oxides, such as alumina, silica, etc. are used as support material for nitrate-and nitrite-reducing catalysts. Due to the about 1000 times lower diffusion coefficients in the liquid phase, the diffusional properties of these materials are sufficient for gas-phase reactions but quite unsatisfactory for liquid-phase reaction. The effective diffusion coefficients (D_{eff}) of reaction components inside these materials generally lie at about 10–20% of the value in solution with unhindered diffusion (D_0), equal to a reduced diffusion coefficient D_{eff}/D_0 of about 0.1–0.2. Therefore, a new type of support material, hydrogels of poly (vinyl alcohol) (PVAL), with superior diffusional properties for liquid-phase reactions, was tested for catalytic nitrate reduction.

3.4. Continuous flow experiments using PVAL-encapsulated catalysts

PVAL-hydrogels prepared by freezing–thawing (PVAL-cryogels) as described in the Section 2 have a macroporous, sponge-like inner structure in which the PVAL has created a three-dimensional network rather than pores known from common materials [23,24,28]. The holes in the network range from 0.5 to about 15 μm. Inside these gels diffusion is possible in three dimensions in contrast to common oxides, where diffusion is possible only in two dimensions along the pores. The gels generally consist of about 10% of polymer, the rest being water, in which diffusion can take place. These PVAL-cryogels combine mechanical stability with high elasticity and are therefore well suited as supports for stirred tank or fluidized-bed reactors, where no abrasion occurs, although their use in fixed bed reactors is also possible. The PVAL-cryogel matrix acts as a support for microscopic catalyst particles, which can be powdered catalysts like the ones described above or even colloidal nanoparticles. These microscopic catalysts are encapsulated inside the macroscopic PVAL matrix. Due to the low polymer content of the gel and the three-dimensional diffusion inside, the reduced diffusion coefficient (D_{eff}/D_0) of this type of support ranges from 0.6 to 0.8, which is about 4 times higher than for common oxide supports [43].

The Pd–Sn catalyst was chosen for encapsulation in PVAL-cryogel beads. Continuous flow experiments were carried out with both hydrogen and formic acid as reductant. Again, as displayed in Fig. 8, the selectivity with formic acid as reductant was considerably higher than if hydrogen had been the reductant. As far as the activity is concerned, the difference be-

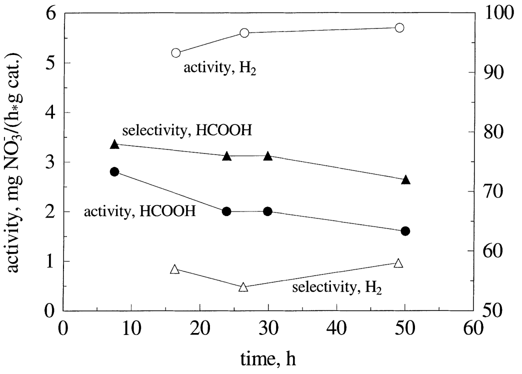

Fig. 8. Activity and selectivity for continuous nitrate reduction with PVAL-encapsulated Pd–Sn catalyst in dependence on the reductant. 2% w/w Pd(5%)Sn(1.25%)/Al_2O_3 catalyst prepared by the deposition–deposition method in PVAL-beads (bead diameter = 0.5–0.6 mm) consisting of 9% w/w PVAL. Reaction conditions: $T = 10°C$, $c(NO_3^-) = 70–80$ mg/l.

tween hydrogen and formic acid is much smaller than it was observed for the use of the hollow fibre dialyser reactor, a demonstration of the superior diffusional properties of the PVAL-cryogel matrix. In the experiments described here the long-term stability of the PVAL-encapsulated Pd–Sn catalyst is high when using hydrogen as reductant and slightly lower when using formic acid. In general, the selectivity for both reductants is somewhat lower than for the use of the catalysts in the hollow fibre dialysers, which is suspected to be caused by an interaction between the metal catalyst itself and the polymer chains. A negative interaction between PVAL and nitrite-reducing monometallic palladium catalysts was not observed [23,24], so that the preparation of more selective PVAL-encapsulated nitrate-reducing catalysts is likely.

