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The electrocatalytic reduction of NO_3^- on Pt, Pd and Pt + Pd electrodes activated with Ge

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Abstract

The electrocatalytic reduction of nitrate has been investigated on Pt, Pd and Pt + Pd electrodes covered with a submonolayer of germanium. Pt + Pd electrodes were prepared by electroless deposition of submonolayers of Pd on Pt by exchange of PdCl_2 for preadsorbed copper. Underpotentially deposited germanium enhances the reduction rate of nitrate strongly. The reduction of nitrite is enhanced to a lesser extent, whereas germanium is inactive for NO and hydroxylamine reduction. Further, cyclic voltammetry shows that the well known inhibition of the nitrate reduction at low potentials is absent for germanium-modified electrodes. Amperometry shows that the current densities for nitrate reduction at 0.1 V depend strongly on the composition of the electrode surface. The activities increase in the order Pd, Pt and Pt + Pd and all electrodes display a proportional relation between the activity and the germanium coverage. This shows that germanium is involved in the rate determining step, which is the reduction of nitrate to nitrite and its role is to bind the oxygen atom of nitrate. The higher activities for Pt + Pd electrodes can be understood in terms of changes in the electronic structure of the metals as a result of alloying. Selectivity measurements with a rotating ring-disk electrode have shown for all electrodes that the hydroxylamine selectivity increases for increasing germanium coverage. Pd displays higher hydroxylamine selectivities than Pt and Pt + Pd electrodes. No gaseous products were observed for Pt, whereas for Pt + Pd and Pd N_2O selectivities up to 8% were found. © 1997 Elsevier Science S.A.

Keywords: Nitrate reduction; Platinum; Palladium; Germanium activation

1. Introduction

The reduction of nitrate has recently gained renewed attention in view of its relevance to pollution control. Both the catalytic reduction [1–3] with hydrogen and the electrochemical reduction [4] can be applied to the treatment of industrial waste water, whereby nitrate is transformed into harmless nitrogen gas. Moreover, the reduction of nitrate to hydroxylamine is carried out industrially in the formation of caprolactam, the monomer of nylon [5].

The electrochemical reduction of nitrate has been investigated on a large number of metals and the half-wave potential has been established to vary periodically with the atomic number of the cathode material [6]. The same periodic dependence is known for the hydrogen evolution reaction. These data were later reinterpreted and the nitrate reduction activity on transition metals displayed a volcano relationship with the M–H and M–O interaction energies; moderate values of M–H and M–O bond energies result in

the optimum activity [7]. A recent study on palladium [8] shows that it is as equally active for nitrate reduction as platinum, whereas rhodium has been found to be much more active [8,9].

Several studies have been carried out with platinum, using different concentrations of the conducting electrolyte and nitrate [8,10–20]. For high nitrate concentrations in concentrated sulphuric acid electrolytes, the reduction was reported to be autocatalytic [10–16], based on the observation that the reaction was accelerated by nitrite and slowed down on stirring of the solution [10,11]. Several reaction mechanisms have been proposed to explain the autocatalytic behaviour: (i) a model with two cycles that comprise a reaction between HNO_3 and HNO_2 as the first step to form two NO_2 molecules [10,11,15], that are subsequently reduced to nitrite [6], or react with a single NO molecule via N_2O_3 to HNO_2 [10,11]. The NO molecule necessary in this step is formed by reduction of HNO_2 . (ii) another model is based on autocatalytic cycles where HNO_3 reacts with HNO_2 to give N_2O_4 , that subsequently reacts with two NO molecules to HNO_2 [17]. (iii) other proposed

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reactions between HNO_3 and NO to form NO_2 [14] and between HNO_3 and NH_2OH to form HNO_2 [14].

In contrast with this, no evidence was found for an autocatalytic mechanism in more dilute electrolytes, using moderate nitrate concentrations [8,18–20]. The reduction of nitrate in these media was observed at potentials where platinum is partially covered with hydrogen, both in acid and alkaline solutions. Therefore, it was concluded that adsorbed nitrate ions and adsorbed hydrogen atoms participate in the reduction reaction. Several studies concerning the electrochemical reduction of NO have been carried out and the most frequently proposed mechanism contains NOH_{ads} or NHO_{ads} as the key intermediate, which determines the selectivity by either reduction to NH_2OH and NH_4^+ or by dimerization to form N_2O [21–28]. On the basis of these results a mechanism for the reduction of nitrate on platinum can be drawn up, Scheme 1.

Competitive adsorption of electrolyte anions affects the nitrate reduction rate. A higher activity was found in perchloric acid than in sulphuric acid [20,29]. Both nitrate and nitrite reduction become inhibited at potentials that impose a high hydrogen coverage. This inhibition, which was also found for N_2O reduction [30], is observed in acid and alkaline solutions and originates from the competitive adsorption of hydrogen [8,18–20]. However, others have explained the passivation by breaking of the autocatalytic cycle [14].

No detailed information is available on the product distribution of nitrate reduction on platinum. DEMS measurements in 0.5 M H_2SO_4 on platinum have shown that no N_2 and N_2O are formed, indicating that NH_4^+ and NH_2OH are the only possible products [31]. A combined rotating ring-disk and mass spectrometry study of the reduction of nitrite in perchloric acid on platinum found selectivities of 60% for NH_2OH , 21% for NH_3 and 19% for N_2O [32]. For NO reduction maximum selectivities for

hydroxylamine of 70% [22] and 78% [25] were found in concentrated sulphuric acid electrolyte.

Germanium is known to enhance the rate of the catalytic hydrogenation of nitrate on supported palladium and palladium + platinum catalysts [5]. Hardly any information is available in the electrochemical literature on the effect of submonolayers of germanium on platinum or palladium electrodes for the electrocatalytic reduction of nitrate [33]. In this study we investigate the activating effect of submonolayers of germanium on nitrate reduction with platinum, palladium and platinum + palladium surface-alloys. We will demonstrate that there is a strong effect of the electrode composition on the activity and selectivity of the reaction.

