Coadsorption of Nitrogen Dioxide and Oxygen on Pt(111)†

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Temperature-programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS) have been used to determine the NO_2 adsorption energy and geometry in the presence of coadsorbed oxygen atoms on Pt(111) at 100 K. NO_2 is adsorbed molecularly, regardless of the oxygen atom precoverage. Coadsorption with oxygen atoms causes a decrease in the amount of irreversible NO_2 adsorption and also a decrease in the amount of the Pt(111) μ-N,O-nitrito surface complex (bridge-bonded NO_2). Coadsorption also causes the formation of a new, low-temperature desorption state for NO_2 which is associated with an NO_2 bonding geometry possessing C_{2v} symmetry. It is proposed that this NO_2 species is bonded to a platinum atom through the nitrogen atom in a nitro configuration. An NO_3 species is not observed spectroscopically at any oxygen atom coverage in this work. However, an NO_3 intermediate may be responsible for some of the features in the adsorption and desorption kinetics. At $\theta_O = 0.75$ monolayer (ML), a chemisorbed NO_2 saturation coverage of 0.15 ML can be achieved and all NO_2 adsorption is reversible, having a chemisorption bond energy of 11 kcal/mol. When the chemisorbed state is saturated, an N_2O_4 multilayer can be formed at 100 K with greater NO_2 exposures.

Introduction

It has recently been established by using temperature-programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS) that NO_2 is adsorbed molecularly at all coverages on clean Pt(111) at 100 K.[1] NO_2 is bonded to this surface exclusively with C_s symmetry as a Pt(111) μ-N,O-nitrito surface complex bridge-bonded between two platinum atoms via an oxygen atom and the nitrogen atom. This surface species is thought to be the necessary precursor to the dissociation of NO_2 that produces adsorbed oxygen atoms and NO when the surface temperature is raised to 170 K. When $\theta_{NO_2} = 0.25$ monolayer (ML), the resulting combined oxygen atom and NO coverage is 0.5 ML and the surface becomes passivated to a degree. NO_2 desorption from greater coverages then becomes competitive with its dissociation.

Schwalke et al.[2] have observed that after initial NO_2 decomposition on Ru(001) at 80 K the surface becomes passivated with the decomposition products oxygen atoms and NO. Further NO_2 adsorption is molecular. NO_2 is bonded to the surface with C_{2v} symmetry via the nitrogen atom in a nitro-bonded configuration. This implies that the nitro adsorption geometry is not the required precursor for dissociation and that Ru(001) is too reactive for the adsorbed NO_2 configuration required for dissociation to be observed spectroscopically.

The NO_2/Ru(001) system is an interesting contrast to the NO_2/Pt(111) system. As long as bridge-bonded NO_2 is available on Pt(111), decomposition continues to take place when the temperature is raised to 170 K. If the possibility for adsorption in a bridge-bonded geometry is removed, the decomposition pathway for NO_2 should be eliminated on Pt(111).

This paper reports the use of coadsorbed oxygen atom coverages as high as 0.75 ML on Pt(111) to investigate modifications in the NO_2 adsorption energy and geometry. At coverages of $\theta_O \geq 0.25$ ML, in addition to bridge-bonded NO_2, NO_2 is found to bond to the surface in the same nitro-bonded configuration that has been observed for NO_2 molecularly adsorbed on Ru(001). When $\theta_O = 0.75$ ML, NO_2 can only bond to Pt(111) in a nitro-bonded geometry and NO_2 decomposition no longer takes place upon warming the sample. Schematic potential energy diagrams are used to rationalize this behavior qualitatively. In addition, we have studied the subtle changes that take place in the low-temperature physisorption states when the Pt(111) surface is precovered with oxygen atoms. This report is one in an on-going series that examines the adsorption and bonding of nitrogen oxides on metal surfaces.[1,3]

Experimental Section

The experiments were carried out in a stainless steel UHV system that has been described previously.[1,4] The system contains the instrumentation necessary to perform HREELS, TPD, Auger electron spectroscopy (AES), and low-energy electron diffraction (LEED). The crystal is heated resistively and is cooled by direct contact between the crystal holder and a liquid nitrogen reservoir. The temperature of the crystal is monitored by a chromel–alumel thermocouple. All data acquisition is accomplished under computer control except for the LEED observations.

Details concerning the Pt(111) crystal used in these experiments and the manner in which it was cleaned and characterized are available elsewhere.[1] The procedure used to synthesize and store the high-purity NO_2, the description of the microcapillary array doser used for NO_2 exposures and the flux enhancement factor achieved with it, the method used to calibrate the coverages of reversibly and irreversibly adsorbed NO_2, and the method used for the TPD and HREELS experiments have been given previously.[1] The only exception is that a 8 K/s heating ramp was used for TPD in these experiments.

