Mechanistic Study on the Electrocatalytic Reduction of Nitric Oxide on Transition-Metal Electrodes

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The mechanism of the electrochemical reduction of nitric oxide (NO) on a series of metals (Pd, Rh, Ru, Ir, and Au) has been studied, both for the reduction of adsorbed NO and for the continuous NO reduction. All metals show a high selectivity to N₂O at high potentials and a high selectivity to NH₃ at low potentials, whereas N₂ is formed at intermediate potentials (although gold forms mainly N₂O, and very little NH₃). The behavior of the transition metals is very similar to that of platinum, suggesting that the reaction schemes are essentially the same (especially the potential windows in which the products are formed are similar). The mechanism that leads to N₂O is believed to involve the formation of a weakly adsorbed NO dimer intermediate, similar to recent suggestions made for the gas-phase reduction of NO. The reduction of adsorbed NO leads only to formation of NH₃ and not to N₂O or N₂. The electrochemical measurements suggest that NH₃ formation involves a combined electron-proton transfer in equilibrium, followed by a nonelectrochemical rate-determining step. The formation of N₂, produced at potentials between the formation of N₂O and NH₃, most likely takes place by the reduction of previously formed N₂O.

Key Words: NO reduction; electrocatalysis; transition metals; differential electrochemical mass spectroscopy.

1. INTRODUCTION

The reduction of nitric oxide (NO) is an important reaction in environmental catalysis, since it determines the performance of wastewater treatment catalysts for nitrate, nitrite, and NO removal (1), and the scrubbing of NO from gas streams (2). Nitric oxide reduction has also been investigated as the cathodic reaction in fuel cells (3), because of its high reduction potential.

The electrodes employed in the electrochemical reduction of NO are usually noble transition metals, because they are the most active catalysts (4) and show the least formation of metal oxides. Palladium has the highest activity and selectivity to N₂ (3), and therefore is the catalyst of choice. Other metals form, depending on potential, undesirable products such as N₂O and/or NH₃.

There is as yet little or no mechanistic insight into why palladium is the best catalyst in the selective reduction of NO to N₂. The only metal for which reasonably detailed mechanistic information is presently available is platinum (5).

Summarizing the results of our previous publication (5), we found that there are two major reaction paths for NO reduction on platinum, one at high potentials (0.3–0.7 V vs RHE) which leads to nitrous oxide (N₂O), and one at low potentials (0–0.3 V) which leads mainly to ammonia (NH₃). The formation of N₂O was observed to take place only in the presence of NO in the solution. From the Tafel slope, the pH dependence, and the kinetic order in NO solution concentration, the following reaction scheme was suggested:

\[ \text{(aq)} + \text{NO} \rightarrow \text{NO}_{\text{ads}} \quad \text{fast} \]
\[ \text{NO}_{\text{ads}} + \text{NO} \rightarrow \text{HNO}_{\text{ads}} \rightarrow \text{unknown intermediate} \rightarrow \text{NH}_4^+ + \text{H}_2\text{O} + \text{*} \quad \text{fast} \]

where * denotes a free site at the surface. The most remarkable feature of this scheme is the rate-determining step, in which we proposed a surface-bonded NO to combine with a solution-phase NO. This latter step may also be interpreted as a weakly bonded N₂O, as long as its concentration is first-order in solution NO to explain the experimentally observed first-order kinetics in NO solution concentration.

