Chapter 6

Adsorption and desorption of NO on stepped Pt(533)

As stated in the introduction not only the structure of a surface is important, but also the interaction of the adsorbates with the surface. In order to unravel this interaction, an experimental and theoretical investigation of the adsorption, desorption and dissociation of NO on the stepped Pt(533) surface is presented in this chapter. By combining temperature programmed desorption and reflection absorption infrared spectroscopy, information about the adsorption sites at different temperatures is obtained. Surprisingly, metastable adsorption structures of NO can be produced through variation of the dosing temperature. We also show that part of the NO molecules adsorbed on the step sites dissociates around 450 K. After dissociation the N atoms can desorb either by combining with an O fragment, or with another N atom, resulting in NO and N$_2$. The N$_2$ production can be enhanced by coadsorbing CO on the surface: CO scavenges the oxygen atom, thereby suppressing associative recombinative desorption of N and O atoms. Density functional theory calculations are used to reveal the adsorption energies and vibrational frequencies of adsorbed NO as well as barriers for dissociation of NO and for diffusion of N atoms. The combined experimental results and theoretical calculations confirm that dissociation of NO is the rate-limiting step in the formation of N$_2$. 
6.1 Introduction

The adsorption and reaction of NO and CO on transition metal surfaces is of significant interest because of the catalytic conversion of NO and CO to N\(_2\) and CO\(_2\) in the car exhaust catalyst. For this reason the adsorption of CO [86-92], NO [3, 86, 88-90, 93-103], and N\(_2\) [101, 104-106] has been studied extensively on well-defined model systems, such as single crystal Pt surfaces under ultrahigh vacuum (UHV) conditions. In this chapter we will focus on the adsorption and dissociation of NO on the surface of a stepped Pt crystal. It is generally agreed that NO adsorbs on the Pt surface with its N-end pointing to the surface. On the atomically flat Pt(111) surface NO adsorbs molecularly and no dissociation of NO occurs [3, 107]. As a result of the lack of dissociation on this flat surface, it is inactive in the conversion of NO and CO to N\(_2\) and CO\(_2\) [90]. In contrast to this low corrugation (111) surface, the Pt(100) surface is highly reactive [2, 95], owing to the presence of surface atoms with a lower degree of coordination. Gohndrone and Masel [95] conclude that at saturation coverage, about 66% of the adsorbed NO dissociates to nitrogen and oxygen upon heating. The reaction proceeds by an autocatalytic mechanism that sets in around 410 K. Recently, Rienks et al. [108] have observed that the rate-limiting step in the NO-CO reaction on a Pt(100) surface is the removal of the NO dissociation products by CO, using synchrotron X-ray photoelectron spectroscopy. NO was found to dissociate at temperatures as low as 250 K, which is much lower than what has been thought previously. In analogy, on stepped surfaces composed of (100) step sites and (111) terrace sites, one might expect dissociation of NO at the step edges. Indeed, on the Pt(211) surface, which contains terraces of three rows of (111)-coordinated atoms and one row of step (100)-atoms, a N\(_2\) peak is observed at 483 K in a temperature programmed desorption (TPD) experiment if NO is adsorbed at the step sites at 95 K [98]. In ultraviolet photoemission spectroscopy (UPS) and x-ray photoelectron spectroscopy (XPS) experiments of NO adsorption on the same surface, Sugisawa et al. [98] do not observe peaks for atomic N and O and therefore they conclude that NO adsorbed at step sites at 95 K does not decompose until around 483 K. They conclude that about half of the NO molecules adsorbed on the step sites decomposes, followed promptly by desorption of N\(_2\). Gohndrone and Masel [95] conclude from their TPD experiments that 80-90% of NO adsorbed on the (100) steps of the Pt(211) surface dissociates. Hu et al. [89] have corroborated this finding that the Pt(211) surface is highly active in the conversion of NO and CO to N\(_2\) and CO\(_2\), and have moreover determined that the products CO\(_2\) and N\(_2\) desorb collimated along the local normal of the (100) steps. Lee et al. [94] have observed that production of N\(_2\)O occurs on a stepped Pt(111) surface strongly resembling the (211) surface, in addition to dissociation of NO on the step sites and subsequent formation of N\(_2\).

On the Pt(533) surface, which consists of four rows of terrace atoms with the (111) geometry and then a row of step atoms with the (100) geometry (Fig. 6.1), the production of N\(_2\) and N\(_2\)O has also been observed and has been attributed to thermal dissociation on the step edges [97, 109]. Upon increasing the amount of N atoms on the surface by electron bombardment, the amount of N\(_2\) and N\(_2\)O increased accordingly [97]. From this previous work it can be concluded that the step sites are the active sites for NO dissociation and show
catalytic activity for the conversion of NO and CO into N\textsubscript{2} and CO\textsubscript{2}. However, little work has been done to unravel the mechanism of N\textsubscript{2} formation. Presumably, N\textsubscript{2} is produced in a three-step process (dissociation and subsequent recombination preceded by diffusion), but it is not a priori clear what the rate-limiting step for this process consists of. Also, the adsorption sites of NO on the stepped Pt(533) surface have not yet been fully characterized.