2. Experimental

Cyclic voltammetry, amperometry and rotating ring-disk electrode (RRDE) measurements were carried out with a Tacussel bipotentiostat and Wenking VSG 72 voltage scan generator, that were connected via an A/D interface to a personal computer. A home-made set-up was used for the RRDE measurements. A $\text{Hg}|\text{Hg}_2\text{SO}_4$ electrode in saturated K_2SO_4 was used as a reference electrode, while all potentials in the text will be referred to the reversible hydrogen electrode (RHE). Platinized platinum electrodes were prepared by electrodeposition from a 0.05 M $\text{H}_2\text{PtCl}_6 + 0.01$ M HCl solution on smooth platinum. A deposition current of 10 mA cm^{-2} was used. Platinized platinum was chosen in order to minimize the influence of impurities on the results. Two different methods were used to prepare platinum + palladium electrodes by the electroless deposition of a submonolayer of palladium on platinized platinum. In the immersion method the electrode was first reduced in hydrogen-saturated ultrapure water for 30 s and then transferred to an oxygen free 10^{-2} M PdCl_2 solution,

Scheme 1.

where it was left for 30 s. Then the electrode was washed with oxygen-free ultrapure water and transferred to the electrochemical cell. The second method consists of the electroless exchange of underpotential deposited copper for palladium. The deposition of copper is carried out at 0.4 V in a 5×10^{-4} M CuSO_4 solution in 0.5 M H_2SO_4 and the coverage is determined directly from the deposition charge Q according to

$$\theta_{\text{Cu}} = Q/2Q_{\text{H}}^0$$

where Q_{H}^0 is the charge involved in the oxidation of a monolayer of hydrogen on the platinum substrate. After deposition, the copper solution was replaced by blank electrolyte, while the potential was held at 0.4 V. The electrolyte was then removed from the cell under an argon atmosphere and an oxygen-free palladium solution was subsequently admitted to the cell at open circuit potential, which rose as a result from 0.4 to 0.85 V. This indicates that copper is fully removed from the surface by exchange with palladium. Palladium electrodes were prepared by electrodeposition of Pd in a 0.05 M $\text{PdCl}_2 + 0.01$ M HCl solution on smooth or platinized platinum. Germanium deposition was carried out by deposition at 0.3 V in a 0.15 mM GeO_2 solution in 0.5 M H_2SO_4 . Before each measurement, potential cycling between 0 and 1.5 V was carried out until a stable voltammogram was obtained. The electrode areas were determined from the oxidation charge for hydrogen desorption in a cyclic voltammogram in 0.5 M H_2SO_4 . All chemicals used were obtained from Merck, p.a. grade. Ultrapure water (18.2 M Ω cm), obtained with an Elga purifying system, was used for preparation of the 0.5 M H_2SO_4 electrolyte solutions. The selectivity of the reaction was determined with RRDE measurements. DEMS measurements were performed with a Leybold Quadruvac PGA 100 mass spectrometer. Details of the experimental set-up are given elsewhere [34]. The products were examined for N_2 ($m/z = 28$) and N_2O ($m/z = 44$).

3. Results

3.1. Preparation of platinum + palladium electrodes

Platinum + palladium electrodes could easily be prepared by the immersion technique. The deposition of palladium takes place by exchange with adsorbed hydrogen according to

It follows from this equation that only half a monolayer can be formed by using the immersion technique. By repeating this sequence, palladium coverages exceeding half a monolayer can be obtained. The cyclic voltammograms recorded after palladium deposition are depicted in Fig. 1(a) and Fig. 1(b). After a single immersion the

Fig. 1. Cyclic voltammograms after electroless Pd deposition by exchange of PdCl_2 with adsorbed hydrogen: (a) clean platinum (---) and after one immersion (—); (b) after one (—), two (····) and three (- · - ·) immersions. Scan rate 20 mV s $^{-1}$. Electrolyte 0.5 M H_2SO_4 .

hydrogen peaks characteristic for platinum at 0.12 V and 0.27 V have decreased considerably and a new hydrogen peak appears at 0.21 V. It is noteworthy that the total charge involved in the hydrogen region as well as the double layer region has decreased slightly. After a second immersion the new hydrogen peak at 0.21 V increases further. The platinum peaks at 0.12 V decrease further and an additional small peak appears at 0.03 V. Surprisingly, this peak grows considerably after the third immersion, and after a fourth immersion the peak height is nearly doubled. Repeated immersions result in a further growth of this peak, while the peak at 0.21 V hardly changes. The peak at low potentials is connected to the presence of multilayer palladium and can therefore be assigned to the dissolution of hydrogen in the palladium bulk. The sudden increase of this peak after the third immersion indicates that during the second immersion palladium is predominantly adsorbed on the platinum substrate and only to a small extent on top of the first layer of palladium. Note that in a single immersion only half a monolayer of palladium can be deposited. The voltammogram for half a monolayer of palladium in Fig. 1(a) is different from both platinum and multilayer palladium and this seems to indicate that palladium is evenly spread on the platinum substrate. However, we cannot exclude the possibility that small islands of palladium atoms are present on the platinum substrate. The platinum substrate used here contains a considerable number of steps and kinks and it is likely that layer growth occurs on these sites. A high density of steps and kinks is expected to favour the spreading of palladium on the platinum substrate.

A disadvantage of this simple immersion technique is that it is not possible to tune the palladium coverage. Therefore, we devised a method to obtain Pd coverages other than 0.5; this consisted of the exchange of dissolved palladium with preadsorbed copper atoms according to

In contrast with palladium, copper can be underpotentially deposited on platinum in submonolayer quantities. Since the exchange between copper and palladium occurs in a 1:1 ratio, also coverages higher than 0.5 can be obtained. The maximum obtainable copper coverage was 0.75 after deposition at 0.4 V. The Pt + Pd electrodes obtained in this way display essentially the same voltammetric response as the electrodes obtained through immersion.

