

Supported bimetallic palladium catalysts for water-phase nitrate reduction

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Abstract

Technologies for the removal of nitrate from drinking water and waste water will be required in the near future, and the catalytic nitrate reduction is one of the most promising methods. So far, the understanding of nitrate reducing catalysts has been very poor. Experimental trends in nitrate removal activity and selectivity for various pH values, and for different bimetallic catalysts, as well as results described in literature were used to set up a mechanistic model for the reaction. The nitrate reduction activity is determined by bimetallic ensembles, at which nitrate is adsorbed and reduced to nitrite by hydrogen, which is supposed to spillover from palladium sites to the bimetallic sites. Formic acid, on the other hand, reacts with nitrate by a transfer hydrogenation mechanism from neighboring palladium sites. The extent of positive charging of the bimetallic sites is supposed to influence the activity at different pH values. At a high pH, strongly adsorbing oxygenated species block bimetallic nitrate adsorption sites as well as palladium sites. The selectivity is determined by the ratio of nitrogen species to reductant species at monometallic palladium sites. At these sites, the reduction of nitrite and other intermediates take place, finally leading to the end products. If this ratio of nitrogen to reductant species changes, the selectivity changes as well, e.g. at different ratios of the two metals. The trends in the experimental data are well described by this model. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Palladium; Bimetallic catalysts; Nitrate reduction; Drinking water; Mechanism

1. Introduction

The nitrate concentration in ground water, which is the main source for drinking water, is still rising throughout the world [1]. As nitrate is a potentially harmful compound to human health (blue baby syndrome, cancer [2]) legislators all over the world set levels for nitrate in drinking water, e.g. 50 mg/l in the European Community [3]. In several regions in the world, drinking water wells have already been

closed because of too high nitrate concentrations. As the water demand is still increasing throughout the world, processes for nitrate removal from drinking water have regained interest in recent years.

The current technologies used for nitrate removal from water are divided into physico-chemical, biological and catalytic processes [4,5]. The main disadvantage of the physico-chemical processes ion exchange, reverse osmosis and electro dialysis 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

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changes. Although, sometimes preferred for economic reasons, in the medium-term these processes should 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 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 and N_2O can arise by incomplete denitrification. In addition, biological denitrification processes are difficult 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, e.g. biomass, turbidity, taste-impairing substances.

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

Palladium–copper catalysts for nitrate reduction and palladium catalysts for nitrite reduction were studied intensively by Vorlop and coworkers [8–11] and later by other groups [12–15]. These investigations dealt mainly with the influence of the catalysts preparation conditions as well as the reaction conditions on the nitrate removal activity and selectivity. The catalytic properties of palladium–copper catalysts were found

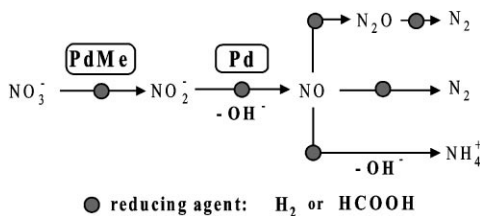


Fig. 1. Scheme of the catalytic nitrate reduction.

to be sensitive to the ratio of the two metals in the catalyst [10,11,15,16]. Both the nitrate removal activity and the selectivity have a maximum at a definite palladium copper ratio, which can differ slightly with the support material and the preparation method used. With palladium copper catalysts having the optimum metal composition, a selectivity for nitrate reduction ranging from 80 to 95% can be reached. This already high selectivity for nitrate reduction can be further improved if a nitrate-reducing Pd–Cu catalyst is used together with a nitrite-reducing Pd catalyst, which has a selectivity for nitrite reduction of >99% [11,17]. Here, the intermediate product nitrite desorbs from the less selective Pd–Cu catalyst and re-adsorbs at the Pd catalyst with the higher selectivity, where it is further reduced to the end products nitrogen and considerably smaller amounts of ammonium.

Some years ago, new selective nitrate-reducing bimetallics, namely alumina supported Pd–Sn and Pd–In, were introduced [18,19]. Compared to alumina supported Pd–Cu catalysts, both alumina supported Pd–Sn and Pd–In catalysts are more active and selective for nitrate removal, although opposite results were found by Strukul et al. for titania and zirconia supported Pd–Sn catalysts [20]. Nevertheless, the major problem of Pd–Cu catalysts, which is the high intermediate release of the problematic intermediates nitrite and nitrous oxide and in the consequence the low nitrogen formation activity, is weakened to a large extent if Pd–Sn and Pd–In catalysts are used for nitrate reduction [21–23]. Another step forward was the use of formic acid instead of hydrogen as reductant, which was first reported by Prüsse and coworkers [24,25]. Formic acid offers several advantages as compared to hydrogen. The major one is an in situ buffering effect: the hydroxide ions formed during nitrate reduction to maintain electro neutrality are neutralized in situ at the catalyst surface by the CO_2 formed by the decomposition of formic acid. This effect lowers the pH-gradient in macroscopic catalyst particles, which otherwise would lead to a decrease in activity and selectivity [26,28].

The decrease of the nitrate removal activity and the nitrogen formation selectivity with increasing pH value was very early recognized as one main drawback in catalytic nitrate and nitrite reduction with hydrogen as a reductant [9]. Several strategies were tested to circumvent this problem, the majority of them focused on

the reduction of (pore) diffusion limitations in the support material, e.g. by the use of hydrogels of polyvinyl alcohol [27,28], membranes [16,20,29,30], structured membranes [31], hollow fibers [26] or cloths [32]. Another approach was the use of metal doped acidic ion exchangers to generate an acidic environment around the active sites [33]. Most of these efforts were more or less successful, but a real breakthrough for the use of hydrogen as reductant and macroscopic catalysts is missing so far. The idea of using a mixture of hydrogen and CO₂, where hydrogen serves as the reductant and CO₂ as a substance to increase the buffering capacity of the water, is useful to some extent, but it was found to be considerably less effective compared to the use of formic acid [26,34].

Nevertheless, hydrogen so far is exclusively used as reductant in all laboratory studies, which are more focused on a subsequent application of this process in a larger scale [35–37], and also in the early pilot-scale studies [38,39]. In addition to the selectivity problems originating from pH-gradients the application of the catalytic nitrate reduction for drinking water treatment will face another problem, which are inhibiting effects caused by water ingredients other than nitrate. So far, these effects have been only scarcely examined [14,21,36,39], but the two stage denitrification process — ion exchanges in combination with a catalytic reactor — recently described by Pintar et al. [37] may be a valuable help to avoid this problem.