The reaction scheme suggested for the formation of NH₃ proceeds through the reduction of adsorbed NO₃⁻:

\[ \text{NO} \rightarrow \text{NNO}_{\text{ads}} \quad \text{fast} \]
\[ \text{NNO}_{\text{ads}} + \text{H}^+ + \text{e}^- \rightarrow \text{HNO}_{\text{ads}} \quad \text{fast} \]
\[ \text{HNO}_{\text{ads}} \rightarrow \text{unknown intermediate} \rightarrow \text{NH}_4^+ + \text{H}_2\text{O} + \text{*} \quad \text{fast} \]

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The reduction of nitric oxide (NO) on a series of metals (Pd, Rh, Ru, Ir, and Au) has been studied, both for the reduction of adsorbed NO and for the continuous NO reduction. All metals show a high selectivity to N₂O at high potentials and a high selectivity to NH₃ at low potentials, whereas N₂ is formed at intermediate potentials (although gold forms mainly N₂O, and very little NH₃). The behavior of the transition metals is very similar to that of platinum, suggesting that the reaction schemes are essentially the same (especially the potential windows in which the products are formed are similar). The mechanism that leads to N₂O is believed to involve the formation of a weakly adsorbed NO dimer intermediate, similar to recent suggestions made for the gas-phase reduction of NO. The reduction of adsorbed NO leads only to formation of NH₃ and not to N₂O or N₂. The electrochemical measurements suggest that NH₃ formation involves a combined electron-proton transfer in equilibrium, followed by a nonelectrochemical rate-determining step. The formation of N₂, produced at potentials between the formation of N₂O and NH₃, most likely takes place by the reduction of previously formed N₂O.
Apparently, the rate-determining step in this scheme involves a breaking of the N-O bond.

Some nitrogen (N₂) is formed in the intermediate potential region (0.2–0.4 V vs RHE), but we did not discuss the mechanism of its formation in our previous work. However, given the fact that N₂ is the most desirable product and that its selective formation is apparently quite sensitive to the nature of the electrode surface, more detailed investigations into the N₂ formation pathway are clearly of interest.

In this paper, we study the metal dependence of the electrocatalytic reduction of NO. The metals investigated are Ru, Rh, Ir, Pd, Pt, and Au. We will show that the two separate pathways for N₂O and NH₃ exist for all these electrodes, and we will argue that they take place via reaction schemes similar to those on Pt. Most importantly, we will present more detailed results on the formation of N₂ on the different metal electrodes. From these results, we will suggest that the key intermediate in the N₂ formation is N₂O rather than surface-bonded N_ads.

2. EXPERIMENTAL

Rotating disk electrodes (RDEs) were used in a homemade setup. Platinum, palladium, and gold were pretreated by repeated cycling in the hydrogen and oxygen evolution region in 0.1 M H₂SO₄, after which the electrolyte was replaced with clean electrolyte. Rhenium, iridium, and ruthenium were electrodeposited from the metal trichloride solution at 0.1 V (vs RHE) onto disk electrodes made from the same metal prior to a measurement in the electrochemical cell, and traces of chloride were removed by thorough rinsing while the electrode was kept at −0.2 V. Iridium was deposited at ca. 80°C. The blank cyclic voltammogram of the disk electrode was compared to that of a flag electrode, to check for the absence of contaminations and surface oxides.

Differential electrochemical mass spectroscopy (DEMS) electrodes consisted of platinum gauzes with the metal of interest electrodeposited onto it, except for gold, in which case a gold gauze was used. The electrodes were pretreated in the same manner as the rotating disk electrodes.

Adsorbate studies were performed on a flag electrode of the bulk concentration of NO, the selectivity to N₂O was 100%.

In this equation, λ is the number of electrons transferred per NO molecule from the Levich equation:

\[
\frac{1}{I} = \frac{1}{I_{\text{kin}}} + \frac{1}{0.62nFC^*D^{2/3}v^{-1/6}o^{1/2}}.
\]

In this equation, \( I_{\text{kin}} \) is the kinetic limited current density, \( n \) is the number of electrons per NO molecule, \( C^* \) is the bulk concentration of NO, \( D \) is the diffusion constant of NO in water, and \( v \) is the kinematic viscosity. The following values were used: \( C^* = 1.40 \times 10^{-6} \text{mol cm}^{-3} \), \( D = 2.5 \times 10^{-5} \text{cm}^2 \text{s}^{-1} \), and \( \nu = 8.5 \times 10^{-3} \text{cm}^2 \text{s}^{-1} \). The kinetically limited current cannot be determined exactly at potentials where several reactions occur simultaneously, and was therefore only determined in potential windows where the selectivity to N₂O was 100%.