3.2. Germanium underpotential deposition

Germanium was deposited for several minutes from a 0.15 mM GeO_2 solution in 0.5 M H_2SO_4 keeping the potential at 0.3 V. Since germanium displays under potential deposition at this potential, submonolayers can easily be obtained. After electrolyte exchange, a voltammogram is recorded starting in the negative direction; a characteris-

Fig. 2. Cyclic voltammogram recorded after germanium deposition on platinized platinum in 0.5 M H_2SO_4 + 0.15 mM GeO_2 at 0.3 V, followed by electrolyte exchange. First (—) and second (---) cycle, scan rate 20 mV s^{-1} .

tic diagram for platinum is shown in Fig. 2. Besides the Pt-H peaks and the broad Pt-O oxidation wave, two oxidation waves occur at 0.7 V and 0.45 V, in accordance with literature results for germanium underpotential deposition on polycrystalline platinum [35]. At moderate coverages, the oxidation wave at 0.45 V broadens and starts to overlap slightly with the hydrogen area. If the upper limiting potential is set to 0.55 V, the reduction and oxidation waves at 0.45 V remain unchanged, indicating that adsorbed species are involved. Experiments performed with platinum single crystals [36] have shown that the redox behaviour of germanium on platinum is structure sensitive. On Pt(100) a transition occurs at 0.54 V from Ge to GeO , that resides on the surface. A second wave at 0.72 V is ascribed to the subsequent transition from GeO to GeO_2 , which dissolves. In contrast with this, a direct transition from Ge to GeO_2 is reported on Pt(110) and Pt(111) around 0.7 V. On Pt(110) the oxidation broadens considerably at more negative potential for increasing coverages. On the basis of these single crystal studies it can be concluded that the oxidation peak at 0.45 V is connected with the formation of GeO , possibly on Pt(100)-related sites, whereas the second oxidation at 0.7 V is due to formation of GeO_2 from both Ge and GeO . The germanium coverage can be determined by evaluating the total charge involved in both germanium oxidation waves using the equation

$$\theta_{\text{Ge}} = Q_{\text{ox, Ge}} / (nQ_{\text{H}}^0)$$

where Q_{H}^0 is the charge involved in the hydrogen desorption in blank electrolyte. Four electrons are involved in the oxidation of germanium to dissolved germanium dioxide. A maximum coverage of 0.25 was reported for Pt(100) with every germanium atom blocking four hydrogen atoms, whereas for Pt(110) a maximum coverage of 0.4 was found [36]. We found a maximum coverage of 0.35 on platinized platinum, a value which is intermediate between those for Pt(100) and Pt(110). Fig. 2 shows that the coverage of adsorbed hydrogen decreases in the presence

of adsorbed germanium, demonstrating that hydrogen does not adsorb on germanium. The ratio $4(Q_H^0 - Q_H)/Q_{Ge}$ represents the number of hydrogen atoms displaced by a single germanium atom and Fig. 3 shows this displacement ratio as a function of the germanium coverage for platinum. Germanium blocks approximately three hydrogen atoms for low coverages, while values around 2.4 are found for high coverage. It was found in a previous report that germanium displaces two hydrogen atoms on polycrystalline platinum, irrespective of the coverage [35]. For single crystals it was found that on Pt(100) every germanium blocks four hydrogen atoms, while on Pt(110) 2.5 hydrogen atoms are blocked. For low coverages the displacement is intermediate between Pt(100) and (110), and for higher coverages the displacement ratio equals the value for (110). The hydrogen blocking of germanium is different from that of underpotentially deposited copper, which displaces a single hydrogen atom per Cu adatom, irrespective of the coverage. This implies that copper adsorbs on the same site as hydrogen does, whereas germanium takes up a different position.

On palladium, only a single germanium oxidation wave was observed at 0.7 V, as shown in Fig. 4, in agreement with previous results for polycrystalline palladium [37,38]. It is remarkable that the oxidation of germanium is not completed at the beginning of the oxide region, but extends throughout the oxide region. Since no single-crystal data are available in the literature for palladium we have no explanation for the difference with platinum. The maximum obtainable germanium coverage on palladium was 0.20, which is considerably lower than on platinum, 0.35. Bakos et al. [37] found higher coverages after deposition from germanium solutions exceeding 10 mM GeO_2 , whereas we used 0.15 mM GeO_2 . However, they found that rapid alloy formation occurs at the deposition potential of 0.85 V. On the platinum electrodes covered with a submonolayer of palladium the germanium oxidation occurred in an intermediate fashion between platinum and palladium. For low coverages two separate peaks were

Fig. 3. Displacement ratio H/Ge, expressing the number of hydrogen adatoms displaced by a single germanium adatom, as a function of the germanium coverage. The ratio H/Ge is determined from a cyclic voltammogram as shown in Fig. 2.

Fig. 4. Cyclic voltammogram recorded after germanium deposition on electrodeposited palladium in 0.5 M H_2SO_4 + 0.15 mM GeO_2 at 0.25 V, followed by electrolyte exchange. First (—) and second (---) cycle, scan rate $20 mV s^{-1}$.

observed at 0.7 V and 0.45 V, whereas at higher coverages these two peaks merge into one broad peak with a small shoulder.

3.3. Effect of adsorbed germanium on NO_3^- , NO_2^- and NH_2OH reduction

Fig. 5 shows the cyclic voltammograms for both clean and germanium-covered platinum in the presence of 0.1 M KNO_3 . The dashed curve represents the nitrate reduction

Fig. 5. Cyclic voltammogram for clean platinum (---) and platinum covered with a submonolayer of germanium (—) in 0.5 M H_2SO_4 + 0.1 M KNO_3 . Scan recorded in 0.5 M H_2SO_4 (···), scan rate $20 mV s^{-1}$.

on platinum in the absence of germanium. The reaction is inhibited in the potential region below 0.05 V, which is ascribed to the blocking of the surface by adsorbed hydrogen [8,18,19]. It is remarkable that there is no inhibition at all in the presence of adsorbed germanium and the current increases continuously with decreasing potential. The effect of adsorbed germanium on the reduction activity is very great, especially at low potentials. Convection of the solution was found to have no effect on the reaction rate, demonstrating that the rate is kinetically limited and not diffusion limited. The same features were observed for the platinum + palladium surface alloy and for pure palladium electrodes. As with platinum, the nitrate reduction is inhibited for low potentials, whereas the inhibition is absent in the presence of adsorbed germanium. A discussion of the quantitative aspects of the effect of germanium on the reaction rate will be given below.