3.5. Practical aspects for technical-scale nitrate reduction

During pilot-plant catalytic nitrate reduction in groundwater, which was carried out by Solvay Germany [44], several problems were observed which have to be taken into account regarding a further scale-up to technical dimensions.

So far most of research work in catalytic nitrate reduction was carried out using aqueous nitrate solution simply consisting of nitrate and deionized water. Of course, ground water or waste water which has to be treated for nitrate removal will have more ingredients which might influence catalyst's activity and selectivity. We removed nitrate from tap water and from different waste waters. Indeed, a decrease in activity and selectivity was often observed compared to the removal of nitrate from deionized water. For nitrate removal from tap water (for composition refer to Table 5) by a hollow fibre dialyser immobilized Pd–In catalyst a significant decrease in activity was observed for both reductants as displayed in Table 6 compared to the values given in Table 4. For the use of hydrogen as reductant selectivity drops dramatically, whereas the selectivity decrease for formic acid as reductant is only minor. It turned out that not a single water ingredient is responsible for the lower activity with both reductants and the lower selectivity with hydrogen as reductant but some of the ingredients, namely $PO_4{}^{3-}$, $SO_4{}^{2-}$ and Cl^-, contribute to the observed effects. It should

Table 5
Composition of the tap water. The pH value was equal to 7.57. For nitrate reduction experiments the nitrate content was adjusted to 100 mg/l by adding $NaNO_3$

Component	Concentration, mg/l
Ammonium	<0.01
Calcium	123
Chloride	54
Iron	0.01
Potassium	2.5
Magnesium	13
Manganese	<0.01
Sodium	27
Nitrate	35
Nitrite	<0.01
Phosphate	0.31
Silicate	19
Sulphate	161
Hydrogencarbonate	181

Table 6
Activity and selectivity for continuous nitrate reduction in tap water using a hollow fibre dialyser reactor and hydrogen or formic acid as reductant. Catalyst: Pd(5%)In(1%)/Al_2O_3 prepared by the deposition/precipitation method. Hollow fibre dialyser: F5 HPS (Fresenius, Germany) filled with 6.3 g catalyst and 13 g of inert Al_2O_3 which also served as support material for the catalyst

Reductant	Reductant (mmol/l)	Nitrate (mg/l)	Activity, mg $NO_3{}^-$/(h·g cat.)	Selectivity (%)
HCOOH	0.92	56	0.4	70
H_2	0.85	54	7.7	17

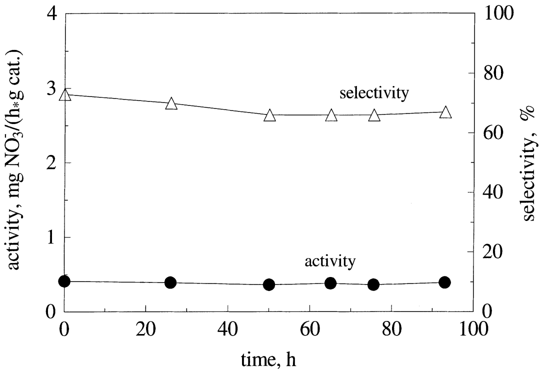

Fig. 9. Activity and selectivity for continuous nitrate reduction in tap water using a hollow fibre dialyser reactor with a Pd(5%)In(1%)/Al_2O_3 catalyst and formic acid as reductant. Reaction conditions: $T=10°C$, $c(NO_3^-)=55–60$ mg/l, $c(HCOO^-)=35–45$ mg/l.

be pointed out, that no catalyst fouling or poisoning occurs but a limited inhibition of the nitrate reduction as can be seen from the long-term stability shown in Fig. 9. A high long-term stability of the catalyst was also observed during the pilot-plant experiments [44].

