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N_2O adsorption and reaction at Pd(110)

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Abstract

The adsorption and decomposition of N_2O on Pd(110) has been studied using molecular beam uptake measurements and reflection-absorption infrared spectroscopy to characterise the reaction products. Nitrous oxide adsorption at 300 K leads to efficient dissociation with an initial sticking probability $S_0=0.65$. The reaction saturates at an uptake of 0.5 ML of adsorbed O, the surface forming an ordered Pd(110)- $c(2 \times 4)O$ overlayer. At higher temperatures the reaction probability drops, consistent with a trapping-dissociation mechanism. Adsorption at temperatures below 100 K leads to efficient dissociation, but the dissociation probability drops rapidly with uptake and thereafter N_2O is adsorbed intact. A secondary maximum in the N_2 product yield is seen for an N_2O uptake of 0.5 ML, with the surface simultaneously ordering to form a (1×2) low-energy electron diffraction pattern that becomes sharp as uptake saturates with a composition of 0.15 ML O and 0.85 ML of N_2O . We suggest that this structure is associated with a row-pairing reconstruction of Pd(110), forming a corrugated Pd surface. The IR spectrum shows bands at 1290 and 2262 cm⁻¹ due to N_2O adsorbed with a component of its axis perpendicular to the surface. Heating this surface leads to desorption of molecular N_2O at 100 K, followed by two further peaks at 117 and 140 K with partial dissociation. We discuss the origin of the off-normal emission of N_2 during N_2O decomposition and the role of N_2O as an intermediate during the reaction of NO on Pd(110). © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Nitrous oxide is one of the products formed in the decomposition of NO at palladium surfaces [1,2], along with gaseous N_2 and adsorbed N and O atoms. NO shows a rich chemistry on Pd(110), adsorbing molecularly at room temperature to reconstruct the metal surface into a complex series of adsorbate phases which have been characterised

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by reflection-absorption infrared spectroscopy (RAIRS) [3]. Heating a surface previously exposed to NO at 300 K results in an NO desorption peak near 495 K [3,4], desorption occurring concomitantly with reaction to form N_2 and N_2O [5], leaving O atoms on the surface that poison further reaction. In the presence of a fuel, such as H_2 , CH₄ or CO, the O atoms can be removed, allowing NO reduction to be run continuously. Under different reaction conditions there appear to be at least two different routes for N_2 formation during NO reduction at Pd(110) [5]: one is the recombination of $N_{(a)}$ [6] and the other is the

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reaction of $N_{(a)} + NO_{(a)}$, which may either give $N_{2(g)}$ directly [7] or by N₂O decomposition [8]. Here we investigate the adsorption and dissociation of N₂O on Pd(110) and discuss its possible role as an intermediate in the reduction of NO.

Reaction of NO to form N₂ and N₂O only begins to occur above 420 K on Pd(110), where NO starts to dissociate slowly or desorb from the surface. Dissociation of NO is rate limiting [6] and can be blocked either by the formation of an O_(a) overlayer or by chemisorbed NO_(a). NO decomposition is catalysed by Pd reconstruction, occurring preferentially at step or defect sites created as Pd reconstructs in response to NO adsorption or desorption [9]. Steps have also been shown to be important in promoting reaction on the Pd(112) face [10,11]. The ratio of N_2O to N_2 product increases with the NO coverage [6,9]. This is consistent with recent isotope experiments by Ikai and Tanaka [7], who showed that N_2O was formed by reaction of NO_(a) with preadsorbed $N_{(a)}$.

At high temperature the N_2 is formed entirely by N_(a) recombination, since insufficient adsorbed NO is present to form N_2O [6,7]. If H_2 is present then O_(a) can be removed as water, allowing the reaction to be run continuously. The N₂ formed under these conditions desorbs with an angular distribution that is symmetric about the surface normal and approximately thermal $(\cos \theta)$ [7]. State-resolved measurements find that the N_2 has a cold translational and rotational energy distribution but does carry considerable vibrational excitation [9]. Nitrogen recombinative desorption occurs indirectly via a short-lived molecular state; the rotational and translational coordinates are cooled by desorption from this well, but some vibrational excitation survives trapping into the precursor state. This picture is consistent with the broad angular distribution seen for N₂ formed during the NO + H_2 reaction [5].