**Figure 6.1:** Schematic picture of the Pt(533) surface, consisting of four atoms wide (111) terraces separated by monatomic (100) steps. The labeling indicates different adsorption sites probed by DFT calculations (see Table 6.1 for the adsorption energies and frequencies). The gray dashed line indicates the unit cell used throughout the calculations; periodic images according to this unit cell are included.

In this chapter we investigate the adsorption, desorption and dissociation of NO on the stepped Pt(533) surface through a combined experimental and theoretical effort. Fig. 6.1 shows a schematic picture of the surface, consisting of four atoms wide (111) terraces and one (100) step. We study the dissociation of NO and the formation of the products N\textsubscript{2} and N\textsubscript{2}O at the steps and defects of our Pt(533) surface using temperature programmed desorption and reflection absorption infrared spectroscopy. From co-adsorption experiments with CO and by comparing the experimental results with density functional theory (DFT) calculations we conclude that the dissociation of NO is the rate-limiting step in the formation of new products.

### 6.2 Experiment and computation

The experiments are performed in the ultrahigh vacuum (UHV) chamber described in chapter 2. The Pt(533) surface is cleaned by sputtering with argon ions and subsequent annealing in oxygen and UHV. The experiments are performed on three different crystals giving identical results (except the formation of N\textsubscript{2} at low temperature, see below). Isotopically labeled \textsuperscript{15}N\textsuperscript{18}O is used in the TPD experiments to distinguish between
background CO (mass 28) and N$_2$ (mass 30 for the isotopomer) and between CO$_2$ with two $^{16}$O (mass 44), CO$_2$ with $^{16}$O and $^{18}$O (mass 46) and N$_2$O (mass 48). After dosing NO and CO via background dosing, TPD spectra are measured with a heating rate of 2 Ks$^{-1}$. Fragments with m/e = 15 (N), 28 (CO), 30 (N$_2$), 33 (NO), 44 (C$^{16}$O$_2$), 46 (C$^{16}$O$^{18}$O) and 48 (N$_2$O and C$^{18}$O$_2$) are monitored simultaneously.

Reflection absorption infrared (RAIR) spectra are recorded at 4 cm$^{-1}$ resolution under grazing incidence by averaging for 19 s per spectrum. The heating rate used in the temperature-dependent RAIRS measurements is 0.25 Ks$^{-1}$. In the RAIRS experiments both normal and isotopically labeled NO is used to obtain additional information about molecules like N$_2$ and N$_2$O possibly formed at the surface through the isotopic frequency shifts of the different vibrations. The NO and CO exposures are given in Langmuirs, defined here as 1 L = 1$ \times $10$^{-6}$ mbar s. The NO exposure can be converted to relative coverage by multiplying the exposure with 0.5, as the uptake curve of NO (see Fig. 6.7) shows approximately a linear behavior between zero coverage and saturation coverage at 2 L.

Structures and binding energies are calculated using the Vienna Ab-initio Simulation Package (VASP) [110-112]. VASP is a plane wave-based density functional code employing the projector augmented wave method [113]. The surface is modeled by a 19 layer slab in a 4×1 cell containing 4 atoms per layer, sampled by a grid of (3×2×1) k-points. A cut-off energy for the expansion of the plane waves of 400 eV is found to be sufficient for an accurate description. For exchange and correlation contributions, generalized gradient corrections (GGA) according to Perdew et al. [114] are applied. The vibrational frequencies are obtained by diagonalization of the dynamical matrix from finite displacements ($\Delta = \pm$0.02 Å) of every atom of the adsorbate into each Cartesian coordinate. Pathways and activation energies for dissociation and diffusion are determined using the nudged elastic band method [115].

6.3 Results and discussion

6.3.1 NO adsorption and desorption

Figure 6.2 depicts TPD spectra of NO from the stepped platinum surface for different coverages dosed at 85 K. At very low coverages only one peak is observed, at 450 K. With increasing coverage desorption of NO is observed also at 345, 280 and 230 K, respectively. The spectral shape for saturation coverage is in good agreement with that reported previously [97], with slightly shifted peak positions. The lower panel shows that the corresponding N$_2$ signals are limited to a temperature range between 400 and 500 K.
To unravel the adsorption sites of NO on the stepped Pt surface, RAIR spectra are measured during dosing at 85 K and during heating of the crystal. Fig. 6.3 depicts RAIR spectra recorded during the dosing, as a function of NO exposure. At very low coverage only one peak is observed at 1594 cm$^{-1}$. With increasing coverage, this peak reaches a maximum intensity around 0.8 L exposure and shifts to 1607 cm$^{-1}$. Additional peaks appear at 1484 cm$^{-1}$ (at 0.2 L; very weak), 1619 cm$^{-1}$ (at 0.5 L; shifting to 1634 cm$^{-1}$) and 1688 cm$^{-1}$ (at 0.3 L; shifting to 1702 cm$^{-1}$). The integrated intensity of the peaks in the RAIRS spectrum cannot be related directly to NO coverage, as the dynamic dipole moment may differ for different adsorption sites [116], as a consequence of variations in the tilt angle with respect to the surface normal, variations in the electronic structure with coverage [117] or due to dipole-dipole coupling [118].
Figure 6.3: (a) Reflection absorption infrared spectra at 85 K of $^{14}$N$^{16}$O on Pt(533) for coverages increasing from left to right. The last spectrum is for a fully covered surface. Dark color represents high absorption ($\Delta_{\text{max}} = -\ln(R/R_0)_{1702\text{ cm}^{-1}} = 0.045$), (b) Cross section of (a) at 0.1, 0.25, 0.5, 1, and 2 L [i.e. the same exposures as the TPD spectra in Fig. 6.2, except the 2 L which should be comparable to 2.5 L, as both correspond to full coverage (see Fig. 6.7)].