All of the HREELS spectra, including those of the warm-up experiments, were taken with the crystal at 100 K. Signal-averaging with repetitive scans in combination with a real-time display of energy losses allowed features due to impurities adsorbed from the background such as NO to be easily identified.

The oxygen atom coverages used in this work were generated by exposing the crystal to NO_2 at 400 K.[5,6] The coverages were measured with AES using the calibration established in ref 5. Oxygen atom and NO_2 coverages reported in this paper are referenced to the Pt(111) substrate.

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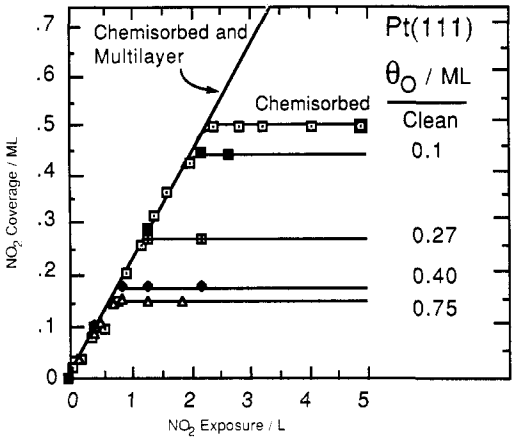

Figure 1. NO_2 uptake curves for several oxygen atom precoverages on Pt(111) at 100 K. The curves are derived from integrated thermal desorption data. A dramatic precursor effect dominates the NO_2 uptake in all cases, and the NO_2 initial sticking coefficient is independent of the surface oxygen coverage.

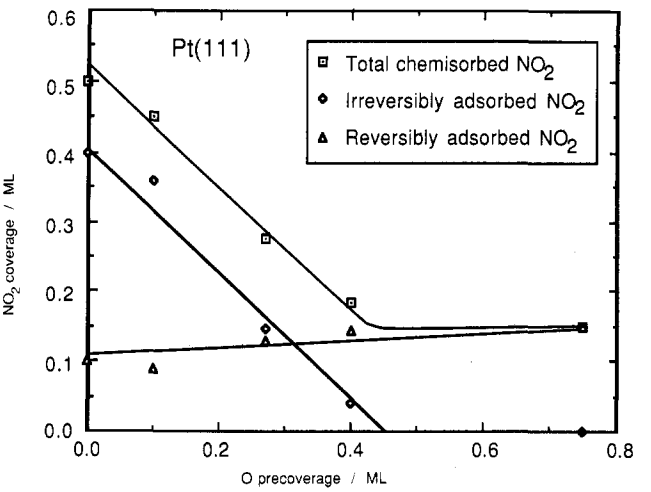

Figure 2. Saturation coverages of chemisorbed NO_2 as a function of oxygen atom precoverage on Pt(111). The amount of irreversibly adsorbed NO_2 decreases to zero when the precoverage of oxygen atoms reaches 0.45 ML.

Results

Temperature-Programmed Desorption and NO_2 Uptake. TPD experiments were performed as a function of NO_2 exposure at 100 K with several precoverages of oxygen atoms on Pt(111). Chemisorbed NO_2 was formed from low exposures of NO_2. The desorption of NO_2 from this state followed first-order kinetics and was detected by monitoring mass 46. This provided a measure of reversibly adsorbed NO_2. Irreversibly adsorbed NO_2 decomposed to NO and oxygen atoms. Monitoring mass 30 for NO during TPD provided a measure of NO_2 irreversible adsorption. The desorption of O_2 from oxygen atom recombination on the surface took place at temperatures well above the desorption states for NO and NO_2. O_2 desorption was detected by monitoring mass 32. The oxygen atoms resulting from irreversible NO_2 adsorption did not create any new features in the O_2 desorption spectra that have been reported for high oxygen atom coverages on Pt(111).[5] Physisorbed N_2O_4 multilayers were formed from higher exposures of NO_2.[1] But only mass 46 was observed during desorption from the multilayer. Desorption from the chemisorbed NO_2 and physisorbed N_2O_4 states can be distinguished, however, by the lower desorption temperature of NO_2 from the physisorbed state. Physisorbed states of N_2O_4 are removed by heating to 170 K. The assignments of the NO_2 and N_2O_4 species in the two states are supported by HREELS results, which will be discussed in the next subsection.