On the other hand, some possible water ingredients are known to influence both activity and selectivity of the catalyst. For the type of inorganic ingredients S^{2-} has to be mentioned, whose poisoning effect on hydrogenation catalysts is a well-known fact. In addition, 'heavy metals' (e.g. iron and manganese) may precipitate due to the reductive conditions in the reaction vessels onto the catalyst's surface thereby altering its properties. If such substances should be present in the water a conditioning step prior to the nitrate removal step has to be installed to protect the catalyst. Likewise, oxygen has to be removed from the water for two reasons. First, as long as oxygen is present no nitrate will be reduced and second, oxygen might also induce corrosion of the bimetallic catalyst, namely of the less precious second metal (Cu, Sn, In). Experiments dealing with the influence of organic compounds on the catalytic nitrate removal are still missing.

As already pointed out, the pH-gradient will negatively influence both activity and selectivity if hydrogen together with macroscopic catalyst particles is used. The use of formic acid eliminates this special problem and has some additional advantages, such as an easy dosage, an unlimited solubility and minor safety requirements. By these advantages formic acid is favored for the removal of high nitrate concentrations (>1 g/l) which are present in many industrial waste water streams or brines originating from physico-chemical nitrate removal technologies. Nevertheless, for some applications hydrogen might still be the desired reductant for economical reasons. Here, some kind of pH adjustment has to be integrated in the reactor. For many applications CO_2 likely will be the most desired acid as its products HCO_3^- or CO_3^{2-} generally are regarded as less critical substances in water than i.e. Cl^-, PO_4^{3-} or SO_4^{2-} although special attention has to be paid to avoid precipitation of carbonates onto the catalyst leading to a rapid deactivation of the catalyst [14]. However, it has to be kept in mind that a catalyst still has a higher activity and selectivity using formic acid than using a combination of hydrogen as reductant and carbon dioxide as acid [22].

Like in many other liquid-phase reactions, internal mass transfer limitations play an important role in catalytic nitrate reduction, too. When using hydrogen as reductant both activity and selectivity are lowered by pore diffusion, whereas mainly the activity is affected in case of formic acid and not the selectivity due to the in situ buffering effect. Whatever reductant might be used, every improvement in diffusion will be a valuable help for a technical-scale nitrate reduction process. As already explained, hydrogels of poly (vinyl alcohol), PVAL, may be used as a new type of support material with superior diffusional and, additionally, superior mechanical properties (high elasticity, no abrasion even in fluidized-bed reactors) compared to the classical ceramic supports.

It should not be forgotten that in technical-scale nitrate reduction not only chemistry may cause problems but also biology. The growth of microorganisms inside the plant resulting in an increase of the pressure drop and finally reactor plugging was already reported, especially if a fixed-bed of the catalyst was used, whereas the biofilm formation on the surface of the catalyst pellets was somewhat lower in a fluidized-bed reactor [44]. However, a desinfective treatment of the whole plant including the catalyst prior to start-up is indispensable and can be done by chemical desinfection (i.e. ClO^-) or irradiation. In addition, nanofiltration or irradiation of the inlet water stream might also be necessary to avoid re-contamination. Again, the use of PVAL-encapsulated catalysts might be helpful, as their application in fluidized-bed reactors does not cause any problem and, furthermore, their surface prevents grafting of the microorganisms to some extent.

4. Conclusions

In the medium-term nitrate removal from drinking water and waste water will become necessary in order to protect the environment and human health. So far, only biological and the described catalytical denitrification provide a sustainable answer to the nitrate problem. Compared to the Pd–Cu catalysts of the first generation [10] two new bimetallic catalysts (Pd–Sn, Pd–In) were presented in this work — the second generation of nitrate-reducing catalysts — that are more efficient than Pd–Cu catalysts regarding the nitrogen formation activity, the selectivity and the long-term stability. These bimetallics have to be taken into consideration as possible technical-scale nitrate reduction catalysts. The new concepts described here, the use of formic acid as reductant instead of hydrogen to solve selectivity problems due to in situ buffering and the application of PVAL-encapsulated catalysts with superior diffusional properties, have a high potential to significantly improve the catalytic nitrate reduction. These concepts may be a valuable help to finally establish a technical-scale nitrate reduction process.

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