Table 6.1 summarizes the IR assignment and connects the observed vibrational frequencies to the different adsorption sites depicted in Fig. 6.1. The peak at 1594 cm$^{-1}$ can be assigned to molecules bound at the upper step edges in a bent geometry or in a two-fold bridge position [99, 119] and the vibrational frequency at 1619 cm$^{-1}$ to NO molecules coordinated at a terrace site immediately adjacent to step sites [119]. The step significantly perturbs this site compared to a normal (111) terrace site resulting in a lower vibrational frequency. The peak at 1688 shifting to 1702 cm$^{-1}$ is assigned to molecules on the terraces bound atop. In the past, this frequency has been attributed to molecules bound in a linear geometry [99, 119]. However, recent work has shown that NO molecules bound atop are
highly tilted [117, 120]. Thus, the vibrational frequency at ~1700 cm\(^{-1}\) is caused by molecules bound atop on terrace sites in a tilted geometry. The peak at 1484 cm\(^{-1}\) is assigned to NO molecules in a threefold fcc or hcp hollow site on the terraces [96, 121]. Traditionally, the peak at 1484 cm\(^{-1}\) has been assigned to NO molecules bound in a two-fold bridge site [99, 119] on Pt(111). However, only the explanation NO bound in a threefold hollow site, is in agreement with the assignment of Materer et al. [122] and with the recently resolved binding structure of NO on flat Pt(111) [107, 120]. According to this structure, NO is bound in threefold hollow sites and in atop sites, but never in a twofold hollow site. At saturation coverage only one narrow peak is observed at 1702 cm\(^{-1}\). This can be understood by noting that the intensities of the lower frequency peaks are transferred to the peak with the highest frequency, due to dipole-dipole coupling [118]. An additional effect may be a reduction of the other RAIR signals due to a change in the electronic structure of the whole adsorbed system with increasing coverage [117].

Table 6.1: Vibrational frequencies of NO on Pt(533) observed in the experiments. Relevant references are given in the text.

<table>
<thead>
<tr>
<th>IR frequency (cm(^{-1}))</th>
<th>Assignment</th>
<th>Site in Fig. 6.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>1480-1484</td>
<td>terrace, 3-fold fcc or hcp hollow site</td>
<td>1, 2, 3, 4, 5, 6</td>
</tr>
<tr>
<td>1594-1607</td>
<td>step, bent or bridge geometry</td>
<td>7, b</td>
</tr>
<tr>
<td>1619-1634</td>
<td>terrace, adjacent to step, possibly tilted*</td>
<td>a*</td>
</tr>
<tr>
<td>1688-1702</td>
<td>terrace, atop and tilted</td>
<td>c, d</td>
</tr>
<tr>
<td>1815</td>
<td>steps, linear geometry</td>
<td>b, but linear</td>
</tr>
</tbody>
</table>

* Tentative assignment

As observed in Fig. 6.3, the IR signal at 1688 cm\(^{-1}\) appears prior to saturation of the step sites. Zhu et al. [107] have observed similar behavior for NO on Pt(111): before the atop sites are fully occupied, the hcp hollow sites become appreciably populated. Zhu et al. [107] have explained this observation by island formation and by limited diffusion during uptake, which could explain our observation as well. An alternative explanation may be that entropy effects cause the atop sites to become occupied before saturation of the step sites.

The integrated NO absorption around 1600 cm\(^{-1}\) – where the initial adsorption upon NO exposure is observed – versus exposure at 85 K is depicted for low coverages in Fig. 6.4. Surprisingly, a sub-linear increase is observed at the lowest coverages: the slope of the absorption curve is gradually increasing until it achieves a steady state value. The initial slow increase of absorption indicates that either the molecules are not IR active, possibly because they lie flat on the surface, or because there is simply no NO on the surface at very low coverage. The latter explanation implies that some NO already dissociates at 85 K and N\(_2\) could be formed.
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Figure 6.4: Integrated absorbed infrared intensity of the peak around 1600 cm\(^{-1}\) as a function of the NO coverage. The straight line is a guide to the eye indicating the linear increase in integrated intensity from 0.10 L.