On all metals the potential window in which NO reduction takes place can be divided into three regions: at high potentials (0.4–0.7 V) N₂O is the main product, N₂ is formed with varying selectivity at intermediate potentials (0.2–0.4 V), whereas NH₃ is the main product at low potentials (0–0.3 V). It is known that hydroxylamine (H₂NOH)
can be formed as a minor product at low potentials (0 V) on platinum (11); however, as the number of electrons per NO molecule at low potentials is close to 5, indicating that NH$_3$ is the major product, and a quantitative determination is quite complicated, we will exclude H$_2$NOH formation from our discussion. Figure 1 shows the selectivity to N$_2$O and N$_2$ of the six metals studied in this paper, as obtained from the DEMS measurements. At high potentials both the electrical current and the DEMS signal become very small, resulting in a large experimental uncertainty, reflected in some of the selectivities reported being higher than unity. The amount of N$_2$ produced varies with the metals used, as do the boundaries of the three potential regions. The selectivity to N$_2$ on palladium, for instance, is very high and covers a larger potential window than on the other metals. As will be further discussed below, we believe that the similarities in selectivity are an indication that the reaction mechanism is similar on all transition metals. The results will be discussed in three separate sections, according to the three potential regions.

### 3.2. Reduction of NO to NH$_3$

The reduction of NO to NH$_3$ can be studied by continuous NO reduction in the potential region 0–0.3 V, or by the reduction of an NO adsorbate layer in a clean NO-free electrolyte. In the latter case, information about the rate-determining step in the overall reaction scheme can be obtained relatively easily by measuring a so-called Tafel plot, which gives the potential dependence of the overall reaction rate. Under the assumption that the reduction rate is first- (12) or second-order (13) in the adsorbate coverage, it can be shown that a plot of the peak potential (i.e., the potential at which a maximum current is measured during the reductive stripping voltammetry) vs the logarithm of the scan rate is equivalent to a Tafel plot. Lateral interactions between NO molecules are neglected, as the coverage at the peak potentials is relatively low (ca. 0.2, i.e., in approximately half of the maximum coverage).

Table 1 summarizes the slopes of the Tafel plots obtained for the NO adsorbate reduction on Pt, Rh, Ir, and Ru in acidic and alkaline solution. The maximum coverage of NO is in all cases similar (0.4–0.5 monolayer), and similar to values reported for single-crystal surfaces (14–16). Pd and Au are not included, as in the case of palladium the peak potential overlaps with the hydrogen evolution reaction, and in the case of gold because no NO adsorbate layer is formed. As an example a typical Tafel plot for the NO reduction of Ru in acidic solution is shown in Fig. 2. A value of ca. 60 mV/dec indicates the existence of an electron-transfer

![FIG. 2. Dependency of the peak position of the NO reduction with the scan rate on ruthenium in 0.1 M H$_2$SO$_4$; surface at maximum NO coverage.](image)

<table>
<thead>
<tr>
<th>Tafel Slope of the Adsorbed NO Reduction, in mV/dec</th>
<th>Pt</th>
<th>Rh</th>
<th>Ir</th>
<th>Ru</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M H$_2$SO$_4$</td>
<td>54 ± 3</td>
<td>70 ± 3</td>
<td>76 ± 5</td>
<td>66 ± 10</td>
</tr>
<tr>
<td>0.1 M KOH</td>
<td>58 ± 3</td>
<td>106 ± 3</td>
<td>88 ± 5</td>
<td>63 ± 1</td>
</tr>
</tbody>
</table>