In contrast to the potential of the catalytic nitrate reduction technology for drinking water treatment, kinetic, characterization and especially mechanistic studies, which can help to explain how nitrate reducing catalysts are working, are rare. Kinetic data for nitrate and nitrite reduction were collected mainly for powdered Pd–Cu and Pd catalysts, respectively. Tacke and coworkers used rate equations of the power law type to describe nitrate and nitrite removal [8,40], whereas Pintar et al. used rate equations based on a Langmuir–Hinshelwood model to describe both reactions [41,42]. The correlation between experimental data and simulations were very good in both cases. Wärnå et al. proposed a detailed mechanism with several elementary steps at the catalyst surface and derived a set of equations to simulate nitrate removal in a monolith reactor [43]. In contrast to Tacke and Pintar, who used powdered Pd–Cu and Pd catalysts, here the Pd–Cu catalysts are supported on a

monolith-fixed alumina washcoat. Although, experimental data could have been fitted in a satisfactory manner, the proposed mechanism has to be modified because the intermediate nitrous oxide (N₂O), which has been detected several times [8,21–23], was not taken into consideration. For the nitrate reduction with a Pd–Sn catalyst power law type rate equations were reported by Hörold [18] and Daum [44].

So far, characterization data for nitrate and nitrite reducing catalysts are scarce. Pd–Cu catalysts were examined with different techniques like SEM, XRD, EDX, AES, EXAFS or TPR by Pintar et al. [45,46] and Strukul et al. [13]. Characterization was mainly done in order to get information about the distribution and the size of the metal crystallites, but both groups also got evidence for an intimate interaction between palladium and copper, which was interpreted as a strong hint for the formation of an alloy. The formation of a Pd–Cu alloy was also reported by Berndt et al. [47] and Mönnich [48] based on chemisorption, TEM and FT-IR measurements. This group also extensively examined differently prepared nitrate reducing Pd–Sn catalysts by chemisorption, FT-IR and ¹¹⁹Sn-Mössbauer spectroscopy [48,49]. They found out that in nitrate reducing catalysts both Pd–Sn ensembles and pure Pd ensembles are present. Furthermore, different Pd–Sn ensembles could have been identified, alloys with different compositions and adsorbed Sn(II) species as well as Sn(IV) species. The alloys are supposed to be active in nitrate reduction, whereas Sn(II) species are suspected to have an inhibiting and Sn(IV) species to have an inert character.

Despite all the studies done so far in this field, up to now only very few and isolated facts are available on how nitrate and nitrite reducing catalysts might work, i.e. how the mechanism might be [8,12,18]. Several points contribute to this lack of knowledge. First, in situ characterization methods for heterogeneous catalysts are rare, especially if the reaction is done in water-phase. Second, similar processes, which have been known for a long time and which, consequently, are well studied, e.g. the catalytic hydration of nitrate to hydroxylamine under acidic conditions (DSM hydroxylamine process) or the electrochemical reduction of nitrate under acidic or alkaline conditions (known for >100 years), are without doubt similar, but not really comparable due to different catalysts and reaction conditions. Nevertheless, van Santen and coworkers

recently used electrochemical methods to gain information about the mechanism of the nitrate reduction for drinking water treatment and got interesting results [50]. And thirdly, the catalytic nitrate reduction considered here is a relative new reaction first described about 10 years ago. So it is quite usual that most of the work done so far was devoted to the development and optimization of the catalysts than to a deeper understanding of the mechanism.

The scope of this work is to discuss some mechanistic aspects of the catalytic nitrate reduction, which are plausible and in line with earlier and new findings of our group, and to compare them with results of other groups. The proposed model will give an explanation for the nitrate removal activity and the selectivity in terms of the reaction conditions and the catalyst composition, i.e. the ratio of the two metals. Different bimetallic catalysts, Pd–Cu, Pd–Sn and Pd–In, and two reductants, hydrogen and formic acid, will be discussed in a more qualitative than quantitative manner. Although, some parts of the model were reported earlier [25,51–53] here the whole model will be introduced to a broader community for the first time. It may be a help for further discussions and the development of better nitrate reducing catalysts.

2. Experimental

2.1. Catalyst preparation

First, the support material, alumina type HL (Martinswerke, Bergheim, Erft, Germany) calcined for 24 h at 1000°C (BET surface = 36 m²/g, main pore diameter = 70 Å, isoelectric point at pH 10.2, particle size = 2–3 μm) was suspended in a 2% Na₂CO₃-solution for 15 min. By dropping a 1.4% Na₂PdCl₄-solution slowly into the suspension, the Pd was let to precipitate and deposit onto the support under vigorous stirring. Then the second metal (Cu, Sn or In) 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 <5%, the desired palladium/second metal ratio (Pd:Me ratio) was always obtained (checked with AAS). In this study, this Pd:Me ratio is given in terms of the weight ratio.

2.2. Nitrate reduction with hydrogen

A 500 ml glass vessel equipped with a magnetic stirrer (500 rpm) was used for the batch experiments with the powdered catalyst (slurry phase). The pH value was adjusted by using an automatic pH control unit by adding 0.2 M 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/h to ensure the maximum possible hydrogen concentration in solution, which is equal to 0.85 mmol/l at 10°C. Before sodium nitrate in the starting concentration of 100 mg/l nitrate 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 2.5.

2.3. Nitrate reduction with formic acid

Experiments were carried out according to 2.2 with the two differences that nitrogen was used as a gas for oxygen stripping and 0.4 M HCOOH 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 (approximately 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. In this experimental setup, the concentration of formic acid or formate, respectively, increases during the reaction course up to a concentration of about 70 mg/l towards the conclusion, i.e. the complete conversion of the nitrate to the products.

In the sets of experiments, in which the pH-dependence of the activity and ammonium formation for the catalysts was examined, 600 mg/l of sodium formate (double stoichiometric amount necessary for nitrate reduction) were additionally put into the reactor in order to ensure a sufficient amount of reductant being present during the whole reaction course.

All nitrate reduction experiments were carried out in a pH range, where formic acid is almost completely deprotonated ($pK_a = 3.74$), so that it is not necessary to distinguish between formic acid and formate, once formic acid is dissolved in the reactor.

2.4. Nitrate reduction with hydrogen and formic acid

Experiments were carried out according to 2.2 with the difference that 0.4 M HCOOH was used to adjust the pH value instead of HCl. Some experiments were also conducted with additional amounts of sodium formate as indicated in Fig. 7.