To assign the peaks in the TPD spectrum to the different adsorption sites (now known from RAIRS, see table 6.1), we heat the sample at a heating rate of 0.25 Ks\(^{-1}\) while RAIR spectra are being measured. The result is plotted in Fig. 6.5 together with a TPD spectrum obtained at the same heating rate.

Figure 6.5: RAIR and TPD spectra during the heating at 0.25 Ks\(^{-1}\) of a Pt crystal fully covered with \(^{14}\)N\(^{16}\)O dosed at 85 K. Dark color represents high absorption. The line at 450 K represents the maximum in NO desorption, illustrating the disappearance of the RAIRS signal already before this temperature.
Up to a temperature of 200 K the spectrum remains unchanged: the signal at 1702 cm\(^{-1}\) is the only peak in the spectrum. At 200 K, the intensity of the peak at 1702 cm\(^{-1}\) decreases and two additional resonances appear, at 1620 (very weak) and 1815 cm\(^{-1}\). This last peak is assigned to molecules bound in a linear geometry on either the steps or the terraces (see below). As this vibrational resonance has never been observed on the flat Pt(111), but is observed for a stepped Pt surface above 220 K [99, 119], it is presumably associated with molecules bound atop in a linear geometry on the step sites. At 270 K the 1620 cm\(^{-1}\)-resonance weakens, and simultaneously a peak at 1580 cm\(^{-1}\) appears. This signal at 1580 cm\(^{-1}\) is most probably due to molecules on the steps in a bent or bridge geometry. Due to dipole-dipole coupling with the NO molecules with a vibrational frequency of 1800 cm\(^{-1}\), the frequency is shifted from ~1600 cm\(^{-1}\) to the observed 1580 cm\(^{-1}\). The decrease in the 1702 cm\(^{-1}\)-peak coincides with the first two desorption peaks in the TPD spectrum. The decrease in intensity of the 1815 cm\(^{-1}\)-resonance is assigned to molecules on step sites, we can conclude that at 340 K (i.e. the third peak in the TPD spectrum) molecules desorb from the steps. In contrast, Wang et al. [97] concluded previously that only the highest temperature NO peak originates from NO adsorbed on the steps and the other three peaks are due to NO desorbing from the terraces. It is obvious that on the Pt(533) surface the distinction between step and terrace atoms is somewhat artificial, and it is also not completely clear where the molecules are located on the step sites. Wang et al. [123] conclude from a high-resolution electron energy loss spectroscopy study that oxygen atoms bind on the outer edge of the step (site 7 in Fig. 6.1) and not at the higher coordination sites in the step trough. As Agrawal et al. [99] and Levoguer et al. [119] observed that the NO signals at around 1600-1610 cm\(^{-1}\) and 1800 are blocked by oxygen coverage, it can be concluded that the NO molecules bind on the outer edge of the steps. Together with the decrease of the 1815 cm\(^{-1}\) signal, an IR signal appears at 1603 cm\(^{-1}\) assigned to NO molecules bound in a bridged or bent geometry at the steps. The decrease of this signal in the RAIRS coincides with the increase of the highest temperature peak in the TPD spectrum. Recently Mukerji et al. [124] assigned the IR resonance at ~1800 cm\(^{-1}\) observed for NO on Pt(211) to an O–NO complex (NO bound on top of an O atom adsorbed on a step bridge site). As we do not observe NO dissociation till ~400 K (see section 6.3.2), no oxygen atoms are available in our case to make an O–NO complex. Also DFT calculations (see below) are in agreement with our assignment to NO bound in a linear geometry to the step sites.

Combining the RAIRS with the TPD spectrum we can conclude that the NO desorption peak above 400 K is due to NO desorbing from the (100) step sites. The Pt atoms at the step edges are less coordinated and therefore interact more strongly with the adsorbate resulting in a higher desorption temperature. The lowest two peaks are from NO adsorbed on the (111) terrace sites. By comparing the desorption structure to the recently derived model for adsorption sites for NO on Pt(111) [107, 120], we assign the peak at the lowest temperature to NO desorbing from the hcp hollow site (visible in RAIRS only as a decrease of the 1702 cm\(^{-1}\)), the peak at 300 K to desorption from the atop sites and probably the shoulder on the high temperature site of this peak to NO molecules desorbing from fcc hollow sites (The spectral signature of this fcc threefold hollow site is visible in some RAIRS experiments, just
after disappearance of the 1700 cm\(^{-1}\) intensity, as a very weak signal at 1480 cm\(^{-1}\) over a narrow temperature range from 260 till 275 K.). Hcp and fcc hollow sites are sites with or without, respectively, a Pt atom in the second row of the crystal. The peak at 345 K in the TPD is from NO molecules on the step sites or from the terrace site directly adjacent to the steps. An interesting feature to note in Fig. 6.5 is that all IR signals vanish before \(T=450\) K, whereas the TPD demonstrates that there is still a significant amount of NO present on the surface (see the line at 450 K in Fig. 6.5). This could indicate that the molecules with the vibrational frequency of \(\sim 1600\) cm\(^{-1}\) lie flat on the surface at very low coverage and are therefore infrared inactive. Such an interpretation is consistent with the infrared invisibility of NO at low coverage during the dosing (Fig. 6.4), implying that this is also due to NO lying flat on the surface.