Germanium also accelerates the reduction of nitrite. As reported earlier [8], this reaction is also inhibited at potentials below 0.05 V on platinum. Surprisingly, germanium has absolutely no activating effect on the reduction of hydroxylamine and as a result the inhibition at low potential is maintained. On the contrary, germanium acts as a site blocker, resulting in a decrease in activity. It has been found by others that germanium is also inactive for the reduction of NO [5].

To compare the effect of germanium on the aforementioned reduction reactions in a more quantitative way, we performed experiments using 10 mM concentrations of the various compounds with and without germanium present on a platinum + palladium electrode. The steady state reduction activity was measured at 0.1 V after 2 min reaction time and the germanium coverage was 0.04. The results are presented in Fig. 6 and the activating effect of germanium for nitrate reduction is clearly shown. The reduction current for NO_3^- on clean platinum is much higher than for nitrate. However, in the presence of germanium, the nitrite reduction current is smaller than for nitrate. It must be considered though that under these conditions the reduction of nitrite is mixed diffusion-kinetically limited, implying that higher rates are possible upon improved mass transport, while the reduction of nitrate and hydroxylamine are kinetically limited. In addition, the rates in Fig. 6 are expressed as microamps per square centimetre, but it should be considered that a decreasing number of electrons is involved in the order nitrate, nitrite, and hydroxylamine. Thus when the current densities are expressed as turnover frequencies (TOFs), the rates for nitrate and nitrite would be approximately equal.

The I - E curves obtained for the various electrodes were investigated for Tafel behaviour. A plot of $\log(I)$ vs. E was found to be linear only for small current densities in the potential region above 0.2 V. However, for higher current densities, which are observed at potentials below 0.2 V, the curve deviates from the straight line that is expected for ideal behaviour.

Fig. 6. Current density for the reduction of 10 mM NO_3^- , NO_2^- and NH_2OH in 0.5 M H_2SO_4 for a clean Pt+Pd electrode and a Pt+Pd electrode covered with a submonolayer of germanium. Current density measured at a constant potential of 0.1 V after waiting 2 min.

The effect of the concentration on the reduction current was also investigated. Fig. 7(a) shows that the steady state reduction current, measured at 0.1 V, increases with the nitrate concentration. If $\log(I)$ is plotted vs. $\log(c_{\text{NO}_3^-})$, shown in Fig. 7(b), a straight line is found. From the slope of this line the reaction order is found to be 0.69 for nitrate according to

$$I \sim (c_{\text{NO}_3^-})^{0.69}$$

The same reaction order in nitrate was found for catalytic experiments on carbon-supported platinum catalysts in the pH range 5 to 8, whereas the reaction order in H^+ was found to be 0.1 [2].

3.4. Effect of electrode composition on nitrate reduction rate

The effect of the electrode material on the nitrate reduction activity is summarized in Fig. 8 for Pt, Pd and Pt + Pd as a function of the germanium coverage. Before the activity measurement, germanium was deposited on the surface at 0.3 V, followed by replacement of the germanium solution by a 0.1 M KNO_3 -containing electrolyte, while keeping the potential at 0.3 V. The activity was determined at 0.1 V after 2 min waiting, to allow the current to reach a semi-steady state. The germanium coverage was determined after the nitrate reduction experiment

Fig. 7. (a) Current density of nitrate reduction, measured at a constant potential of 0.1 V, as a function of the NO_3^- concentration in 0.5 M H_2SO_4 electrolyte. Measurements were performed on a Pt + Pd electrode covered with a submonolayer of germanium. (b) The logarithm of the current density as a function of the logarithm of the NO_3^- concentration.

in a positive scan after electrolyte exchange. Fig. 8 shows that the activity for platinum, expressed in microamps per square centimetre, is linearly related to the germanium

Fig. 8. The current density in 0.5 M H_2SO_4 + 0.1 M KNO_3 , measured at a constant potential of 0.1 V, as a function of the germanium coverage for Pd, Pt, and 0.3 and 0.6 monolayers (ML) of palladium on platinum.

coverage up to $\theta_{\text{Ge}} = 0.25$. For higher germanium coverages the activity drops rapidly to a much lower level. For palladium the rate likewise increased for increasing germanium coverage; however, the current densities observed for palladium are approximately four times lower than for platinum. Surprisingly, the current densities on platinum + palladium electrodes are much higher than on platinum and palladium. The activity is linearly correlated with the germanium coverage in the low coverage region, reaches an optimum and then decreases. In the linear regime, the activity can be expressed as a TOF per germanium adatom when the reduction is assumed to give 100% hydroxylamine with six electrons involved. For platinum, a TOF of 0.5 NO_3^- molecules per germanium atom per second is found, whereas for palladium a value of 0.1 is found. In the presence of submonolayers of palladium, TOFs of 1.0 and 2.5 are found for palladium coverages of 0.3 and 0.6 respectively. However, as shown below, the selectivity toward hydroxylamine deviates from 100% and therefore the true TOFs will be somewhat lower.