![FIG. 1. Selectivity of the reduction of NO in the solution. Solution saturated with NO, (a–f) 0.1 M H$_2$SO$_4$, (g–l) 0.1 M KOH, (a, g) Pt, (b, h) Ru, (c, i) Ir, (d, j) Rh, (e, k) Pd, (f, l) Au. Solid lines and filled circles, selectivity to N$_2$O; dotted lines and rectangles, selectivity to N$_2$. The error bars given in (a) and (g) also apply to the other figures.](image)
3.3. Reduction of NO to N₂O

The Tafel slopes of the NO reduction to N₂O on the various metals, as derived from the kinetic limiting current of the RDE measurements, are given in Table 3. The Tafel slope was found to be close to 120 mV/dec in three cases: platinum and ruthenium in acidic solutions, and iridium in alkaline solutions. This implies that the first electron-transfer step is rate-determining in these three cases. In all other cases the Tafel slope was found to be significantly higher than 120 mV/dec, indicating that the rate-determining step is a chemical step prior to the electrochemical steps. The values given in Table 3 are significantly different from those given by Colucci et al. (8) (78, 116 and 408 mV/dec on respectively Pd, Rh, and Ru in acidic solutions), as determined from voltammetry at stationary electrodes. Since reactions with mass-transport limitations should preferably be studied at rotating electrodes, and because we took extreme care to avoid surface oxidation of the less noble transition metals (17, 18), we believe our values reflect more accurately the "real" Tafel slopes.

Colucci et al. (8) suggested that the mechanism of the NO reduction to N₂O on platinum, palladium, rhodium, and ruthenium includes only species which are adsorbed at the surface. Gootzen et al. (19) suggested for platinum electrodes that the key step in the N₂O formation is the dissociation of NO, which also implies that only adsorbed species are involved in the formation of N₂O. However, we find that NO from the solution must be involved in the reaction scheme for two reasons. The first reason is that the potential window in which the reduction of adsorbed NO takes place (0–0.3 V) is much lower than the potential window considered here (0.4–0.7 V). Second, N₂O is not produced during the reduction of adsorbed NO. Since the only difference between the reduction of adsorbed NO and the reduction of NO at high potentials is the presence of dissolved NO, solution NO must be directly involved in the reaction sequence to produce N₂O. Since these observations hold for all metals studied here, we suggest that the formation of an (NO)₂ dimer as the rate-determining step, as has been proposed for platinum (5), is also valid for the other metals. The higher Tafel slopes observed for some of the systems could be explained by assuming that the first electron transfer shifts to a stage after the rate-determining step, and the surface dimerization reaction becomes the rate-determining chemical step.

### Table 2

<table>
<thead>
<tr>
<th>Solution</th>
<th>E&lt;sub&gt;peak&lt;/sub&gt;</th>
<th>RDE</th>
<th>Pt</th>
<th>Pd</th>
<th>Rh</th>
<th>Ir</th>
<th>Ru</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M H₂SO₄</td>
<td>0.21</td>
<td>0.25</td>
<td>0.11</td>
<td>0.17</td>
<td>0.102</td>
<td>0.18</td>
<td>0.14</td>
</tr>
<tr>
<td>0.1 M KOH</td>
<td>0.18</td>
<td>0.2</td>
<td>0.15</td>
<td>0.15</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*<sup>a</sup> Measured on a gold electrode with a thin (2–3 ML) palladium overlayer, and at 1 mV/s.

*<sup>b</sup> There is no change in the selectivity.

### Table 3

<table>
<thead>
<tr>
<th>Solution</th>
<th>Tafel Slopes of the NO Reduction between 0.4–0.7 V in a Solution Saturated with NO, in mV/dec</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M H₂SO₄</td>
<td>117 ± 4</td>
</tr>
<tr>
<td>0.1 M KOH</td>
<td>322 ± 23</td>
</tr>
</tbody>
</table>
It is unclear whether dissolved NO reacts directly from the solution, or from a weakly adsorbed state at the surface. Either possibility will lead to the same N\(_2\)O formation kinetics and the same adsorbate reduction kinetics, since this weakly adsorbed NO will desorb when the solution is replaced with clean electrolyte.