<table>
<thead>
<tr>
<th>site</th>
<th>(E_{\text{ads}}) (eV) N</th>
<th>(E_{\text{ads}}) (eV) O</th>
<th>(E_{\text{ads}}) (eV) NO</th>
<th>(v_{\text{N-O}}) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.81</td>
<td>-0.76</td>
<td>-1.65</td>
<td>1487</td>
</tr>
<tr>
<td>2</td>
<td>0.77</td>
<td>-0.65</td>
<td>-1.75</td>
<td>1549</td>
</tr>
<tr>
<td>3</td>
<td>0.41</td>
<td>-1.10</td>
<td>-1.98</td>
<td>1526</td>
</tr>
<tr>
<td>4</td>
<td>0.59</td>
<td>-0.76</td>
<td>-1.82</td>
<td>1547</td>
</tr>
<tr>
<td>5</td>
<td>0.51</td>
<td>-1.23</td>
<td>-1.91</td>
<td>1523</td>
</tr>
<tr>
<td>6</td>
<td>0.33</td>
<td>-1.20</td>
<td>-2.06</td>
<td>1553</td>
</tr>
<tr>
<td>7</td>
<td>0.52</td>
<td>-1.50</td>
<td>-2.50</td>
<td>1621</td>
</tr>
<tr>
<td>a</td>
<td></td>
<td>-1.99</td>
<td></td>
<td>1834</td>
</tr>
<tr>
<td>b</td>
<td></td>
<td>-2.02</td>
<td></td>
<td>1621</td>
</tr>
<tr>
<td>c</td>
<td></td>
<td>-1.04</td>
<td></td>
<td>1869</td>
</tr>
<tr>
<td>d</td>
<td></td>
<td>-1.05</td>
<td></td>
<td>1855</td>
</tr>
</tbody>
</table>

The TPD and RAIRS assignments are corroborated by the results of DFT calculations presented in Table 6.2. From these calculations it can be concluded that the most favorable adsorption sites are indeed on the upper end of the step (Table 6.2 and Fig. 6.1, site 7). The molecule adsorbs in a two-fold coordinated site at the step and leans over towards the lower terrace. The binding with the substrate is established exclusively via the nitrogen atom. Step-bound molecules exhibit the strongest binding (lowest adsorption energies) and therefore are expected to desorb at the highest temperature. Compared to other possible adsorption sites, the adsorption energy in the hollow sites (Site 1, 3 and 5 are fcc hollow sites, while 2, 4 and 6 are hcp hollow sites) decreases, when going towards the step. Adsorption becomes less favorable at the lower end of the step. In addition to this general behavior, the adsorption energy alternates between slightly more and less favorable values for odd and even labeled sites, reflecting the preference of NO for fcc hollow sites on the (111) terrace. This general
trend, when comparing sites at the terrace to those close to the steps, is observed for adsorption to atop sites, as well. The promoting effect of the step is so large, that atop sites at the step are even lower in energy than hollow sites at the terrace. The optimal adsorption site is in line with the recent calculations of Ge and Neurock for NO on Pt(410) [125].

The calculated stretching frequency for these NO molecules at the step edge (site 7) is around 1620 cm\(^{-1}\), in good agreement with the \(\sim 1600 \text{ cm}^{-1}\) that is observed for low coverages at elevated temperatures (see Figs. 6.3 and 6.6 at low exposure, and Fig. 6.5 at temperatures exceeding 350 K). The calculated vibrational frequencies for NO bound on atop sites in a linear geometry and for NO in hcp/fcc hollow site are \(\sim 1850 \text{ cm}^{-1}\) and \(\sim 1550/1530 \text{ cm}^{-1}\) respectively, corroborating the site assignments of the infrared peaks given above. A limitation of the calculations is that the vibrational frequencies are calculated for isolated molecules. Isolated NO molecules adsorbed in atop sites preferentially adopt a linear geometry, whereas at higher coverages atop adsorbed NO molecules at the terraces are highly tilted [117, 120]. As a result, the calculated (1850 cm\(^{-1}\)) and measured (1700 cm\(^{-1}\)) frequency for the atop molecules adsorbed on site c and d differs significantly (Table 6.1 and 6.2).

RAIRS spectra during NO uptake were recorded not only at 85 K, but also at temperatures between 175 and 350 K. In all these experiments the initial IR absorption feature is observed at 1600-1640 cm\(^{-1}\). In contrast to the results at 85 K, at temperatures between 175 and 300 K a resonance appears at \(\sim 1800 \text{ cm}^{-1}\) with increasing coverage indicating that the molecules originally bound bridge/bent (partially) move to a linear binding state. The \(\sim 1800 \text{ cm}^{-1}\) peak becomes increasingly intense with increasing temperature from 175 K to 300 K (at 350 K only an absorption is observed at \(\sim 1600 \text{ cm}^{-1}\), because the temperature is too high to occupy other sites) from which it seems apparent that the molecules have to overcome a barrier before they can bind in the linear geometry.