In contrast, the N₂ formed during temperature programmed desorption (TPD) of an adsorbed NO layer shows very different behaviour. Although NO and N₂O desorb with a $\cos \theta$ and a $\cos^2 \theta$ distribution respectively, both centred around the surface normal, nitrogen showed a lobular distribution, with a sharp maximum at ca 40° to the normal along the [001] direction and $\cos^{4.2} \theta$ in the $[1\overline{1}0]$ direction [4,5]. Sharp angular peaks result from a preferential repulsive energy release along the axis of the desorption lobe, usually the local surface normal [12]. Angular time-of-flight (TOF) measurements confirm that this N_2 is translationally hot [8], quite unlike the N_2 formed by recombination at high temperatures [9]. The source of the lobular distributions was suggested to be either a local reconstruction forming tilted sites where N_2 is produced, or a preferred collision geometry for the $N_{(a)} + NO_{(a)}$ reaction [7]. A recent study on the stepped Pd(211) surface shows that N₂ produced during NO desorption is peaked at 25° to the surface along the [111] direction, normal to the (100) steps [13].

Recently, Matsushima and co-workers have compared the production of N₂ during TPD of N_2O and NO from Pd(110) using angular TOF measurements [8]. Decomposition of N₂O produced translationally excited N₂ that desorbed in a lobe at 45° to the surface normal, the distribution being very similar to that from NO decomposition. Since N₂O dissociates at temperatures below 200 K, where the Pd(110) surface is immobile [3], the off-normal desorption cannot be attributed to facetting of the surface by bulk displacive reconstruction of the Pd. It was proposed that the desorption angle was determined by a balance between repulsion of the nascent N₂ from the metal surface and from the O atom as the N₂O bond breaks [8]. This implies a transition state that lies flat, with the N_2O bond axis parallel to the surface and closely aligned along the [001] direction. The similarity of the N₂ angular TOF distributions from NO and N₂O decomposition suggests that N_2O is the common intermediate that leads to N₂ production during NO flash desorption [8].

Here we describe the adsorption behaviour of N_2O on Pd(110). We find that partial reaction to form N_2 and adsorbed O atoms occurs even at 85 K. The resulting surface shows a (1×2) lowenergy electron diffraction (LEED) pattern, with N_2O adsorbed upright on the surface. RAIR spectra for N_2O adsorption are compared with those obtained for non-dissociative adsorption on Pt(111). We discuss the proposed mechanisms for formation of N_2 during NO or N_2O dissociation at high coverage and compare this with NO decomposition on Pd(110) at higher temperature [9,14].

2. Experimental

A thermal (effusive) molecular beam source was used to monitor the adsorption of N₂O and NO on a Pd(110) surface using the direct reflection technique to determine sticking probabilities. Scattered molecules and reaction products were detected by a quadrupole mass spectrometer (OMS). The relative sensitivities to different species (N₂O, NO and N₂) were calibrated from the QMS signals using beams whose relative fluxes are known for effusive flow conditions. The signals at masses 28 and 30, due to N₂ and NO, were subject to interference from N₂O cracking. This background was removed by measuring the N₂O cracking ratios and subtracting the appropriately scaled N₂O signal, as described later. Absolute gas fluxes were calibrated by determining simultaneously the sticking probability $S(\Theta)$ and the exposure required to form a well-defined overlayer. All coverages are referenced to the saturation uptake of CO on an 85 K surface, which has a coverage of 1 ML and a sharp (2×1) p1g1 LEED pattern [15]. RAIR spectra were recorded at 85 K using a Mattson 6020 FTIR spectrometer. Adsorption spectra were all obtained for background dosing, accumulating 200 scans per trace with 4 cm^{-1} resolution.