Finally, we note that reaction scheme [1] predicts the rate of the reaction to be first-order in the concentration of solution NO, because the surface is always covered with NO\(_{ads}\) and hence only the amount of NO(aq) changes with the NO concentration. A kinetic order of unity has indeed been observed on platinum in acidic solutions. Due to the large error bars in the determination of the kinetic limited current (Table 3), we have not pursued these measurements for the other systems, but both DEMS measurements and an analysis of the RDE data for palladium, using the procedure suggested by M arkovic et al. (20), suggest a kinetic order close to one.

### 3.4. Reduction of NO to N\(_2\)

As mentioned in the Introduction, there is only scant mechanistic information available on the formation of N\(_2\) from the electrocatalytic NO reduction. However, it seems that one may assume two alternative working hypotheses. The first hypothesis is that N\(_2\) is formed by the reduction of N\(_2\)O, i.e., in series with the N\(_2\)O formation. This is a known reaction in electrocatalysis that has been studied by a number of authors (21–25). The second hypothesis is that N\(_2\) is formed by a reaction of surface species (such as NO\(_{ads}\), N\(_{ads}\), NOH\(_{ads}\), or other yet unidentified species), i.e., in parallel with the N\(_2\)O formation.

If the first hypothesis would be true, i.e., N\(_2\) would be formed from the reduction of N\(_2\)O, one would expect a correlation between N\(_2\)O reduction activity and the selectivity toward N\(_2\) in the reduction of NO. Figure 3 gives the activity of the various metals in the N\(_2\)O reduction in alkaline solutions. The activity found in alkaline solutions increases in the order Au < Ru < Ir < Rh ≈ Pt < Pd, with the onset of the reaction being 0, 0.1, 0.4, 0.45, 0.45, and 0.6 V, respectively (Fig. 3). This ordering is comparable to the production of N\(_2\) in alkaline solutions shown in Fig. 1, the potentials of the onset showing a reasonable agreement with the onset of the N\(_2\)O reduction (Au ≈ Ru < Pt < Rh < Ir < Pd, the onset of the reaction being 0, 0.45, 0.45, 0.55, and 0.6 V, respectively). Iridium is more active in the N\(_2\) production than suggested by its N\(_2\)O reduction activity, which makes it an exception.

To compare the activity and selectivity in acidic solutions is more problematic, since the N\(_2\)O reduction is known to be very sensitive to the competitive adsorption of SO\(_4^{2-}\) anions (21, 22). The measurements should therefore be carried out in an HClO\(_4\), since these metals can reduce ClO\(_4^-\) to Cl\(^-\) (26), which is known to adsorb strongly. In general, however, the series for the N\(_2\) production from NO in acidic solutions is similar to the series of the N\(_2\)O reduction activity. Gold, for instance, is inactive in both cases, followed by iridium, rhodium, and ruthenium, whereas palladium is very active. Platinum does not fit in the series, as the rate in N\(_2\)O reduction in both HClO\(_4\) and H\(_2\)SO\(_4\) is higher than on palladium, whereas palladium is more active in the selective formation of N\(_2\) from NO.

The qualitative agreement between the N\(_2\)O reduction activity and the selectivity in the NO reduction to N\(_2\) is a strong argument in favor of the "N\(_2\)O serial pathway." Also the fact that no N\(_2\) is produced during the NO adsorbate reduction in the absence of NO in the solution disfavors the "adsorbate parallel pathway." In fact, the NO adsorbate is generally not reactive at all at potentials for which N\(_2\) is produced during the continuous NO reduction.