2.5. Sample analysis

Periodically withdrawn liquid phase samples were analyzed for the reaction components nitrate, nitrite and formate by HPLC and UV detection, whereas ammonium was analyzed in an automatic flow-injection-analysis system using a fluorescence detector. Both procedures are described in detail in [53].

2.6. Activity and selectivity

The activity, which indeed is the nitrate removal activity, for all catalysts and reductants used relates to complete conversion. In the experiments with formic acid as sole reductant an induction period prior to nitrate reduction is observed. After this period, nitrate reduction proceeds with zero order kinetics until complete conversion. For the calculation of the nitrate removal activity, the slope of the linear concentration–time curve was used, which, formally, is a maximum activity. In the runs with hydrogen as reductant, no induction period is observed and the reduction proceeds with an positive reaction order until complete conversion. Here, the time until complete conversion was used for the calculation of the activity, which in this case, formally, is an average activity. Nevertheless, these two different kinds of activity can be directly compared to each other, as they both describe the nitrate removal from the starting concentration until complete conversion. This procedure was already described in detail in [21,25,53].

In each nitrate reduction experiment described here, nitrogen and ammonium are the only two products

after complete conversion of nitrate. Nitrogen is the desired product, whereas ammonium is the undesired one. The selectivity of nitrate removal is given in terms of the ammonium formation, which is a “negative” selectivity. That means, that the more ammonium is formed in an experiment, the less selective is the catalyst. The ammonium formation is also related to complete conversion.

3. Results and discussion

3.1. Effect of the pH value

It is generally accepted, that for nitrite reduction with hydrogen at palladium catalysts both the activity and the selectivity are decreasing with increasing pH value. For nitrate reduction, mainly Pd–Cu catalysts have been examined with hydrogen as reductant, but only little information is available about the pH dependence of activity and selectivity. Generally a negative impact of higher pH values on the selectivity is reported [8,18,20,25], whereas Pintar et al. observed no effect [41]. The activity reaches a maximum at moderate pH values, slightly differing by the preparation method used for the Pd–Cu catalyst [8,18]. This is also observed with the Pd(5%)Cu(1.25%)/Al₂O₃ catalyst used in this study as indicated in Table 1. In case of formic acid as reductant, the maximum activity is reached at a lower pH value than in the case of hydrogen, whereas the ammonium formation decreases with increasing pH value.

The pH dependence of the nitrate removal activity and ammonium formation for the Pd(5%)Sn(1.25%)/Al₂O₃ catalyst and the Pd(5%)In(1%)/Al₂O₃ catalyst are displayed in Fig. 2. With hydrogen as reductant, the maximum activity is reached at pH 6 for the Pd–In catalysts, whereas it is further increasing at lower pH values in case of the Pd–Sn catalyst, although the curve is flattened significantly. Similar dependencies are obtained for formic acid, although the activity values are higher in this case and the maximum, or the point where the curve flattens, respectively, is moved one pH unit to more acidic conditions, as it was already observed for the Pd–Cu catalyst. Obviously, the activity decrease at higher pH values is a general phenomenon, as it is observed for all catalysts and

Table 1
Activity and ammonium formation for nitrate reduction with hydrogen or formic acid in dependence of the pH value^a

pH value	Hydrogen		Formic acid	
	Activity (mg NO ₃ ⁻ /(h g _{cat.}))	Ammonium formation (mg/l)	Activity (mg NO ₃ ⁻ /(h g _{cat.}))	Ammonium formation (mg/l)
5	14	2.3	36	6.5
7	57	2.0	64	4.2
9	65	3.3	46	2.3
10.5	45	6.3	10	2.0

^a Catalyst: Pd(5%)Cu(1.25%)/Al₂O₃.

reductants, whereas the decrease or flattening at lower pH values is quite similar for the two reductants but characteristic for each catalyst, i.e. for each second metal (Cu, Sn or In) used to generate the bimetallic catalyst. These phenomena will be further discussed in Section 3.4.

The ammonium formations corresponding to the activities in Fig. 2 are shown in Fig. 3. For each catalyst and reductant the ammonium formation rises with increasing pH value. This is no discrepancy to the in situ buffering effect of formic acid, because such high pH values, as adjusted in these experiments, will not occur even under strong diffusion limitations due to the buffering of CO₂. Except for nitrate reduction with formic acid using the Pd–Cu catalyst (Table 1) the increasing ammonium formation at higher pH values is a general phenomenon (Section 3.4).

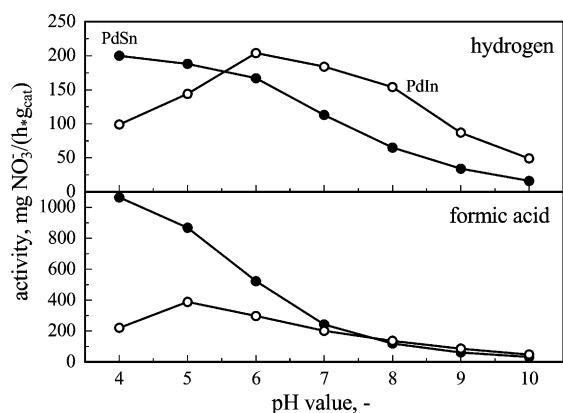


Fig. 2. Nitrate removal activity in dependence of the pH value for hydrogen or formic acid as reductant. Catalysts: Pd(5%)Sn(1.25%)/Al₂O₃, Pd(5%)In(1%)/Al₂O₃.

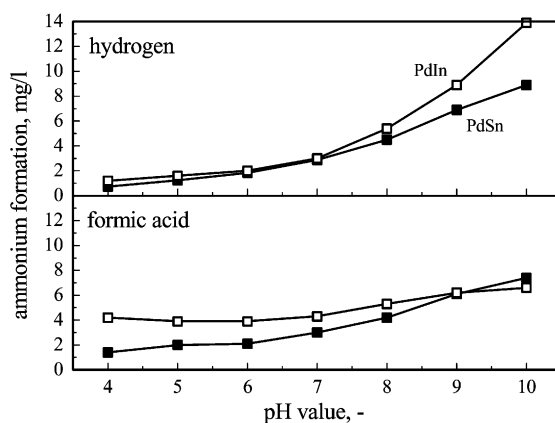


Fig. 3. Ammonium formation corresponding to the nitrate removal activity in Fig. 2 in dependence of the pH value for hydrogen or formic acid as reductant. Catalysts: Pd(5%)Sn(1.25%)/Al₂O₃, Pd(5%)In(1%)/Al₂O₃.