Moreover, if dosing is started at a surface temperature of 350 K, which is subsequently lowered whilst dosing, we end up with a different NO layer at 85 K compared to the situation of dosing directly at 85 K. This is apparent from the RAIR spectra collected during the dosing process, shown in Fig. 6.6.

![RAIR spectra of 14N16O (P_{\text{background}}=5\times10^{-9}\text{ mbar}) dosing during cooling down of the crystal at 0.25 Ks\(^{-1}\). The total cooling time is 20 minutes. Dark color represents high absorption.](image)

**Figure 6.6:** RAIR spectra of 14N16O (\(P_{\text{background}}=5\times10^{-9}\text{ mbar}\)) dosing during cooling down of the crystal at 0.25 Ks\(^{-1}\). The total cooling time is 20 minutes. Dark color represents high absorption.
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The integrated intensity of the 1700 cm\(^{-1}\) signal is roughly 10 % smaller and the peak is 1.5 times broader compared to the signal obtained by dosing directly at 85 K. From 300 K downwards, molecules can adsorb in a linear geometry at the step sites (resulting in a signal at around 1800 cm\(^{-1}\)). During cooling part of the molecules stay at this adsorption site. Indeed, the total integrated RAIRS intensity (1700 and 1800 cm\(^{-1}\) signal) for a layer obtained by dosing from 350 K downwards is twice as large as that for a layer dosed at 85 K. This is not due to a larger amount of NO on the surface, however: a TPD spectrum of a layer obtained by dosing during cooling the crystal shows a slight decrease of intensity in the first two desorption peaks as shown in Fig. 6.2a, indicating that slightly (~5 %) less NO is adsorbed at the surface. This lower saturation coverage could be explained by the fact that if the NO molecules are bound linear on the steps at higher temperatures (vibrational frequency ~1800 cm\(^{-1}\)), they could hinder the molecules in site 6 (hcp hollow site), resulting in a lower amount of molecules in these sites and a lower first TPD peak.

6.3.2 \(\text{N}_2\) formation

The \(\text{N}_2\) desorption signal (corrected for the formation of \(\text{N}_2\) in the mass spectrometer from filament-induced dissociation of desorbing NO) for different coverages of NO is depicted in figure 6.2b. At low coverage only one desorption signal is observed at 455 K, slightly higher than the last desorption peak of NO. At higher coverage a second peak at 410 K is appearing. The two peaks can indicate two possible pathways for the dissociation of NO with comparable, but slightly different activation energies. This double peak structure is not as clearly visible in spectra recorded by Skelton et al. [109], most probably due to the higher heating rate (10 Ks\(^{-1}\) instead of the 2 Ks\(^{-1}\) used in our experiments).

Figure 6.7: Integrated desorption signal for NO (circles) from 150 to 550 K and for \(\text{N}_2\) (squares) from 350 to 550 K. The signal for \(\text{N}_2\) is multiplied by a factor of 50.

In Fig. 6.7 the integrated intensities for the desorption signal of NO and \(\text{N}_2\) (integrated from 350 to 550 K) are plotted versus the NO exposure. The \(\text{N}_2\) signal is 50 times weaker than that of NO (corrected for the difference in detection efficiency between NO and \(\text{N}_2\)): only ~2 % of NO is converted to \(\text{N}_2\). As around 25 % of the molecules adsorbs on the step sites (inferred from the ratio of the TPD signals), it can be concluded that around 8 % of the NO adsorbed on the step sites in a bent or bridge conformation (~1600 cm\(^{-1}\) in RAIRS) is converted to \(\text{N}_2\).
The $\text{N}_2$ desorption signal is saturated once these step sites are fully covered with NO and decreases if these sites are blocked for NO by adsorption of CO (result not shown), indicating that, as expected, the steps play a pivotal role in the formation of $\text{N}_2$. The observed relative amount of $\text{N}_2$ formed and the key role of steps in the formation is in good agreement with previous measurements by Skelton et al. [109]. The observation that NO only dissociates on the step sites is also consistent with our calculations (see below) and with previous experiments where no significant NO dissociation on the Pt(111) surface has been observed [3, 107]. As $\text{N}_2$ adsorbed on step sites already desorbs before 180 K [105] while $\text{N}_2$ adsorbed on terrace sites desorbs below liquid nitrogen temperatures [106], it can be concluded that the $\text{N}_2$ molecules desorbing at 410 and 455 K have to be formed at that temperature. For a stepped Pt(211) crystal it has also been shown that NO adsorbed on the step sites at 95 K does not decompose until 483 K [98].