### 3.5. Mechanistic Issues and Comparison to Gas-Phase Reduction of NO

#### 3.5.1. NO dissociation

As noted in Section 3.2, it is known that NO may dissociate at room temperature on metals such as Rh, Ir, and Ru, whereas it is generally adsorbed molecularly on Pt and Pd. An overview of the NO dissociation behavior on metal surfaces was recently given by Brown and King (27). At higher coverages, the NO dissociation process may be inhibited because of the lack of adjacent empty sites or because strong lateral interactions between the dissociation products render the molecular state more stable. The necessity of having empty surface sites for triggering NO dissociation has been shown recently in detailed UHV surface science studies of NO reactivity on Rh (28, 29). In most UHV studies, the N\(_{ads}\) species is considered as an intermediate in the N\(_2\)O, N\(_2\), and NH\(_3\) formation. Hence, we will have to consider the possibility of NO dissociation on Rh, Ru, and Ir in the electrochemical context.
It is difficult to obtain any direct evidence for NO dissociation from electrochemical experiments. Gootzen et al. (19) suggested that the observation of an oxide reduction peak after NO adsorption on Pt at open-circuit potential (OCP) was due to the reduction of the adsorbed oxygen formed from NO dissociation. However, we showed recently that the peak is observed only on roughened electrodes (5), suggesting quite a different mechanism, and in keeping with the gas-phase situation where NO adsorbs molecularly on Pt at room temperature. Interestingly, an oxide reduction peak is observed, at ca. 0.5 V, on a smooth flame-annealed Rh electrode after adsorption of NO at OCP (ca. 0.8 V), as illustrated in Fig. 4. When NO is adsorbed at 0.45 V, no oxide reduction peak is observed, and a much higher NO reduction charge is measured (see Fig. 4), indicating a higher coverage of NO under these conditions. However, these observations still do not prove the occurrence of NO dissociation. On Rh, surface oxides are known to be more stable than on Pt, and therefore on Rh, certainly at a potential of 0.8 V, a more competitive co-adsorption of oxides and NO is expected than on Pt. The peak at 0.5 V can hence be explained by the reduction of co-adsorbed oxides, which are not formed by NO dissociation, but similar to the formation of surface oxides on roughened platinum.

An interesting observation to be made from Fig. 4 that could point toward the role of NO dissociation is the fact that the apparently lower coverage of NO formed at 0.8 V starts to be reduced at a significantly less negative potential than a saturated layer formed at 0.45 V. This could mean that the surface sites that become available after reduction of the surface oxides trigger the NO dissociation. The saturated NO adlayer is not reactive or is much less reactive at these potentials, as is also evidenced by the observation of a stable NO stretching peak in FTIR experiments of NO on single-crystal Rh (14). A similar—though less pronounced—shift in the reduction peak is observed when a nonsaturated NO adlayer is formed at 0.45 V by dosing from a less concentrated NO solution. These observations are in stark contrast with the coverage effects observed for the NO adsorbate reduction on Pt, where no such positive shifts in reduction potential with lower NO coverage are observed.

If NO dissociation plays a role on Rh, Ir, and Ru, then the observed Tafel slopes for the adsorbate reduction may suggest that it is not the rate-determining step in the ammonia formation. However, it should be realized that it is not a priori clear to what extent the NO dissociation has to be considered as potential or even pH dependent, as the overall NO dissociation process at electrochemical interfaces involves protonation of the oxygen:

\[
\text{NO} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}. \quad [3]
\]

It is obvious that the above experiments are not decisive in pinning down the possible role of NO dissociation on the less-noble transition metals Ru, Ir, and Rh. More direct spectroscopic information is clearly needed.

The results in Fig. 4 do suggest, however, that at high NO coverages, which seems the relevant surface condition for the continuous NO reduction experiments, NO dissociation is not likely to take place at potentials above 0.3 V. Hence, it is suggested that NO dissociation does not play a significant role during N2O and N2 formation. Evidence for alternative mechanisms, in relation to gas-phase and UHV experiments, is discussed in the next two sections.