The palladium crystal was polished to within 0.25° of the Pd(110) surface and was cleaned by Ar^+ ion sputtering and O_2 treatment. The crystal was mounted on two heating wires and could be cooled to 85 K and heated resistively as required. The surface showed a sharp LEED pattern, whereas CO adsorption reproduced the (2×1) p1g1 LEED pattern and the thermal desorption spectrum reported previously [15]. CO thermal desorption is very sensitive to the presence of contaminants which inhibit reconstruction of the surface during desorption, providing a sensitive test of the surface quality. N₂O uptakes and RAIR spectra were also recorded for N2O adsorption on

Pt(111), which was prepared using standard techniques.

3. Results

3.1. N₂O adsorption at 300 K

A beam of nitrous oxide was scattered from the Pd(110) surface and the uptake of N_2O and formation of products monitored using the QMS to detect molecules scattered into the chamber. As the beam is admitted to the chamber it reflects from a flag in front of the sample, giving a constant signal, proportional to the N_2O flux (Fig. 1). When the flag is removed and the beam strikes the Pd(110) surface N_2O adsorption is seen as a decrease in the mass 44, 30 and 28 signals due to N_2O and its fragment ions. At temperatures above 150 K N_2O is not stable on Pd(110) and dissociates to give molecular N_2 , which desorbs promptly, and O, which remains on the surface. The mass



Fig. 1. Mass spectrometer trace showing the uptake of N_2O (m=44, solid line) and formation of nitrogen (m=28, points) as the beam is admitted to the chamber and then exposed to Pd(110) at 300 K. Mass 28 is also a cracking fragment of N_2O and the traces have been normalised to give the same signal at masses 44 and 28 from N_2O alone. The beam is admitted to the chamber and reflects from a flag, giving a constant signal due to the N_2O flux. When the flag is removed and the beam strikes the Pd surface the N_2O traps and dissociates to give N_2 , which desorbs, and O atoms, which remain on the surface, poisoning further adsorption.

44 and 30 signals, which are due solely to N_2O , show an identical decrease as N_2O is removed by reaction at the surface, followed by a recovery as O poisons the surface to further reaction, Fig. 1. The mass 28 signal shows a different behaviour, increasing due to nitrogen production before falling as reaction ceases. Since mass 28 is both a cracking fragment of N_2O and the N_2 product mass, this signal is made up of a combination of a decrease in the cracking signal due to N_2O and a (larger) increase caused by formation and desorption of nitrogen. We find that the N_2 desorption signal is a mirror image of the N_2O removal (Fig. 1) and no other products, such as NO, were formed.

The uptake of N₂O and the N₂ yield was calibrated by using the molecular beam to provide known gas fluxes and measuring the sticking probability and relative exposures required to form well-defined overlayer structures on the Pd surface. Since the beam operates in the effusive, lowpressure limit, the flux of molecules depends on $(mass)^{-0.5}$. By running known fluxes of N₂ and N₂O into the chamber we are able to calibrate the sensitivity of the mass 28 signal to nitrogen formed by reaction compared with N₂O cracking in the ion source. This allows us to confirm that N₂O dissociation forms only N₂ and O, with no N atoms remaining on the surface. The absolute N₂O uptake was determined by measuring the uptake of CO required to form the (2×1) p1g1 LEED pattern, which is the saturation overlayer of CO at 85 K and has a coverage $\Theta = 1$ ML. Thermal desorption spectra of CO were similar to those reported previously [15]. Integrating the uptake curves for CO and N₂O adsorption, and allowing for the difference in beam fluxes, gave a saturation N₂O uptake of 0.50 ML at 300 K.

After N₂O adsorption the surface showed a $c(2 \times 4)$ LEED pattern due to an ordered O overlayer. Oxygen adsorption on Pd(110) at 400 K gives rise to $c(2 \times 4)$ and (2×3) LEED structures [16], which are associated with (1×2) and (1×3) missing-row reconstructions of the Pd(110) surface [17]. Only one O species is seen by EELS [18,19] and the oxygen coverage of the $c(2 \times 4)$ -O structure was determined to be 0.5 ± 0.05 ML by nuclear reaction analysis [20,21] and by O₂ uptake [22], exactly the same coverage observed here for the saturation N₂O uptake at 300 K. An LEED analysis suggests the $c(2 \times 4)$ -O structure has O atoms adsorbed in threefold sites on the (111) microfacets in a zig-zag pattern along the top layer Pd rows, each O bonding to two Pd atoms from the top layer and one from the second layer, with O atoms out of phase on neighbouring [110] chains [17]. This model is consistent with the images observed in STM studies [23–25]. In contrast to oxygen adsorption, reaction with N₂O forms a well-ordered O overlayer even at 300 K, but reaction ceases at 0.5 ML coverage and does not continue to form the (2 × 3) structures seen during oxygen adsorption.