3.5. Selectivity measurements with RRDE and DEMS

RRDE experiments were performed to study the effect of the electrode material on the selectivity of the nitrate reduction toward hydroxylamine. From all possible products that are formed in the reduction of nitrate, only nitrite and hydroxylamine are sensitive towards oxidation at the platinum ring electrode, whereas other possible products like NH_4^+ , N_2 and N_2O are not susceptible toward oxidation at the platinum ring electrode. The measurements in Fig. 6 have shown that the reduction rate of nitrite is higher than that of nitrate, so that it is unlikely that nitrite will be formed as a product. This opens the way for the direct detection of hydroxylamine by oxidation at the Pt ring electrode. However, a drawback is the non-ideal oxidation behaviour of hydroxylamine. A typical cyclic voltammogram for hydroxylamine is shown in Fig. 9. The positive scan does not reach a limiting current, but con-

Fig. 9. Cyclic voltammogram recorded at a Pt ring electrode. The Pt disk electrode, covered with a submonolayer germanium, was polarized at 0.1 V in 0.5 M H_2SO_4 + 0.1 M KNO_3 . Rotation frequency 4 rev s^{-1} , scan rate 20 mV s^{-1} .

Fig. 10. Inverse current density as a function of the inverse square root of the rotation frequency measured at a rotating Pt electrode in 0.5M H_2SO_4 + 10mM NH_2OH .

tains a peak at 1.3 V, that originates from hydroxylamine adsorbates formed in the positive scan between 0.4 and 0.8 V. On the contrary, the negative scan does contain a limiting current, that was used for determination of the hydroxylamine selectivity. It is found that the hydroxylamine oxidation current is not proportional to the square root of the rotation frequency ω , indicating that the reaction rate is not diffusion limited, but that a kinetic limitation is involved. Indeed, a linear curve is found when $1/I$ is plotted vs. $1/\sqrt{\omega}$ in Fig. 10, as predicted by Koutecky for a reaction rate that is mixed kinetic-diffusion limited. The reciprocal current can be represented by the following equation:

$$\frac{1}{I} = \frac{1}{I_{\text{kin}}} + \frac{1}{k\sqrt{\omega}}$$

From the slope of the curve k can be determined, enabling the reconstruction of the $I-\sqrt{\omega}$ plot that would have been obtained in the absence of kinetic hindrance. The deviation between the measured and the corrected curve can be substantial for higher current densities. The corrected value was taken to determine the ratio $I_{\text{ring}}/I_{\text{disk}}$ of the ring and disk current. The molar selectivity for hydroxylamine can be obtained according to

$$S_{\text{NH}_2\text{OH}} = \frac{1}{N} \frac{I_{\text{ring}}/n_{\text{ring}}}{I_{\text{disk}}/n_{\text{disk}}}$$

where $N = 0.25$ is the collection factor, I_{ring} and I_{disk} are the ring and disk current and n_{ring} and n_{disk} the number of electrons involved in the reactions at the ring and the disk electrode. Several products can be formed at the disk electrode: N_2 , N_2O , NH_2OH and NH_4^+ , each having a different number of electrons involved in the formation out of NO_3^- . As a result n_{disk} is a weighted average of the values for the various products. However, the selectivities for the various products are not known in advance, and therefore the average value n_{disk} is unknown. An estimated hydroxylamine selectivity can be obtained by assuming that $n_{\text{disk}} = n_{\text{ring}}$. This would hold for the situation that the

selectivity for hydroxylamine is 100%. In this case the molar selectivity can be written as

$$S_{\text{NH}_2\text{OH}} = \frac{1}{N} \frac{I_{\text{ring}}}{I_{\text{disk}}}$$

As our measurements have shown, the major side product is NH_4^+ and therefore the selectivities indicated in Fig. 11 are somewhat underestimated. Another difficulty in the measurement of the hydroxylamine selectivity was the fast deactivation of the ring electrode when it was held at a constant potential. This is probably caused by the slow formation of strongly bonded oxides on the platinum ring. To circumvent this problem the disk electrode was held at a constant potential of 0.1 V to reduce nitrate and a potential scan was made on the ring electrode to ensure that the hydroxylamine detection took place on a freshly activated surface.

Fig. 11 shows the hydroxylamine selectivities obtained after correction of the measured ring currents as a function of the electrode composition. For all electrodes studied, it is found that the selectivity rises with the germanium coverage up to ca. 0.25. For higher coverages, the selectivity remains more or less equal, in spite of a decreasing reduction activity. For platinum the selectivity reaches 50% for $\theta_{\text{Ge}} = 0.25$. In the case of platinum electrodes covered with a submonolayer of palladium approximately equal selectivities are observed. For palladium the slope is higher, and a maximum selectivity of 60% is reached at $\theta_{\text{Ge}} = 0.20$. These results clearly demonstrate that the germanium coverage is a crucial factor for the selectivity and that palladium has a higher tendency to form hydroxylamine than platinum.

DEMS measurements were performed to establish the N_2 and N_2O selectivity as a function of electrode composition. The mass spectrometer was calibrated by oxidation of

Fig. 11. NH_2OH selectivity measured at a constant potential of 0.1 V as a function of the germanium coverage for Pt (●), Pd (○) and Pt + Pd (+) electrodes measured with an RRDE. Ring material was Pt. Electrolyte 0.5M H_2SO_4 + 0.1M KNO_3 .

Fig. 12. DEMS measurement on a Pt+Pd electrode covered with a submonolayer of germanium in 0.5 M H_2SO_4 + 0.1 M KNO_3 , $m/z = 44$ (N_2O^+). Scan rate 20 mV s^{-1} .

a monolayer of adsorbed CO to CO_2 . For platinum, no gaseous products were found, indicating that only hydroxylamine and ammonia are formed. In the case of palladium and platinum + palladium electrodes N_2O was formed, whereas no N_2 was observed. A typical measurement for a Pt + Pd + Ge electrode is shown in Fig. 12; the N_2O production increases along with the reduction current. The maximum of the N_2O production is observed in the positive scan, but this originates from a retarded registration of the gaseous products by the mass spectrometer, as its response time is 3 s. The simultaneous change in current and N_2O response shows that N_2O is a true product of bulk NO_3^- reduction instead of being a product of reduction of an adspecies that is formed at higher potential as observed by Nishimura et al. [31] for NO_3^- reduction on platinum. The selectivity for N_2O was determined after keeping the electrode potential at 0.1 V for 2 min, allowing the current to reach a semi-steady state. The N_2O selectivity was found to be slightly dependent on the reduction potential: decreasing toward higher potentials and remaining equal for lower potentials. Relatively low selectivities, up to 8%, were found for all electrodes studied. The N_2O selectivity was found to increase with germanium coverage.