3.5.2. NO dimerization. The reaction scheme [1] suggested for the N2O formation in Pt involves the formation of a (protonated) surface-bonded (NO)2 dimer. The very similar conditions under which N2O is formed on the other metals is suggestive of a more general applicability of this reaction scheme.

In fact, there is a growing surface science literature on the formation of NO dimers on silver, copper, molybdenum, tungsten, and palladium, and it has also been suggested to exist on platinum and rhodium (27). It has been shown that silver is the key intermediate in the N2O formation. NO is adsorbed weakly on Ag (27). Apparently, strongly adsorbed NO is not required for the formation of the NO dimer or the production of N2O. Theoretical DFT studies have also supported the existence of the NO dimer on Ag (30).

Even though we are not aware of similar UHV-based evidence for the NO dimer on Au, the generic similarity between Ag and Au suggests that it is reasonable to assume a similar N2O formation mechanism on Au. This would certainly explain the unique selectivity of Au in reducing NO to N2O as observed in our electrochemical study. Silver in fact has a similarly high selectivity toward N2O in the electrochemical NO reduction (31). A low, weakly adsorbed state of NO involved in the dimer formation may explain the first-order kinetics in the NO solution concentration, as mentioned in the Introduction. Interestingly, there is no clear catalytic effect of any metal in reducing NO to N2O.
mechanism of the NO electro reduction on transition metals

4. CONCLUSIONS

In this paper, we have studied the mechanism of the electrocatalytic reduction of NO on Ru, Rh, Pd, Ir, Pt, and Au electrodes by a combination of electrochemical measurements and on-line mass spectrometry. Our objectives were to assess to what extent the mechanistic schemes for NO and NH₃ formation recently suggested for the NO reduction on platinum can also be applied to the other metals. In addition, we have studied the mechanism of N₂ production from NO.

All transition metals show a high selectivity toward N₂O at high potentials and, with the exception of Au, a high selectivity toward NH₃ at low potentials. At intermediate potentials, all metals, again with the exception of Au, produce N₂, though with varying selectivity.

The NO reduction to N₂O is suggested to take place via the formation of an NO dimer, similar to the mechanism proposed for platinum (5). The varying Tafel slopes found for the different metals may reflect a shift in the rate-determining step with the metal or, more precisely, a shift in the occurrence of the first electron-transfer step in this mechanism. Despite the varying Tafel slopes, the similarities in the onset of the N₂O formation (i.e., at potentials much more positive than the onset of the adsorbate reduction) suggest a common mechanism for the N₂O formation on all metals. The existence of an NO dimer has been proved on various metal surfaces in UHV. Moreover, its weak adsorption strength would explain why all metals show a similar activity in the NO reduction to N₂O.

We have also presented evidence that the mechanism of formation of N₂ is similar on all metals (except for Au, which does not produce N₂), and involves N₂O as the key intermediate. This deduction was based on the correlation between the selectivity of a certain metal toward producing N₂ from NO and its activity in reducing N₂O. Metals that actively reduce N₂O also produce more N₂ in their NO reduction. Moreover, no N₂ and N₂O are formed in the NO adsorbate reduction in the absence of NO in solution, suggesting that there is no parallel pathway for N₂ formation.

The situation for NH₃ formation is less clear. Certainly for the reduction of the NO adsorbate on Rh (and presumably also Ru and Ir) we cannot exclude the role of NO dissociation, which was not considered for Pt. Tafel slope measurements nevertheless suggest an electron-transfer step to be involved in, or prior to, the rate-determining step, even though this cannot be taken as proof for similar mechanisms. At high NO coverages, NO reactivity on Rh is lower, though this cannot be taken as proof for similar mechanisms. At high NO coverages, NO reactivity on Rh is lower, suggesting a suppression of the NO dissociation by the blocking of free sites.

Finally, the best electrocatalyst for the selective reduction of NO to N₂ is palladium. At high potentials this is related to its high activity in reducing N₂O to N₂. At low potentials this is related to its low activity in the reduction of adsorbed NO to NH₃.

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