3.2. Effect of the metal ratio

Very often, the ratio of two metals in a bimetallic catalysts is crucial for its catalytic properties. For the catalytic nitrate reduction, this effect was already investigated in the first study [6]. It was found out, that the ratio of palladium to copper is of major importance for both the nitrate removal activity and the ammonium formation. In subsequent studies, this effect was confirmed several times by different groups and for differently prepared Pd–Cu catalysts [11,15,16]. In general, a definite metal ratio exists at which the nitrate removal activity and, surprisingly, also the selectivity, reaches a maximum value. The ratio of the two metals is also of major importance for the activity and ammonium formation of Pd–Sn and Pd–In

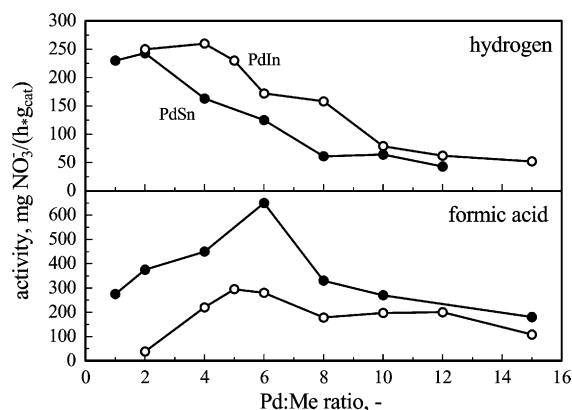


Fig. 4. Nitrate removal activity in dependence of the Pd:Me ratio (Me: second metal) for hydrogen or formic acid as reductant. Catalysts: Pd(5%)Sn(x%)/Al₂O₃, Pd(5%)In(x%)/Al₂O₃ (x: various).

catalysts (Figs. 4 and 5, respectively). These two catalysts exhibit a rising activity with increasing content of the second metal (Sn or In), i.e. decreasing Pd:Me ratio, if hydrogen is used as reductant (Fig. 4). In contrast, in the case of formic acid a volcano-type curve with a sharp maximum for both catalysts at Pd:Me ratios of about 5:1–6:1 is observed. Thus, the two different catalysts are quite similar to each other, whereas a significant difference is observed for the two different reductants.

As far as the ammonium formation is concerned (Fig. 5) at a Pd–Sn as well as Pd–In ratio of 6:1

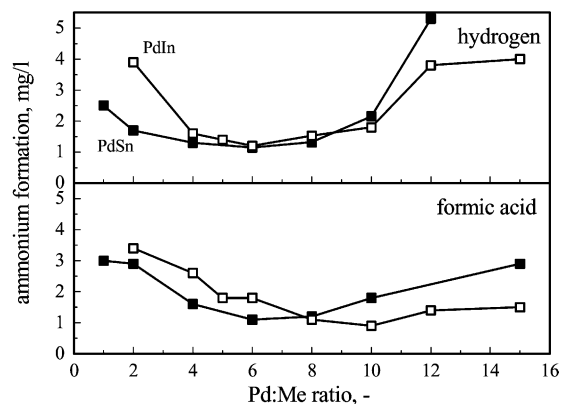


Fig. 5. Ammonium formation corresponding to the nitrate removal activity in Fig. 4 in dependence of the Pd:Me ratio (Me: second metal) for hydrogen or formic acid as reductant. Catalysts: Pd(5%)Sn(x%)/Al₂O₃, Pd(5%)In(x%)/Al₂O₃ (x: various).

minimum ammonium formation is observed for hydrogen as reductant. The optimum ratio is shifted to 10:1 for the Pd–In catalysts and formic acid as reductant, whereas again 6:1 is the best for the Pd–Sn catalyst and formic acid. These findings imply that there must be a more general reason, which is rather independent from the reductant and the type of second metal. Furthermore, if the two reductants are compared, one can state a different characteristic as far as the activity is concerned but a similar characteristic for the ammonium formation. One can therefore suggest that different types of active sites are responsible for the nitrate removal activity on the one hand and the ammonium formation on the other hand.

3.3. Nitrate reduction with hydrogen and formic acid

So far, nitrate reduction was carried out either with hydrogen as reductant or with formic acid. But it is also of interest to see whether activity and/or selectivity are changing when both reductants are used simultaneously. In Fig. 6 the nitrate removal activity and the ammonium formation of a Pd(5%)In(1%)/Al₂O₃ catalyst are compared for the use of hydrogen, formic acid and hydrogen plus formic acid as reductant. Whereas the ammonium formation is equal for each experiment, the nitrate removal activity for the experiment, in which both reductants are used, is almost the sum of the activities for each single reductant. Two different explanations are possible for this results:

1. The activity for the combined use of both reductants is higher, simply due to the fact that the to-

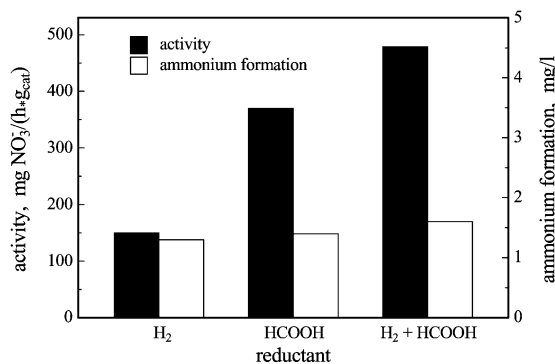


Fig. 6. Nitrate removal activity and ammonium formation in dependence of the type of reductant. Catalysts: Pd(5%)In(1%)/Al₂O₃.

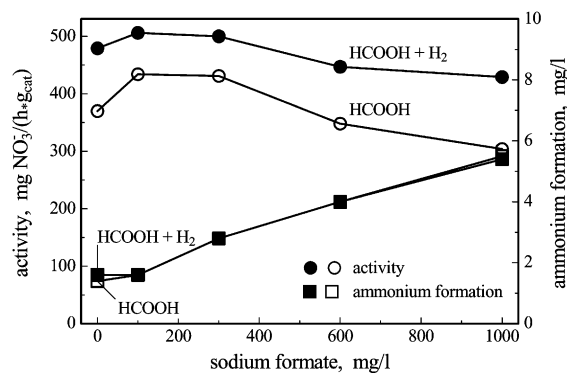


Fig. 7. Nitrate removal activity and ammonium formation in dependence of the sodium formate concentration added to the reactor for the use of either hydrogen or hydrogen plus formic acid as reductant. Catalysts: Pd(5%)In(1%)/Al₂O₃.

tal concentration of reductants is higher in this experiment.