4. Discussion

Our measurements have shown that the activity of the nitrate reduction on non-activated Pt, Pd and Pt + Pd electrodes is very low, as has been found earlier [8,18]. In addition, the reduction is inhibited at potentials that impose a high hydrogen coverage, which implies that the nitrate

ion is unable to adsorb on the surface if covered with hydrogen, as was also concluded by Horányi and Rizmayer [18,19]. This inhibition is caused by the low adsorption enthalpy of nitrate on platinum and palladium compared to hydrogen. The adsorption strength of nitrate is comparable with that of phosphate, sulphate and perchlorate that all display weak reversible adsorption on these metals. A submonolayer of germanium on the metal surface has a strong enhancing effect on the activity of the nitrate reduction and it is important to note that the inhibition by hydrogen no longer occurs in the presence of germanium, which does not adsorb hydrogen itself. This shows that germanium is directly involved in the adsorption of the nitrate ion on the catalyst surface. The enhancing effect of germanium is also observed for nitrite, although to a lesser extent. The reduction activity on the Pt + Pd + Ge electrode is lower for nitrate than for nitrite, which indicates that the reduction of nitrate to nitrite is the rate determining step. It is remarkable that germanium is not active for the reduction of NO [5] and NH_2OH and due to this inability of germanium it is possible to obtain high hydroxylamine selectivities upon activating the precious metal electrodes with germanium.

The proportional relation between the activity and the germanium coverage shows that germanium is involved in the rate determining step, which is the reduction of nitrate to nitrite. What might the specific action of the germanium atom be in catalysing both the reduction of nitrate and nitrite? Our cyclic voltammograms demonstrate that germanium adatoms on platinum and palladium show oxygen uptake at lower potentials than platinum and palladium, which means that the adsorption energy of oxygen on germanium is considerably higher than on platinum and palladium. In analogy with the sulphate, chlorate and phosphate anions, bonding of nitrate with the noble metal surface is expected to occur via interaction with an oxygen atom. On the basis of the cyclic voltammetry data, this interaction with oxygen is expected to be higher for germanium adatoms than for platinum and palladium.

The strong interaction between germanium and oxygen is important for the reduction of the nitrate molecule. For the dissociation of an N–O bond in an NO_3^- ion to occur, the bond has to be activated by interaction of both the N and O atom with the catalyst surface. Charge has to be transferred from the metal into an antibonding orbital of the nitrate molecule, enabling dissociation. The role of the electrode potential is to increase the Fermi level such that effective charge donation into these antibonding orbitals can occur. A stronger interaction of the catalyst surface with the oxygen atom of the nitrate molecule will automatically lead to a weakening of the N–O bond in the nitrate molecule and therefore facilitate dissociation. On the basis of these arguments, we believe that in the transition state of the dissociation reaction the oxygen atom is bonded to the germanium atom and the nitrogen atom becomes bonded to a platinum or palladium atom, as shown in

Scheme 2. We must also consider that the nitrate ion contains negative charge on the oxygen atoms and a positive charge on the nitrogen atom, which may also influence the bonding of nitrate to the surface. The GeO species that is formed in the dissociation reaction is not stable at the potential of 0.1 V used in our experiments and will be reduced immediately to water. Owing to the low potential, this regeneration reaction is not expected to be rate determining.

A similar effect of germanium has been proposed in the catalytic reduction of crotonaldehyde ($\text{CH}_3\text{--CH=CH--CHO}$) to crotyl alcohol on platinum catalysts with hydrogen as reductor [39]. As a result of its Lewis acidity, germanium is proposed to interact with the lone pairs of the oxygen atom of crotonaldehyde resulting in a weakening of the C=O bond, and hence an increasing reactivity toward hydrogenation of this bond.

A second possible reaction mechanism for the nitrate reduction is dissociation of an N–OH bond in HNO_3 to form GeOH and NO_2^- . However, this possibility can be disregarded since we found that the hydrogenation of hydroxylamine to ammonium is not enhanced by germanium. The hydroxyl group of hydroxylamine is apparently not subject to the specific interaction of the germanium adatom and therefore we expect the same inactivity towards N–OH bond breaking in nitrate.

After the first reduction step to form nitrite, the reaction can proceed in the same way: one of the oxygen atoms of nitrite interacts with the germanium atom, followed by dissociation of the N–O bond to form GeO and subsequently regeneration to Ge, as shown in Scheme 2. After this reduction, NO_{ads} resides on the precious metal surface where it is subsequently hydrogenated. The reduction of nitrite to form adsorbed NO has recently been demonstrated with FTIRS to occur at 0.5 V on single-crystal electrodes [40]. At this potential, in the double layer region, platinum is uncovered with adsorbed hydrogen, which indicates that this species is not necessary in the

reduction of NO_2^- to NO_{ads} . As a consequence this reaction is certainly possible at lower potentials, as used in our reaction. The deoxygenation reactions on the germanium-activated catalyst can be summarized as follows:

It seems somewhat surprising that NO dissociation is not enhanced by germanium. Several factors might explain the inactivity of germanium for this reaction. First, the N–O bond energy in NO is higher than the N–O bond energy in NO_3^- and NO_2^- , discouraging dissociation. Secondly, for dissociation to occur, the oxygen atom of the NO molecule has to interact with germanium, which is energetically unfavourable because of the high M–N–O angle, whereas for nitrate and nitrite this is not so much the case. Possibly germanium only interacts efficiently with negatively charged oxygen atoms as present on nitrate and nitrite. Another possibility is that the residence time of adsorbed NO is very short due to a fast follow-up hydrogenation reaction. The inactivity of germanium for the reduction of NH_2OH might be related to the formation of GeOH in this reaction, as no stable compounds of germanium containing OH groups are reported [41]. If NH_2OH reduction to NH_4^+ was to proceed via dehydrogenation to NO, followed by dissociation of the NO intermediate, the same inactivity of germanium would be expected as for NO reduction itself.