3.2. Temperature dependence of N_2O reaction

As the surface temperature is increased, the sticking probability for N₂O decreases, Fig. 2, $S(\Theta)$ decreasing roughly linearly with coverage for T > 473 K, consistent with dissociation on bare Pd(110) terraces and the surface being blocked to further adsorption by formation of the $c(2 \times 4)$ -O overlayer. For temperatures of 300 K or below, $S(\Theta)$ shows clear evidence of trapping, the sticking probability falling relatively slowly with coverage, consistent with an indirect, trapping-dissociation mechanism with both intrinsic and extrinsic precursor states. At 85 K the sticking probability is



Fig. 2. Coverage dependence of N₂O sticking as a function of surface temperature. The saturation uptakes of N₂O at 85 and 300 K have been determined from the adsorption curves, while the uptake remains approximately constant for $T \ge 300$ K.

independent of coverage until very close to saturation, sticking saturating with an uptake of 1.0 ML of N₂O, twice the uptake at 300 K. N₂O traps into a weakly bound precursor (physisorption) state and either dissociates or desorbs back to the gas phase, depending on the temperature. As the lifetime of the precursor state drops at higher temperatures, the coverage dependence $S(\Theta)$ becomes linear and only the intrinsic state has a significant reaction probability. The difference in activation energy for desorption or dissociation of the intrinsic precursor can be estimated if we assume that the trapping probability is approximately independent of temperature. Plotting $\ln(1/S_0-1)$ against 1/T gives an estimate of 14 kJ mol^{-1} for the difference in the activation barrier to desorption compared with dissociation.

Below 100 K the adsorption behaviour changes and N_2O adsorbs intact on the surface. A beam of nitrous oxide hitting the surface at 85 K results in a decrease in the mass 44 and 30 signals due to N_2O uptake, Fig. 3. The sticking probability for N_2O is 0.75 and is independent of coverage until adsorption is almost complete, Fig. 2. However, adsorption is not entirely molecular and a proportion of the N_2O dissociates to form O and N_2 . The molecular nitrogen desorbs immediately, giving an increase in the mass 28 signal, Fig. 3, but N_2 formation falls off rapidly as uptake proceeds, with a small secondary maximum at a coverage of half the saturation N_2O uptake. At higher doses the mass 28 signal returns to follow the mass 44 and 30 signals, indicating that N_2 evolution has ceased and N_2O is adsorbed molecularly without significant dissociation

The probability for N₂O dissociating to $O_{(a)} + N_{2(g)}$ was obtained by using the molecular beam to calibrate the sensitivity of the QMS, as described above. Using the relative OMS sensitivities and the absolute sticking probabilities obtained from the uptake measurements allows us to obtain the probability for N₂O dissociation as a function of uptake, Fig. 4. Initially, nitrous oxide adsorption leads to efficient dissociation on the clean Pd(110) surface, with around 60% of the N₂O dissociating, but this channel drops to just 5% once half the saturation uptake has been achieved and the remaining N₂O adsorbs without significant dissociation. Overall, some 15+3% of the N₂O which has adsorbed at saturation is dissociated to give adsorbed O atoms and N₂. N₂O adsorption at 85 K produces a surface with 0.15 ML of adsorbed O atoms and 0.85 ML of undissociated N_2O .

The secondary maximum in the N_2 evolution curve for an N_2O uptake of 0.5 ML is entirely



Fig. 3. Mass spectrometer trace showing the time behaviour of N_2O adsorption and N_2 evolution at 85 K (cf. Fig. 1). Exposing the surface to the N_2O beam leads to a decrease in the mass 44 signal (solid line) while the mass 28 signal (\bullet) increases initially, due to the formation of N_2 , and then decreases as nitrogen production ceases and N_2O adsorbs intact.