- Two different active sites are present in the catalyst. At one site hydrogen is activated for nitrate reduction, whereas formic acid is activated for nitrate reduction at another site.

It can be distinguished between these two explanations by the experiment depicted in Fig. 7, where the activity and ammonium formation for nitrate reduction with formic acid and with hydrogen plus formic acid are shown in dependence of the formic acid (formate) concentration. In these sets of experiments with either of the reductant, nitrate reduction was carried out with different amounts of sodium formate additionally added to the reactor in order to enhance the total concentration of formate being present. The activity of nitrate reduction with formic acid first increases with rising total formate concentration. At higher formate concentration the activity decreases (Langmuir–Hinshelwood). Obviously, all active sites accessible to formic acid are occupied at higher formate concentration. For the combined use of both reductants the activity is higher for a nearly constant amount over the whole range of formate concentrations examined. This is an evidence for the existence of two different types of active sites, where the reductant are activated for nitrate reduction, one which is accessible to formic acid, and maybe also for hydrogen, which is not excluded by this experiment, and another one which is solely accessible to

hydrogen. We also made the contrary experiment, in which a definite amount of formic acid was put into the reactor at various hydrogen partial pressures up to 8 bar [44]. The result was equal to the one described here. The nature of these two active sites will be discussed in the Section 3.4.

The ammonium formation of these two sets of experiments are equal. Obviously, for these experiments the selectivity is determined only by the concentration of formic acid or formate, respectively. This is a surprising result, which can be interpreted in terms of the well known high adsorption strength of formate compared to hydrogen, and will be discussed more in detail in the following section.

Another conclusion can be drawn from the experiments shown in Fig. 7. There is some addition in the nitrate removal activity for the two reductants but not for the ammonium formation. This is another sign, that the sites controlling the activity and the selectivity are different.

3.4. Mechanistic aspects of nitrate reduction

In the following sections, experimental data from our own experiments as well as from experiments carried out by other groups will be used to set up a model of the nitrate removal activity and the selectivity of nitrate reducing bimetallic catalysts. This reaction is a rather complicated one, consisting of consecutive and parallel parts, in which numerous stable intermediates and products — the ones containing nitrogen are summarized in Table 2 — and surely even more adsorbed species take part or are supposed to take part. The catalysts used so far in nitrate reduction studies are manifold in their type, composition and preparation procedure. Thus, the derivation of a model will only be successful if simplifications are made. Furthermore, at the current stage of research the discussion of trends is much more useful for the understanding of the mechanism than definite values of activity or selectivity for any of the catalyst.

3.4.1. The catalyst

As already mentioned, only very few characterization data are available for nitrate reducing catalysts, namely for Pd–Cu [45–47] and Pd–Sn [48,49] catalysts, whereas nothing is known about nitrate reducing Pd–In catalysts. From the results described in

Table 2
Nitrogen compounds involved in catalytic nitrate reduction

Oxidation number	Formula	Name	Remarks
+5	NO_3^-	Nitrate	Substrate
+4	NO_2	Nitrogen dioxide	Possible intermediate
+3	NO_2^-	Nitrite	Known intermediate
+2	NO	Nitric oxide	Probable intermediate
+1	N_2O	Nitrous oxide	Known intermediate
± 0	N_2	Nitrogen	Known product
-1	NH_2OH	Hydroxylamine	Product at pH < 4
-2	N_2H_4	Hydrazine	No informations
-3	$\text{NH}_3/\text{NH}_4^+$	Ammonia/Ammonium	Known product

literature, a picture of nitrate reducing catalysts can be drawn as displayed in Fig. 8. Small metal crystallites are distributed onto an inert support material. The crystallites consist of bimetallic ensembles, probably alloys, next to pure palladium ensembles. No evidence could be found thus far, that monometallic ensembles of the second metal are present in the catalyst. For the following discussion the exact nature of the bimetallic ensembles does not matter, as it will only be distinguished between bimetallic and monometallic sites.

3.4.2. Reaction sites for N-containing compounds

The reduction of nitrite via the probable intermediate NO and the known intermediate N_2O to nitrogen and ammonium can be performed with monometallic palladium catalysts. No second, activating metal is necessary for any of these reaction steps. Nitrite is known to be a strongly adsorbing substance. This was confirmed by Daum and coworkers [44,54], who investigated nitrite adsorption at Pd catalysts. Therefore, it can be concluded, that nitrite adsorbs at monometallic palladium sites, where it is further converted to following N-containing intermediates as

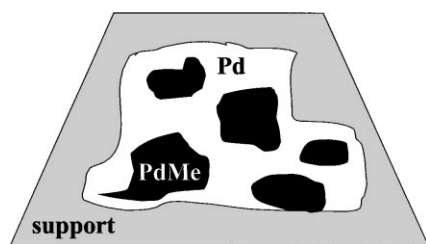


Fig. 8. Scheme of nitrate reducing bimetallic catalysts.

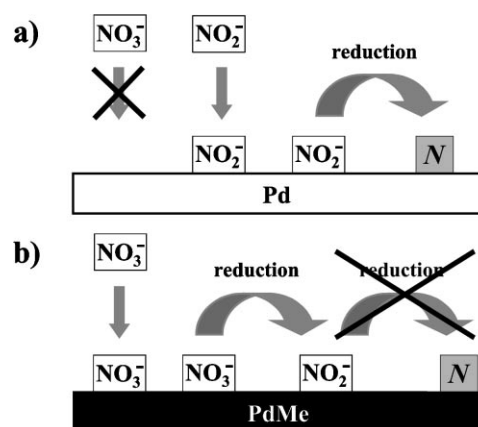


Fig. 9. Schematic representation of adsorption and reduction steps of nitrogen-containing compounds at monometallic palladium and bimetallic sites. Me: metal, N: reduced N-species.

it is depicted in Fig. 9a. As monometallic palladium catalysts exhibit no activity for nitrate reduction, it can be further concluded, that nitrate does not adsorb at monometallic palladium sites, which was also confirmed by Daum and coworkers [44,54].