Now we will discuss the effect of electrode composition on the activity pattern. It is remarkable that the highest TOFs per germanium atom are found on platinum + palladium + germanium electrodes, whereas platinum and palladium display much lower TOFs. The question is what the characteristic properties of this alloy are that cause the higher turn over frequencies with respect to Pt and Pd. We

Scheme 2.

should consider electronic effects as a possible cause for the observed activities of the alloy. Recent theoretical work has suggested that electronic effects are present when mixing platinum and palladium. Density functional theory calculations were carried out for a Pt overlayer on Pd, and vice versa, as well as for a single Pt atom in a Pd matrix, and vice versa [42]. According to these authors, a good measure for the effect of alloying on the reactivity is the shift of the d-band centre. For complete Pt and Pd overlayers hardly any electronic effect was found, whereas for the isolated atoms in the substrate matrix shifts of the d-band centre of +0.19 eV and –0.17 eV respectively were found. This difference between a full overlayer and an isolated atom placed in a matrix suggests that the electronic effect on a metal as a result of alloying depends on its content in the alloy. A high electronic effect on a metal is expected when its content in the alloy is low and a small electronic effect is expected when its content in the alloy is high.

A shift of the d-band centre caused by alloying has a clear effect on the reactivity; an upshift of the d-band centre, as expected for Pt in a Pt + Pd alloy, implies a stronger interaction of the metal atom with for instance adsorbed CO, due to an increased interaction between the metal d-band with the $2\pi^*$ orbitals of the CO molecule, that lie above the Fermi level [42,43]. For example, whereas theory found a d-band centre shift of –0.47 eV for an overlayer of palladium on Ru [42], experimentally the CO desorption was found to shift 120 K to lower temperature for Pd on Ru(0001), corresponding to a decrease of the CO binding energy of 30 kJ mol^{-1} [43]. The calculated electronic effects in the case of Pt + Pd are lower [42], but are nevertheless expected to have a substantial effect on bonding properties.

However, one cannot straightforwardly translate these results to the germanium-activated reduction of nitrate to nitrite, which is the rate determining step. The reaction rate of this step is determined by the activation Gibbs energy ΔG_{act} , the energy difference between the ground state and the transition state. The transition state that we have proposed in Scheme 2 is bonded with oxygen to germanium and with nitrogen to a precious metal atom in the surface. As a result the energetics of the reaction can be influenced via both the M–N bond and the Ge–O bond. The M–N interaction can be different for Pt and Pd and can therefore affect the activation energy and thus the reaction rate. In addition, the electronic effects on Pt and Pd due to alloying will also affect the metal–N interaction directly.

The predicted downshift of the d-band centre for Pd in a Pt + Pd alloy implies a weaker interaction of the Pd d-band with antibonding orbitals of the nitrate molecule just above the Fermi level, like the situation for adsorbed CO [42]. This interaction results in a bond between the metal and the nitrogen atom, whereas filling of the antibonding nitrate orbital at the same time weakens the N–O bonds in the nitrate molecule. It is expected that this interaction is

dominant in the bonding between the metal and the nitrate ion and more important in enabling breaking of the N–O bond in nitrate. Thus the downshift of the d-band centre for Pd upon alloying results in a weaker interaction of Pd with the NO_3^- ion and therefore the activation energy for the reaction increases, resulting in a lower rate. In the case of platinum, the opposite holds; the predicted upshift of the d-band centre for Pt implies a stronger interaction between the d-band and the antibonding orbitals of the nitrate molecule. This strengthening of the M–N interaction in the ground state corresponds with a weakening of the N–O bond and, therefore, the activation energy for the reaction is lowered. As a result we would expect an increased activity of platinum upon alloying with palladium and a decreased activity of palladium upon alloying with platinum. Since both effects counteract, we might expect a zero effect on the reaction rate upon alloying of Pt and Pd. However, this is not necessarily true. We should recall that the reaction occurs on M–Ge pairs on the surface. Our experiments have shown that for increasing Pd coverage the current density per germanium adatom increases. Theory predicts that Pt becomes more active for increasing Pd content, whereas Pd itself recovers toward the value for pure Pd. This suggests that the observed increase of current density upon adding Pd to Pt originates from Pt + Ge ensembles on the surface, since Pd + Ge ensembles in the surface alloy are expected to be less active than Pd + Ge ensembles on pure Pd electrodes.

This model can also explain the shift of the observed activity optimum to lower Ge coverage for increasing Pd content. In the case of Pt + Pd the Pt surface concentration decreases for increasing Pd coverage, resulting in a lower density of active sites on the surface. A Pt atom becomes activated in the presence of a Ge adatom on a nearby site. With the surface compositions Pd:Pt = 30:70 and 60:40 used in this study, a germanium atom that is randomly deposited on the surface will have one or more Pt neighbours that are activated for nitrate reduction as a result. However, since the Pt surface concentration is lower than for pure Pt, less Ge will be needed to activate all Pt atoms in the surface and additional Ge deposition can block Pt sites, resulting in a decrease of the activity. This explains the shift of the optimum activity toward lower germanium coverages increasing Pd content in the surface. For a further increase in the palladium coverage than the coverages studied here, we expect a further shift of the optimum to lower germanium coverage.

The optimum that is observed in the activity curve for pure platinum at a germanium coverage of 0.25 has a different cause. The reduction of NO_3^- can be divided into two parts: first, the successive deoxygenations of nitrate to nitrite and NO, which require germanium; second, the hydrogenation of NO to hydroxylamine that proceeds on the precious metal. In the case of platinum the activity is proportional to the germanium coverage up to $\theta_{\text{Ge}} = 0.25$ and drops for higher coverages. For increasing germanium

coverage the amount of available precious metal surface for the reaction decreases. Both the deoxygenation reaction, as shown in Scheme 2, and the hydrogenation require precious metal sites and one of these two reactions is the rate determining step above $\theta_{\text{Ge}} = 0.25$.