Fig. 4. Absolute probability for N_2 formation from N_2O as a function of the total N_2O uptake at 85 K. The calibration of the N_2O uptake and N_2 yield is discussed in the text.

reproducible and is associated with ordering of the Pd(110) surface. Halting adsorption on the 85 K surface at an uptake of 0.4 ML results in a very faint (2×1) LEED pattern, whereas by 0.6 ML uptake the pattern has changed to a (1×2) pattern, which becomes intense as adsorption continues up to 1.0 ML total uptake. The van der Waals radius of N_2O (1.55 Å) is larger than the atomic radius of the palladium atoms (1.375 Å), and the faint (2×1) pattern at $\Theta < 0.5$ ML is probably due to ordering of N₂O along the close-packed direction, just as seen for 0.5 ML NO [3] and CO [26] coverage, during adsorption at 180 K where Pd(110) is unable to reconstruct to form a missingrow structure. Local ordering of O formed by N₂O dissociation could also produce this pattern (oxygen adsorption typically forming streaks at the half-order positions even when ordering to form the missing-row reconstructions is incomplete along the [001] direction [16,18]), but this is not consistent with the disappearance of the weak (2×1) spots at higher N₂O coverages. The intensity and range of N₂O coverage over which the (1×2) LEED pattern is observed suggest that this ordering is associated with reconstruction of the substrate, rather than simply due to formation of an ordered N₂O overlayer. Since N₂O is too large to pack at full monolayer coverage along [110], the overlayer must involve some displacement or tilting of the N₂O (cf. both NO [3] and CO [26] adsorption on this surface at high coverage) and could not form the simple (1×2) symmetry seen in LEED. Although adsorption of NO and CO can also lead to ordered (1×2) LEED patterns, in this case the reconstruction only proceeds at temperatures above 240 K where the surface is sufficiently mobile to allow adequate transport of Pd atoms to form the missing-row Pd structures [3,26,27]. Since the Pd(110)– $(1 \times 2)N_2O$ surface forms a sharp LEED pattern at 85 K a missingrow reconstruction can be excluded, leaving a rowpairing or rumpled-surface reconstruction as the prime candidates. The Pd(110) surface undergoes a row-pairing reconstruction for H adsorption even at 120 K [28,29] and a pairing reconstruction of Pd has also been proposed for the (2×2) p1g1 structure seen for high coverages of NO at 180 K Thus the (1×2) periodicity of the [3].

 O/N_2O -covered surface following N_2O adsorption below 100 K is attributed to a displacive reconstruction of Pd(110), resulting in a (1 × 2) periodicity for the substrate, although a direct structural technique such as STM would be required to prove this conclusively.

3.3. Desorption of N_2O from Pd(110)

Heating a surface saturated with N₂O at 85 K resulted in a complex desorption peak, Fig. 5a, with three desorption features. The first peak, at 101 K, is predominantly due to desorption of molecular N₂O, with little dissociation. Cracking of the N₂O begins to dominate at higher temperatures, producing an N2 desorption peak near 117 K with a further shoulder at 140 K. Desorption of N₂O from a surface pre-adsorbed with ca 0.2 ML of O, Fig. 5b, leads to increased dissociation at 100 K but a 30% lower overall yield of N₂ compared with N₂O desorption. After desorption the surface shows a $c(2 \times 4)$ LEED pattern due to adsorbed O atoms. N₂O adsorption on a $c(2 \times 4)O$ surface at 85 K gave primarily molecular N₂O desorption at 100 K, with a small amount of residual N₂O dissociating at temperatures up to 140 K. The presence of O on the Pd(110) surface reduces the dissociation probability of N₂O and does not increase the binding energy of N₂O in the same way as observed on Ru(001) [30], where a large upward shift in the desorption temperature was observed.