There is no question, that for nitrate reduction a second, activating metal, e.g. Cu, Sn or In, is needed. Obviously, the second metal, or the bimetallic ensemble (Section 3.4.1), enables nitrate adsorption. Indeed, nitrate adsorption at different bimetallic catalysts could have been confirmed [44,45]. After adsorption the nitrate is converted to the next intermediate, which probably will be nitrite rather than NO_2 , at these bimetallic ensembles. This can be achieved either by an electron transfer from the bimetallic ensemble to the adsorbed nitrate with a subsequent regeneration of the ensemble

Table 3

Activity, ammonium formation and maximum intermediate nitrite release for nitrate reduction with hydrogen at pH 9 in dependence of the Pd:Sn ratio

Pd:Sn ratio	Activity (mg NO ₃ ⁻ /(h g _{cat.}))	Ammonium formation (mg/l)	Intermediate nitrite release (mg/l)
1:1	58	12.4	7.6
2:1	50	11	8.5
4:1	25	6.5	2.6
8:1	10	6.9	0.6
12:1	4	14.4	0.3

by the reductant or by the direct transfer of the reductant to the nitrate. This is uncertain so far, and it will not be easy to distinguish between these two pathways. But this point is not really crucial for the following discussion.

After nitrate is transformed to nitrite at the bimetallic sites, we assume that no further reaction to following intermediates will occur at these sites (Fig. 9b). Nitrite cannot be further converted, so it will desorb or spillover from these sites and will finally re-adsorb at monometallic palladium sites, where it can be further reduced. This is in sharp contrast to the ideas of Pintar and coworkers [12,42], who think that nitrite may also be converted in an unselective manner at bimetallic sites. Nevertheless, there are several findings that support our assumption:

1. The nitrite reduction activity of bimetallic catalysts decreases with increasing content of Sn [18] or Cu [15].
2. The intermediate release of nitrite during nitrate reduction increases with rising content of the second metal in bimetallic Pd–Cu [53] as well as Pd–Sn catalysts (Table 3).
3. The nitrate reduction is inhibited at higher nitrite concentrations [44,53].

Another support of this assumption will be given in the discussion of the selectivity later on in this paper.

3.4.3. The reductant

In some cases the trends in nitrate removal activity are different for the two reductants, e.g. for catalysts rich in Sn or In, respectively (Fig. 4). Furthermore, there is some evidence that two different active sites are present in nitrate reducing catalysts, at which either of the reductants is activated for nitrate reduction (Section 3.3).

It is well known, that formic acid strongly adsorbs as surface formate species at palladium catalysts, where it also can be decomposed to hydrogen and CO₂ [55,56]. If other reducible species are present, the adsorbed formate species act as reductant by transfer hydrogenation rather than by supplying hydrogen from the previous decomposition (Fig. 10a) [57]. It is further known that the decomposition of formic acid in the gas phase is inhibited if bimetallic catalysts, e.g. Pd–Cu or Pd–Ni, are used [58]. Furthermore, palladium catalysts exhibit only a very small activity for nitrite reduction probably caused by a too high coverage of the two strong adsorbents nitrite and the formic acid [53]. Thus, it can be concluded, that formic acid will adsorb and act as reductant by transfer hydrogenation exclusively at monometallic palladium sites. This means that the reduction of nitrate which is solely adsorbed at bimetallic sites, can only be performed at

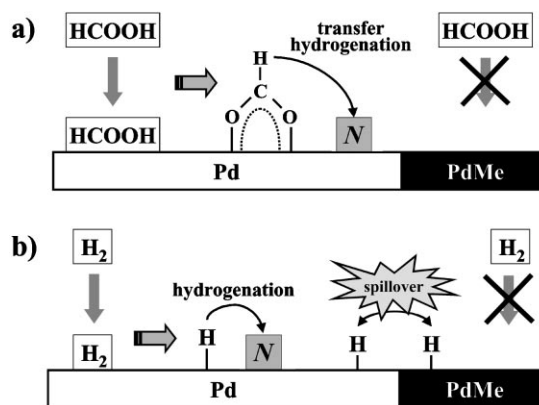


Fig. 10. Schematic representation of adsorption and reaction steps of the two different reductants at monometallic palladium and bimetallic sites. Me: metal, N: reduced N-species.

Table 4

Specific activity and ammonium formation for nitrate reduction with hydrogen or formic acid in dependence of the ratio of surface palladium atoms to total tin atoms ($\text{Pd}_s/\text{Sn}_{\text{total}}$)^a

$\text{Pd}_s/\text{Sn}_{\text{total}}$	Hydrogen		Formic acid	
	Specific activity ($\text{mg NO}_3^-/(\text{D h g}_{\text{cat.}})$)	Ammonium formation (mg/l)	Specific activity ($\text{mg NO}_3^-/(\text{D h g}_{\text{cat.}})$)	Ammonium formation (mg/l)
0.6	628	5.7	65	6.0
3.0	264	6.4	195	8.9

^a The specific activity is given in terms of $\text{mg NO}_3^-/(\text{D h g}_{\text{cat.}})$, in which D represents the palladium dispersion measured by CO chemisorption [48,49]. The catalysts were prepared by the CSR method described in detail elsewhere [48,49].

such bimetallic sites neighboring monometallic palladium sites, where formic acid is adsorbed.

The dissociate chemisorption of hydrogen at palladium surfaces is out of the question [59]. Hydrogenation is performed when a surface hydride species is transferred to a substrate, as it is shown in Fig. 10b. Hydrogen chemisorption data presented in [48,49] indicate that the direct chemisorption of hydrogen at bimetallic ensembles is very unlikely to occur in nitrate reducing catalysts. But it is known for several different catalytic metals, that hydrogen spillover can occur between different metals, e.g. $\text{Ru} \rightarrow \text{Cu}$ or $\text{Pt} \rightarrow \text{Re}$, or even from monometallic to corresponding bimetallic sites, e.g. $\text{Pt} \rightarrow \text{PtRe}$ or $\text{Rh} \rightarrow \text{RhSn}$ [60]. Therefore, it can be assumed that in case of nitrate reducing catalysts hydrogen spillover from monometallic palladium sites to bimetallic ensembles occurs. In other words it can be said that hydrogen is activated for nitrate reduction at bimetallic ensembles. Thus, we have the two different active sites for nitrate reduction with the two reductants, which are monometallic palladium sites, accessible to formic acid, and the bimetallic ensembles, which are accessible for hydrogen by spillover but not for formic acid.

This hypothesis is supported by the results shown in Table 4. In this table the nitrate removal activity and ammonium formation of two Pd–Sn catalysts with different ratios of surface palladium atoms to total tin atoms ($\text{Pd}_s/\text{Sn}_{\text{total}}$) are compared for the use of hydrogen and formic acid as reductant. These catalysts were prepared by a controlled surface reaction (CSR) procedure described in detail elsewhere [48,49]. The number of surface palladium atoms were calculated from the results of chemisorption, TEM and FT-IR data. The results indicated in Table 4 clearly show, that Pd–Sn catalysts with few monometallic

palladium sites and therefore many bimetallic sites are more active in the nitrate reduction with hydrogen, whereas the contrary is observed if formic acid is the reductant. In that latter case, the catalyst rich in monometallic sites is much more active than the catalysts having only few surface palladium sites.