The composition of the precious metal surface not only influences the M–N interaction but also the Ge–O interaction. Our experiments show that the interaction of germanium with platinum differs from that with palladium, as indicated by the presence of an oxidation wave at lower potential in the cyclic voltammogram. The different interaction with germanium is also expressed by the formation of intermetallic compounds after germanium deposition on palladium [37,38], whereas no alloy formation is known for platinum. As the interaction between Ge and the metal is different, this can also hold for the Ge–O interaction. It could be possible, for example, that whereas Pt is necessary for a beneficial interaction with the nitrogen atom of nitrate, Pd induces a beneficial interaction between germanium and the oxygen atom of nitrate. This might further enhance the activity of the Pt + Pd alloy with respect to pure Pt and Pd.

The selectivity measurements for hydroxylamine give a different picture than the activity measurements. We found for all electrode compositions that the selectivity for hydroxylamine increases with increasing germanium coverage. The slope of the selectivity plots for low coverages in Fig. 11 is about the same for Pt and Pt + Pd and is higher for Pd. Platinum is less selective for hydroxylamine than palladium. Comparison of the activity plots in Fig. 8 with the selectivity plots in Fig. 11 shows that the selectivity remains constant for germanium coverage exceeding 0.25 while the activity decreases. There appears to be no clear correlation between the activity of the reaction and the selectivity for hydroxylamine. However, there seems to be a distinct correlation between the germanium coverage and the hydroxylamine selectivity. We can explain this correlation in the following way. The formation of hydroxylamine proceeds by hydrogenation of adsorbed NO intermediates to hydroxylamine according to

The formation of the other main product ammonia can proceed via different pathways: via dissociation of adsorbed NO or via dissociation of an adsorbed NH_2OH intermediate according to

It is well known that dissociation of the N–O bond is strongly subject to the ensemble effect, thus requiring large metal ensembles for dissociation, while hydrogenations are not. Thus, with increasing germanium coverage dissociation of the N–O bond will be suppressed, leading to the

observed increase in hydroxylamine selectivity. In fact, it is known that the selectivity for the catalytic hydrogenation of NO with hydrogen on precious metals is increased by the presence of carbon monoxide or sulphur coadsorbates [23].

As to the production of N_2O , our DEMS measurements have shown that some N_2O is found for palladium-containing electrodes, whereas platinum does not display N_2O formation. The gaseous product N_2O can be formed via two possible reaction routes. The most frequently reported mechanism [21–28] consists of a single electron reduction of the NO molecule, followed by dimerization and N_2O formation according to

Some authors have proposed HNO_{ads} instead of NOH_{ads} as an intermediate in the formation of N_2O [21–23,28]. So far, no direct evidence has been presented for the existence of NOH or HNO as an intermediate in the N_2O formation. However, we concluded in a previous paper [44] that in the potential region between 0.4 and 0.8 V, N_2O is formed via dissociation of NO, followed by recombination of NO with N. This conclusion was supported by the findings from ultra high vacuum experiments that NO dissociates at room temperature on Pt(100), Pt(310) and Pt(410) [45–47]. The NO dissociation mechanism is, in principle, also possible at lower electrode potentials, since we expect that lower potentials further enhance NO dissociation, due to an increased donation of charge in the antibonding $2\pi^*$ orbitals of the NO adspecies.

The formation of N_2O can be influenced by several factors. Both NO_{ads} and N_{ads} have to be present on the surface in each other's vicinity. Not only can there be a difference in the dissociation ability of the two metals, but also in the rate of hydrogenation of adsorbed NO and N. The low selectivity towards N_2O shows that the rate of hydrogenation is substantially larger than the association rate of N and NO to form N_2O . This might be related with the fact that the reduction of nitrate to nitrite is rate determining, which implies that the coverage of intermediates should be low. A low intermediate coverage suppresses N_2O formation. On the other hand, the reduction potential of 0.1 V imposes a high hydrogen coverage, which enhances reduction of the intermediates that are necessary for N_2O formation. Previous work of Hörold et al. [1] on nitrite reduction at pH = 6 has shown that Pd gave a 99.9% selectivity to N_2 , whereas Pt gave approximately 60% N_2 and 40% NH_3 . This finding supports the idea that the rate of hydrogenation is higher for platinum than for palladium. In our situation this results in a lower coverage of NO and N intermediates and thus a lower N_2O selectivity. The increase in N_2O selectivity with increasing germanium coverage on Pt + Pd electrodes is in accordance with this; an increasing germanium coverage results

in a higher intermediate coverage due to an increased rate of nitrate reduction. As a result the N_2O selectivity will increase, as has been observed.

5. Conclusions

Underpotentially deposited germanium enhances strongly the reduction rate of nitrate on Pt, Pd and Pt electrodes modified with a submonolayer of Pd. The reduction of nitrite is also enhanced, whereas germanium is inactive for NO and hydroxylamine reduction. The inhibition of the reaction at low potentials that is known for Pt and Pd is completely absent for germanium-modified electrodes. Germanium is involved in the rate determining step, which is the reduction of nitrate to nitrite and its role is to bind to the oxygen atom of nitrate.

The current densities for nitrate reduction depend strongly on the composition of the electrode surface. The activities increase in the order palladium, platinum and platinum + palladium. In all cases the activity increases with the germanium coverage. The higher activities for Pt + Pd electrodes can be understood in terms of changes in the electronic structure of the metals as a result of alloying. Pt–Ge sites become more active in the presence of palladium whereas Pd–Ge sites become less active in the presence of platinum.

The selectivity toward hydroxylamine increases for increasing germanium coverage. Palladium has a higher tendency to form hydroxylamine than platinum and platinum + palladium electrodes. For increasing germanium coverage the size of the available metal ensembles decreases, which suppresses N–O dissociative reactions that generate N_2O and NH_4^+ . No gaseous products were observed for Pt, whereas for Pt + Pd and Pd N_2O selectivities up to 8% were found.

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