3.4. RAIRS of N_2O adsorption on Pd(110) at 85 K

The RAIR spectrum for N₂O adsorption at 85 K is shown in Fig. 6 as a function of exposure. Since some of the N₂O dissociates, O atoms are always co-adsorbed along with the N₂O, although the proportion of O to N₂O drops rapidly at higher exposures. Initially the spectra show two bands at 1290 and 2255 cm⁻¹, with a shoulder near 2240 cm⁻¹. These peaks grow in together (traces 1–4) until an exposure corresponding to ca 0.5 ML uptake of N₂O. For higher exposures the surface adsorbs N₂O without any dissociation (Figs. 3 and 4) and the peaks at 1290 and 2255 cm⁻¹ continue to grow in intensity, with a





Fig. 5. (a) Thermal desorption spectrum following uptake of 1 ML of N_2O at 85 K. (b) Desorption spectrum of a saturation dose of N_2O from a surface which has 0.2 ML of O already on the surface from a previous dose of N_2O . In both cases the heating rate is 0.9 K s⁻¹ and the N_2O signal (mass 44) has been scaled to show the cracking signal it contributes at mass 28. The difference signal (dotted lines) represents the formation of N_2 as a function of temperature.

slight shift in the latter towards 2262 cm⁻¹ at saturation (trace 6). These bands correspond to the fundamental parallel vibrational modes of N₂O, with corresponding gas-phase frequencies of 1285 cm⁻¹ (v_(NO)) and 2224 cm⁻¹ (v_(NN)) respectively [31]. The presence of these bands in the spectrum indicates that N₂O is adsorbed upright, rather than lying down with its molecular axis parallel to the surface. The v_(NO) band is only slightly shifted with respect to the gas phase value, whereas the v_(NN)=2262 cm⁻¹ band is shifted up in frequency 38 cm⁻¹ compared with the isolated molecule.

The orientation of N₂O, whether bound via the N or the O atom, is not immediately clear. The shift of the $v_{(NN)}$ band is consistent with the molecule being bound to the surface via N, interaction with the surface shifting up the frequency of the $v_{(NN)}$ mode [32] but not influencing significantly the $v_{(NO)}$ band at 1290 cm⁻¹. The absence of any weakening of the N₂O bonds during chemisorption reflects the non-bonding nature of the filled 7σ and 2π orbitals, which are available for e⁻ donation to the metal from the terminal N, and the absence of back donation into the antibonding 3π orbital, which lies rather high in energy [32,33]. The $v_{(NN)}$ band shifts are similar to those seen for

chemisorption on Ru(001) [34] and Pt(111) [32]. However, unlike these surfaces, no bands due to physisorbed N₂O could be observed for adsorption on Pd(110) at 85 K and nor did the TPD indicate any state other than the chemisorbed species that desorbs above 100 K.

The growth of the band at 2240 cm^{-1} on Pd(110) seems to be associated with N₂O dissociation to form O, only the higher frequency band growing once N₂O dissociation ceases at $\Theta > 0.5$ ML, Fig. 6. This suggests that this band may be associated with N₂O binding at sites adjacent to adsorbed O atoms. Annealing the surface briefly up to 103 K (trace 7, Fig. 6) desorbed roughly half the N₂O from the surface, dissociating some of the N_2O and increasing the O coverage. The high-frequency band loses the sharp 2262 cm⁻¹ peak, leaving a broad band centred around 2249 cm⁻¹. On re-adsorbing 0.2 L of N₂O the spectrum now shows two sharp, overlapping peaks at 2260 and 2243 cm⁻¹, suggesting that the O/N₂O structure has become more ordered, sharpening up the low-frequency feature. In contrast, Pt(111) does not dissociate N₂O, as no N₂ production is observed during beam adsorption experiments at either 85 or 300 K. N₂O adsorption on Pt(111) was reversible, desorption and



Fig. 6. IR absorption spectra of the Pd(110) surface as a function of exposure to N_2O . Traces 1–6 show the IR spectrum for exposure to 0.1, 0.2, 0.3, 0.5, 1.0 and 2.0 L of N_2O respectively at 85 K. The lower traces show the effect of annealing to 103 K followed by re-exposing the O-covered surface to 0.2 L of N_2O at 85 K. The features near 1900 cm⁻¹ arise from miss-cancellation of CO adsorbed on the IR windows.

re-exposure simply regenerating the original N_2O RAIR spectra with no N_2 evolution [32].