3.4.4. Nitrate removal activity

The experimental data concerning the influence of the ratio of the two metals in Pd–Sn and Pd–In catalysts on the nitrate removal activity were already discussed (Section 3.2, Fig. 4). From the mechanistic point of view, these data can now be explained with the scheme displayed in Fig. 11. In this picture, schematic representations of Pd–In catalysts with different Pd:In ratios are shown. It is assumed, that with increasing indium content, first the number and then the size of the bimetallic ensembles are increased. If hydrogen is used as reductant (Fig. 11, right), the activity rises with increasing indium amount (Fig. 11, right, points A \rightarrow D), as more nitrate is adsorbed, because more active sites are present in the catalyst, which finally leads to a higher reaction rate. Hydrogen, which, of course, is also necessary spillover to the bimetallic ensembles, no matter which size these ensembles are.

On the left hand side of Fig. 11 the same situation is shown for the use of formic acid as reductant. At high Pd:In ratios, i.e. low indium contents, the catalyst contains of only few and small bimetallic ensembles (Fig. 11, left, point A). Nitrate reduction is performed at neighboring mono- and bi-metallic sites in a way that nitrate adsorbed at the bimetallic sites is reduced by transfer hydrogenation of formic acid, which is adsorbed at neighboring monometallic sites. With increasing indium amount, the activity reaches a maximum value (Fig. 11, left, point C). At this point

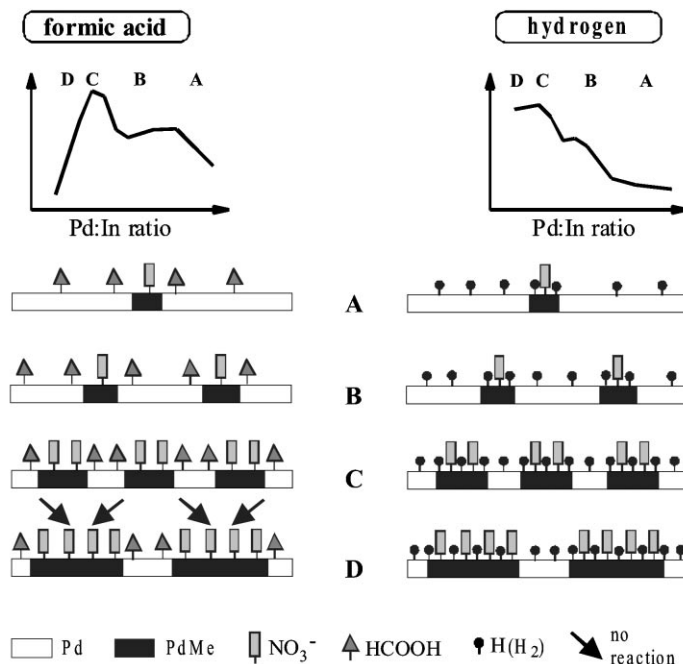


Fig. 11. Schematic representation of nitrate reduction with hydrogen or formic acid as reductant, respectively, in dependence of the second metal content in bimetallic catalysts. Me: metal.

the number of bimetallic sites and thus also the nitrate adsorption have increased and the size of the bimetallic ensembles are in a range, where each nitrate adsorption site in these ensembles can be reached by transfer hydration of adsorbed formic acid surrounding the bimetallic ensembles. If the indium content is further increased, the activity drops rapidly (Fig. 11, left, point D). At this stage, the bimetallic ensembles have reached sizes where the inner nitrate adsorption sites of the bimetallic ensembles can no longer be reached by formic acid.

Based on this model, it can be predicted, that the addition of activities for each single reductant, which has been already described (Figs. 6 and 7), should be more pronounced for catalysts with higher contents of the second metal, as in these cases larger bimetallic ensembles would be present in the catalyst. Such experiments were carried out with Pd–Sn catalysts. The results, which are summarized in Table 5, indeed support the predicted trend.

The nitrate removal activity is also deeply influenced by the pH value. It was already mentioned in

Section 3.1 (Fig. 2, Table 1), that for the two reductants similar trends could have been observed, whereas these trends differ significantly for each second metal. This implies, that nitrate adsorption at the bimetallic ensembles should be taken into consideration for an explanation of the observed trends.

The metal crystallites in nitrate reducing catalysts can be to some extent be compared with electrodes in water. At different pH values, the metal surface will be covered with different adsorbed species, which are hydrogen species at low pH values and hydroxide or even oxide species at high pH values. In other words, the catalyst is in a more reduced state at a low pH, whereas it is more oxidized at a higher pH [61,62]. Since nitrate has to adsorb prior to its reduction, the repulsion between the negative nitrate ions and the reduced or more negatively charged metal surface at lower pH values leads to the observed drop in activity at lower pH values. This effect is markedly different for the three second metals under consideration. Copper is more noble than the other metals and should therefore be negatively charged at higher pH values

Table 5

Activity and ammonium formation for nitrate reduction with hydrogen, formic acid or hydrogen + formic acid, respectively, in dependence of the Pd:Sn ratio

Pd:Sn ratio	Hydrogen		Formic acid		Hydrogen + formic acid	
	Activity (mg NO ₃ ⁻ /(h g _{cat.}))	Ammonium formation (mg/l)	Activity (mg NO ₃ ⁻ /(h g _{cat.}))	Ammonium formation (mg/l)	Activity (mg NO ₃ ⁻ /(h g _{cat.}))	Ammonium formation (mg/l)
1:1	506	1.9	327	2.3	1197	1.9
2:1	453	2.2	475	2.8	1068	1.7
4:1	280	0.9	700	1.2	798	0.7
8:1	89	2.3	375	0.8	408	0.7
12:1	44	4.9	229	0.8	315	0.4

than the other two metals. Indeed, the maximum in activity is observed at about pH 9 for the Pd–Cu catalyst, which is a pH value considerably higher than for the other two catalysts. With this hypothesis, the maximum activity for the Pd–Sn catalyst should be at a higher pH value than for the Pd–In catalyst, which is not the fact (Fig. 2). Two effects may contribute to the fact, that contrary results have been observed. Firstly, studies on equally prepared Pt–In and Pt–Sn catalysts indicated, that indium is in a more reduced state in these bimetallic catalysts than tin [63]. Secondly, tin is known to have a very strong metal–oxygen bond [64] — oxygenated species are the dominant adsorbates at higher pH values — which may hinder its reduction at higher pH values. The observation, that the maximum activity for the use of formic acid is shifted one pH unit towards higher pH values compared to hydrogen, may be caused by the higher reduction strength of surface hydride species compared to adsorbed formate species.