The process of $\text{N}_2$ formation is a multi-step process, which requires first the dissociation of NO and subsequently the formation of $\text{N}_2$. This is corroborated by the observation that if CO is coadsorbed with NO (at low exposure of 0.1 L for both CO and NO, so that both molecules only bind on the step sites and NO dissociation is not greatly hindered by CO site blocking), the production of $\text{N}_2$ is increased by around a factor of 2 compared to the case of only NO. This increase is observed despite the fact that CO adsorbs onto the step sites, and thereby blocks potential NO dissociation sites. After dissociation the nitrogen and oxygen atoms on the surface can recombinatively desorb or $\text{N}_2$ can be formed. Recombinative desorption is confirmed by the appearance of a TPD signal for m/e 31 ($^{15}\text{N}^{16}\text{O}$) and m/e 32 ($^{14}\text{N}^{18}\text{O}$) at 450 K if a 50/50 mixture of $^{14}\text{N}^{16}\text{O}$ and $^{15}\text{N}^{18}\text{O}$ is dosed. A comparison of the integrated TPD areas of m/e 31 and 32 with m/e 30 and 33, reveals that around 8% of the NO molecules desorbing from the step sites results from recombinative desorption, rather than from simple intact desorption. From the fact that the amounts of $\text{N}_2$ and NO produced from recombinative desorption are comparable (both ~8%), it can be concluded that after NO dissociation the chance to form NO or $\text{N}_2$ is statistical. This indicates that NO dissociation is the limiting step for the $\text{N}_2$ formation, as will be further demonstrated below. If CO is present on the surface, the CO scavenges the oxygen, thereby suppressing recombinative desorption of NO resulting in an increase in the $\text{N}_2$ production. In this coadsorption with $^{15}\text{N}^{18}\text{O}$ experiment only $^{16}\text{O}^{18}\text{O}$ and no $^{16}\text{O}_2$ is detected, indicating that CO is not dissociating on the surface. The fact that $\text{N}_2$ and CO$_2$ desorb at the same temperature (see Fig. 6.8) corroborates the observation that the NO dissociation is the rate-limiting step. Following dissociation, CO$_2$ and $\text{N}_2$ are formed and desorb more or less instantaneously. Wang et al. [97] have also observed that the dissociation is the rate-limiting step after which $\text{N}_2$ is formed instantaneously. In their experiments NO is dissociated by electron bombardment and an $\text{N}_2$ peak is observed in the TPD spectra at lower temperature (435 K) than the $\text{N}_2$ formed via thermal dissociation (520 K). This peak at 435 K is assigned to recombinative desorption of N atoms while the peak at 520 K is assigned to thermal dissociation of NO followed directly by $\text{N}_2$ formation.
Figure 6.8: \( N_2 \) (mass 30) and \( C^{16}O^{18}O \) (mass 46) desorption signals from Pt(533) after dosing below 100 K of 0.1 L of \( ^{15}N^{18}O \) and 0.1 L \( ^{12}C^{16}O \). The two fragments desorb at the same temperature, indicating that the dissociation of NO at this temperature is the rate-limiting step in the \( N_2 \) formation.

To confirm the conclusion that the NO dissociation is the rate-limiting step for the formation of \( N_2 \), the activation energies for the dissociation of NO and the diffusion of N atoms over the surface are calculated. Both processes require the knowledge of the adsorption behavior of the atomic dissociation products, nitrogen and oxygen. For the atomic adsorbates only the hollow sites on the substrate were considered to be relevant (see Fig. 6.1). The corresponding adsorption energies are compiled in Table 6.2. Oxygen behaves very much like nitric oxide discussed above. A strong preference for fcc hollow sites is combined with an adsorption-promoting effect of the upper step edge, leading to a lowest energy site at a two-fold coordinated site directly at the step edge.

In the case of nitrogen, the high binding energy of the molecular reference dinitrogen in the gas phase leads to positive (endothermic) adsorption energies. Besides this, the general adsorption behavior is similar. However, in this case, the most favorable adsorption site is the last three-fold coordinated site at the upper (111) terrace (site 6 in Fig. 6.1).

Based on this knowledge, the energetics associated with the three reaction steps leading to \( N_2 \) formation (NO dissociation, diffusion of molecular nitrogen and recombinative desorption of \( N_2 \)) have been calculated. Starting from the equilibrium adsorption site at the upper step edge, several pathways for the dissociation of NO on Pt(533) are calculated. A pathway with low activation energy is shown in Fig. 6.9a. An NO molecule adsorbed at the upper end of the terrace site tilts down onto the terrace. The NO molecule dissociates resulting in oxygen and nitrogen atoms both in bridge sites in the transition state, with an activation energy of 2.10 eV. The oxygen atom subsequently moves away from the step to the next three-fold hollow site. On the stepped Pt(533) surface dissociation of NO is possible, as the barrier for dissociation is slightly smaller than the desorption energy of NO from the step sites. On Pt(111), in contrast, desorption is energetically much more favorable than dissociation of NO. In addition, another dissociation mechanism as proposed by Ge and Neurock [125] could be relevant. The dissociation is preceded by diffusion of NO to the last hollow site on the lower terrace (site 1 in Fig. 6.1), a process, which is connected with energy costs of about 1 eV (taking into account the last diffusion barrier between sites 2 and 1, Fig. 6.9b). From that site, the molecule can dissociate with an even lower barrier (Fig. 6.9b). Dissociation via this
pathway costs less energy, because the N and O atoms do not have to share substrate atoms at the transition state, leading to stronger adsorbate substrate bonding. Through either mechanism, dissociation on the stepped surface is indeed well possible according to the energetics derived from the DFT calculations.