4. Discussion

Adsorption of N₂O proceeds via a precursor mechanism, molecules trapping into a physisorption well that then leads to dissociation, desorption or transfer into the chemisorption state, depending on temperature. At low coverage the desorption channel has an activation barrier some 14 kJ mol⁻¹ greater than the barrier to N₂O dissociation. This trapping–desorption mechanism is consistent with the thermal angular distributions observed for N₂O formed during NO TPD [8,13]. N₂O dissociation occurs even at 85 K, leading to the formation of a mixed O/N_2O overlayer with a total adsorbate coverage of 1.0 ML. The adsorption behaviour is similar to that seen on W(110)and Ru(001), where N₂O dissociation at low coverages is followed by molecular adsorption, with N_2 desorbing on Ru(001) but forming adsorbed N on W(110) [35]. Cu(110) also reacts in a similar way [36], except that in that case dissociation of N₂O dominates over molecular adsorption even at 85 K. Why Cu(110) should be more reactive to N_2O than Pd(110) or Pt(111) is unclear. The high initial dissociation probability on Pd(110) at low temperature is probably associated with reaction at step or defect sites. On Ni(755) N₂O dissociation is associated exclusively with the step sites [37], whereas NO shows a similar preference for dissociation at steps on Pd [10,11]. Alternatively, it is possible that the formation of O atoms on the surface helps to stabilise chemisorbed N₂O by providing electron acceptor sites [30], although judging from the TPD and RAIRS data the stabilisation of N₂O by O_(a) seems to be minimal on Pd(110). At higher temperatures the total N_2O uptake is reduced (Fig. 2), dissociation of N₂O saturating with the formation of a $c(2 \times 4)$ -O LEED pattern, corresponding to a coverage of 0.5 ML of O atoms.

N₂O adsorption at 85 K forms an overlayer with a (1×2) LEED pattern that is ascribed to a row-pairing or rumpling reconstruction of the Pd(110) surface. The RAIR spectrum for N₂O adsorption at 85 K is characterised by two strong bands at 1290 and 2262 cm⁻¹ due to chemisorbed N₂O. Just as on Pt(111) and Ru(001), the $v_{(NN)}$ band is blue shifted due to the interaction with the surface [32]. During TPD the dissociation probability is sensitive to the amount of O adsorbed on the surface, a complete $c(2 \times 4)O$ overlayer leading primarily to molecular desorption, while intermediate O coverages reduce the N₂O uptake and the dissociation probability. However, the presence of additional O on the surface does not significantly alter the N₂O binding energy. This contrasts with the behaviour on Ru(001) where O stabilised N₂O adsorption, shifting the desorption peak up in temperature by 40 K [30]. However, at low N₂O coverage, an additional band due to chemisorbed N_2O is seen near 2240 cm⁻¹ and

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appears to be associated with O coadsorption. This band becomes sharper and more distinct when N_2O is readsorbed on a surface that has been annealed to dissociate some of the N_2O , Fig. 6.

A physisorption state was observed for N₂O on O-covered Ru(001) and also formed at high N_2O coverages on the clean surface, showing an intense perpendicular bending mode near 589 cm^{-1} in electron energy loss spectroscopy due to N₂O physisorbed with its axis parallel to the surface [34]. In addition to the upright chemisorbed species, weak $v_{(NN)}$ and $v_{(NO)}$ bands were seen for physisorption on Pt(111) at 83 K. Avery [32] reported a multilayer state that desorbed near 86 K, the strong bending mode again suggesting a flat-lying species. The observation of weak $v_{(NN)}$ and $v_{(NO)}$ bands indicates that the axis of the physisorbed species seen here on Pt(111) is tilted from the surface plane. No evidence was seen for physisorption of N₂O on Pd(110) at T=85 K. although the adsorption kinetics indicate such a state is important during adsorption.