A drop in activity is observed for all the catalysts at high pH values. Here, the active sites at the catalyst surface are blocked more and more by strongly adsorbing oxygenated species (e.g. OH, OH⁻, O^{x-}), i.e. the bimetallic site is oxidized. These species shall simply be named hydroxide ions for the following discussion. The higher the pH value, the more and the stronger hydroxide ions will cover the surface. Thereby, the nitrate adsorption sites are blocked, finally leading to the observed decrease in activity. Thus, a high activity of nitrate reducing catalysts is favored at pH values, at which the second metal or the bimetallic ensemble, respectively, is positively charged to some extent to facilitate the adsorption of the opposite charged nitrate ion. If the positive charge of the bimetallic sites will exceed a certain limit depending on the type of the

second metal, these sites will be blocked by strongly adsorbed oxygen species leading to a drop in activity.

3.4.5. Selectivity

In the previous section, bimetallic sites were identified as the sites controlling the nitrate removal activity. It was also postulated, that at these sites nitrate is reduced to the intermediate product nitrite. As no further reduction will occur at these sites, nitrite desorbs and re-adsorbs at monometallic palladium sites, where it will be further reduced finally leading to the end products. Many of the experimental results presented here indicated that different sites are responsible for the activity on the one hand and the selectivity on the other hand. Thus and in contrast to statements of Pintar and coworkers [12,42], the sites controlling the selectivity have to be monometallic palladium sites, which will also be supported by the following discussion.

Nitrogen is the main product in the catalytic nitrate reduction. As nitrogen contains two nitrogen atoms, whereas the substrates nitrate or nitrite, respectively, contain only one nitrogen atom, a pairing of two nitrogen-containing surface species (N-species) has to occur. Therefore, the selectivity is a function of the surface coverage of N-species. The surface is also covered by the reductant. N-species, which diffuse over the surface, may also meet diffusing reductant species. Such an event will lead to the formation of ammonium, if the N-species is already reduced to a larger extent. Thus, the selectivity is a function of the ratio of the surface coverage of N-species to reductant species (N:reductant ratio). If N:reductant is high, e.g. at low reductant concentrations, the selectivity will be high, if N:reductant is low, e.g. at low nitrate concentrations existing at the end of nitrate

reduction batch experiments, the selectivity will be low. This hypothesis was introduced by Tacke [8] and is generally accepted today.

Regarding the results already presented and the previous discussion, this hypothesis can be expanded. The selectivity of nitrate reduction will be determined by the N:reductant ratio at the monometallic palladium sites. Furthermore, catalysts with different ratios of the two metals probably will have different surface compositions and therefore differently sized palladium ensembles. As the palladium ensembles control the selectivity, a different selectivity should result, as it can be observed. A nitrate reducing catalyst with a maximum selectivity should have a moderate amount of bimetallic ensembles and medium sized palladium ensembles. During reaction course, nitrate is reduced at the bimetallic ensembles, nitrite is re-adsorbed at the palladium ensembles, where it is further reduced to N-species and finally the products. The palladium ensembles will have a high coverage of N-species and therefore a high selectivity, as the bimetallic ensembles are “producing” N-species during the whole reaction course with an optimal rate.

If catalysts with a low content of the second metal are used, only few bimetallic and large monometallic palladium ensembles are present in the catalyst. Now the situation is different. The nitrate removal activity is lower, as fewer bimetallic ensembles are present. During reaction course, the now larger palladium ensembles will be provided with nitrite and therefore N-species with a slower rate, whereas the palladium ensembles will be covered with the reductant species as usual. This leads to a remarkable shift in the N:reductant ratio, which now is smaller with a corresponding low selectivity, which indeed is observed in the experiments (Fig. 5).

If catalysts with a high content of the second metal are used, these catalysts exhibit many and large bimetallic ensembles, whereas monometallic palladium ensembles are few and small, even if the total crystallite size is broadened to some extent in these catalysts. Now the situation is again different. Nitrate now is reduced at a high rate and a corresponding high rate will be obtained for the production of nitrite. As in this case the palladium ensembles are fewer and smaller, not every nitrite molecule which is produced can directly re-adsorb at the palladium surface, which is “overcrowded”. Therefore, the intermediate

nitrite release is much higher for these catalysts, than for catalysts with a lower content of the second metal (Table 3). The high ammonium formation, which is observed for these catalysts simply results from such palladium ensembles, which are too small to enable the pairing of two N-species, so that in the end ammonium is formed.

The pH value as well is of major importance for the selectivity, not only for nitrate reducing bimetallic catalysts (Fig. 3) but also for nitrite reducing monometallic palladium catalysts [8,18,25]. Obviously, the pH value has some effect on palladium sites. As already mentioned above, the catalyst surface is more and more covered with strongly adsorbing oxygenated species (hydroxide ions) with rising pH value. These hydroxide species may act as blocking barriers disabling the pairing of N-species diffusing on the surface. In a way, this effect resembles the negative effect, which catalysts with a high content of the second metal have on the selectivity, in both cases the size of the palladium ensembles is decreased, leaving more and more small palladium sites, at which only ammonium can be formed. Regarding this picture, it is not surprising that the intermediate nitrite release rises with increasing pH value [21,25,53]. Again, nitrite ions formed can not directly re-adsorb at the palladium ensembles, which are blocked by hydroxide ions.

4. Conclusions

In the medium-term, the removal of nitrate from drinking water and waste water will become necessary in order to protect the environment and human health. So far, the understanding of nitrate reducing catalysts was very poor. In this work, experimental trends in nitrate removal activity and selectivity for various pH values and for different bimetallic catalysts as well as results described in literature were used to set up a mechanistic model for the reaction.

Although, many simplifications were made, the model is able to explain the nitrate removal activity, which is connected to the bimetallic ensembles, and the selectivity, which is determined by the ratio of the coverage with nitrogen-containing species to the coverage with reductant species at monometallic palladium sites. Nevertheless, it is simply a model and not reality. Probably, some expansion, differing

interpretations or maybe even corrections have to be made in the future. More spectroscopic and characterization data, which are not available at the moment, are needed to get a more detailed mechanism in the future. In the meantime, the model described here may serve as a basis to stimulate the discussion and, hopefully, will provide some ideas for the further improvement of nitrate reducing catalysts.

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