**Figure 6.9:** Reaction pathways for the dissociation of NO and the diffusion of nitrogen on the stepped Pt surface. The zero energy equals an NO (half an N₂ and O₂) molecule in the gas phase, not adsorbed on the surface. Panel a illustrates dissociation starting directly from the equilibrium adsorption site (site 7 in Fig. 6.1), in panel b the NO molecule diffuses first to position 1 at the lower step edge and dissociates there. In panel c the energetics for several nitrogen diffusion pathways are shown. The numbering corresponds to the different sites depicted in Fig. 6.1.
The second step in the formation of $N_2$ is the diffusion of $N$ atoms over the surface. Fig. 6.9c illustrates the most important diffusion pathways. Diffusion of a $N$ atom directly towards the lower step is activated by around 1 eV (connecting sites 6$\Rightarrow$7$\Rightarrow$1). Diffusion from the step edge onto the terrace (from site 6 to site 5 in Fig. 6.1) is also activated (around 0.8 eV). If the adatom continues towards the next site 7 along the edge, this is the minimum pathway for diffusion along the step. Moving more directly along the step, implies passing less favored substrate positions (atop or leaning over the step). Hence such pathways are activated by 1.5 eV (not included in Fig. 6.9).

As the activation energy for dissociation (1.68 eV) is appreciably higher than the barrier for diffusion (~1 eV), the diffusion of one $N$ atom to another will follow directly after the dissociation. However, the repulsion between neighboring nitrogen atoms is rather high; two $N$ atoms adsorbed in neighboring adsorption sites 6 (Fig. 6.1) repel each other with 0.42 eV, and when they approach even closer, so that one atom adsorbs in position 6 and the second one in position 5, the repulsion increases to 1.46 eV. Therefore, the step also plays a crucial role in the third and final step of $N_2$ formation: the recombination of $N$ atoms, in addition to enabling $NO$ dissociation in the first place. With one $N$ atom adsorbed at the lower and the second at the upper terrace no substrate atoms have to be shared between both adsorbates and hence the recombination becomes easier. The transition state for such a pathway is characterized by an “adsorption energy” of 1.90 eV. This results in an effective barrier of 1.25 eV relative to two isolated nitrogen atoms at the surface (i.e. twice the adsorption energy of a nitrogen atom in position 6). As the dissociation barrier of $NO$ is higher than the diffusion and recombinative desorption barriers, desorption of $N_2$ will follow directly after the dissociation of $NO$, as is also evident from the experimental data.

Already at low $NO$ coverage, two additional, distinct desorption $N_2$ peaks appear in the TPD spectra around 120 and 150 K (not shown). The origin of these peaks is unclear. Differences in the intensity with respect to the peaks around 400 K are observed performing the experiments on three different Pt(533) crystals. This indicates that the chemistry resulting in these $N_2$ signals is most probably related to defects, like kinks or vacancies. Also, in the IR spectra at very low coverage a very weak signal can be observed at $\sim$2240 cm$^{-1}$, which displays an isotopic frequency shift upon dosing $^{15}N^{18}O$, so that it can be assigned to $N_2$ molecules on defect sites on Pt [104]. Due to the high activation energy for dissociation on the step sites it is impossible that the molecules on the step sites already dissociate at 85 K. There have to be other, more active, defect sites on the crystal where the barrier for dissociation is much lower which result in the formation of small amounts of $N$ and $O$ already at 85 K.

A small, but observable signal is seen for $N_2O$ in the TPD spectra. This product desorbs at 120, 200, 270 and 455 K. With increasing coverage the integrated $N_2O$ signal becomes bigger. The $N_2O$ at 455 K is most probably formed via a reaction of a $N$ atom with $NO$. The $N_2O$ desorbing at lower temperature could be formed via a ($NO$)$_2$ intermediate [126].

No desorption signal is observed for $NO_2$ and $O_2$. Oxygen atoms that remain on the surface after dissociation of $NO$ can dissolve into the subsurface region as observed previously for Pt(211) [98]. From TPD results on this Pt(211) surface, it has been concluded
that the presence of subsurface oxygen does not significantly affect the adsorption and desorption behavior of NO on the surface.

6.4 Conclusions

We have investigated adsorption and dissociation of NO on a stepped Pt(533) surface and find that N\(_2\) is formed on the stepped Pt(533) surface due to dissociation of NO molecules on the step sites around 400 K. The formation of N\(_2\) is a three-step process consisting of the dissociation of NO followed by diffusion of nitrogen atoms and recombinative desorption of N\(_2\). This can be deduced from the enhancement of the N\(_2\) production if CO is coadsorbed with NO. CO scavenges the oxygen atom thereby suppressing recombinative desorption of NO. Density functional theory calculations confirm the adsorption states of NO on Pt(533) and the fact that the dissociation of NO is the rate-limiting step in the formation of N\(_2\).
Chapter six