Adsorption of NO on Ag(111) [38], Cu(111) [39] and Cu(110) [36] at low temperature produces N₂O via the formation of (NO)₂ dimers. On Ag(111) the N₂O formed is stable, whereas on Cu(110) some decomposes to give N₂ and adsorbed O atoms. Adsorption of NO on Pd(110) between 180 and 230 K also creates (NO)₂ dimers [3], but in this case no evidence was seen for formation of N₂O. We have extended these measurements down to 85 K to see if N₂O is formed at lower temperatures as the density of NO increases. The RAIR spectra of NO adsorbed at 85 K were identical to those reported previously at 180 K [3], with no evidence for formation of N₂O. Heating an NO-covered surface reproduced the TPD behaviour observed previously [3,6], with no N₂O formation until NO starts to dissociate at temperatures above 420 K [9]. We conclude that there is no evidence for the direct reaction of adsorbed NO to form N₂O on Pd(110). N₂ and N₂O products are only formed once the surface is sufficiently hot to dissociate NO [6,7], probably at a step or defect site as the Pd surface reconstructs [9].

The similarity of the N₂ translational energy

distributions formed by N₂O and NO decomposition suggests that N₂O may be a common intermediate to N₂ formation during thermal desorption of NO from a dense overlayer [8]. The angular distribution of N₂ formed during N₂O flash desorption has two components, one peaked at 45° to the surface along the [001] direction, while the second is symmetric about the surface normal. This distribution has been ascribed to a transition state with the N₂O axis parallel to the surface, the angle of desorption being controlled by the repulsive energy release between N2 and both the O and the Pd surface [8]. However, the LEED evidence that Pd reconstructs following N₂O adsorption suggests that the metal surface may be corrugated. N₂O decomposition does not occur on a flat surface, providing an alternative interpretation of the lobular N₂ product distributions. Decomposition of N_2O at the (1×2) surface may lead to off-normal desorption peaks simply because this reflects the local surface normal at the site where N₂ is created. This is indeed the model proposed for N₂ formation by reaction of NO at Pd(211) [13], where the N₂ angular distributions can be interpreted as a repulsion along the local surface normal from different step and terrace sites. During NO desorption N₂O is formed by the $N_{(a)} + NO_{(a)}$ reaction [7], initiated by $NO_{(a)}$ decomposition which is rate limiting [6]. Some of the $N_2O_{(a)}$ formed then dissociates to give $O_{(a)}$ and N_2 , which promptly desorbs. NO-covered Pd(110) shows a (1×3) missing-row reconstruction for both low and high NO coverage [3], and N_2 desorbs from this surface in a lobular distribution, peaked along the (111) microfacets [4,5]. The Pd(110) surface is very mobile during this reaction and clearly there is every chance that reaction occurs on Pd(111) microfacets, irrespective of the insensitivity of the N₂ angular distribution to the overall reconstruction of the NO phase [7]. Therefore, although the similar energy release into N₂ translation certainly suggests that N₂O may be a transient intermediate in both reactions [8], we propose that the lobular energy release is caused by the local normal of the reaction site and not by the balance of repulsion between O, the surface and the nascent N₂. This explanation for the offnormal desorption distributions removes the very specific repulsion between N_2 and the O/Pd(110) surface proposed by Ohno et al. [8], but is consistent with the vast body of desorption data that finds the product repulsion aligned along the local surface normal [12,40].

5. Conclusion

N₂O dissociation proceeds rapidly even at 85 K. the O formed poisoning further reaction and allowing N₂O to adsorb into a molecular chemisorption state. The O/N₂O-covered surface shows a (1×2) LEED pattern, suggesting a row-paired or rumpling reconstruction of the Pd(110) surface. The RAIR spectrum shows bands at 1290 and 2262 cm^{-1} due to N₂O adsorbed upright on the surface, bound via the N. A shoulder to the $v_{(NN)}$ feature near 2240 cm⁻¹ is associated with N₂O adsorption adjacent to coadsorbed O. No evidence could be found for N2O formation during NO adsorption at low temperature, N₂O only being produced once NO starts to dissociate at temperatures above 420 K. Reconstruction of Pd(110) in the presence of N₂O suggests that N₂O decomposition does not occur on a flat surface, providing an alternative explanation for the off-normal desorption of the N₂ produced during TPD.

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