The results of each set of TPD experiments are summarized by using the integrated thermal desorption data to construct the uptake curves shown in Figure 1. Each curve that ends as a horizontal line in Figure 1 represents the sum of reversibly and irreversibly chemisorbed NO_2 for a given oxygen atom precoverage. The straight line that is common to each of the uptake curves and which extends above the uptake curve for chemisorption on the clean surface represents the amount of NO_2 adsorbed in both the chemisorbed and physisorbed states as a function of exposure. The data points used to construct the upper portion of this line have been left out of the figure for clarity. The fact that this line is common to each uptake curve indicates that the sticking coefficient for NO_2 is the same for chemisorption as it is for physisorption. It also indicates that the NO_2 initial sticking coefficient is constant and independent of the preadsorbed oxygen atom coverage. The initial slope of each curve matches the slope of the curve for the clean Pt(111) surface, determined previously to represent a sticking coefficient of unity.[1] The high sticking coefficient and the shape of the uptake curve have been attributed for Pt(111) to the existence of precursor states that can be populated with a high probability due to the availability of a large number of short-lived adsorption intermediates for NO_2.[1] Considering that oxygen atoms are present on the surface, an important factor in the adsorption kinetics may be the formation of an NO_3 intermediate. This subject will be treated in greater detail in the Discussion section.

For the NO_2 uptake curve at θ_O = 0.75 ML, the initial slope and the saturation chemisorption coverage are both the same whether adsorption takes place at 100 or 170 K. Exposures at 170 K were performed to remove the possibility of any features of physisorbed layers being included in the integration. Besides having the same initial sticking coefficients of unity, the θ_O = 0.75 ML and the clean uptake curves also have similar functional forms versus exposure with relatively abrupt breakpoints. This allowed the other curves in Figure 1 to be adequately characterized by determining the onset of the multilayer formation for each oxygen coverage.

It is clear from Figure 1 that the saturation coverage of chemisorbed NO_2 decreases as the oxygen atom precoverage increases. The specific dependence is shown in Figure 2 to be the result of two effects by plotting the amount of NO_2 that is irreversibly and reversibly adsorbed, in addition to the total chemisorbed coverage, as a function of oxygen atom precoverage. Up to precoverages of θ_O = 0.45 ML, NO_2 uptake and the amount of irreversibly adsorbed NO_2 are reduced linearly. We attribute this to simple site-blocking by oxygen atoms on the surface. The slope of these lines implies that one adsorbed NO_2 is eliminated for every preadsorbed oxygen atom. This is in contrast to the amount of NO_2 that is reversibly adsorbed. At least 0.1 ML of NO_2 is reversibly adsorbed for each saturation NO_2 coverage, reaching a maximum of 0.15 ML on the oxygen-saturated surface. Thus, this state is largely independent of oxygen atom precoverage. The HREELS spectra will be used in the next subsection to show that nitro-bonded NO_2 populates this state at θ_O = 0.25 ML and above. Thus, nitro-bonded NO_2 becomes an adsorption alternative that allows the surface to be populated by NO_2 at oxygen atom coverages where the uptake of bridge-bonded NO_2 would otherwise be expected to go to zero. If the coadsorbed oxygen atoms that result from NO_2 decomposition during TPD are considered, then the total oxygen atom coverage including preadsorbed oxygen atoms is essentially constant up to an oxygen precoverage of 0.45 ML. Above this value, where essentially no NO_2 decom-

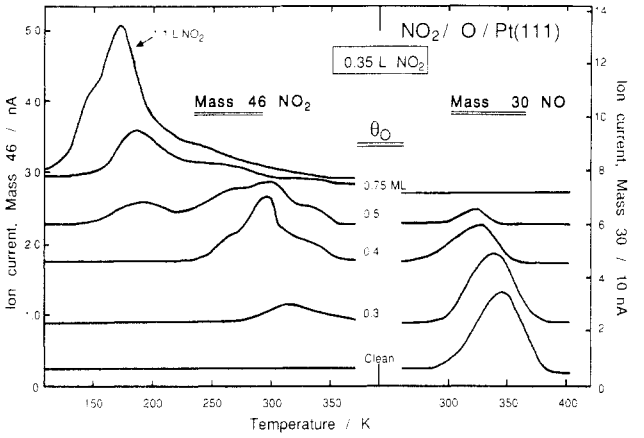

Figure 3. NO_2 and NO desorption spectra resulting from oxygen atom precovered Pt(111) exposed to 0.35 langmuir of NO_2 at 100 K. This exposure provides the same initial coverage of NO_2 for each experiment.

position takes place, the oxygen atom coverage is due only to the oxygen atoms that are preadsorbed.

It can be seen from Figure 1 that exposures below 0.75 langmuir provide the same amount of chemisorbed NO_2 regardless of the amount of preadsorbed oxygen that is on the surface. Using a constant exposure of 0.35 langmuir for a series of TPD experiments as a function of oxygen atom precoverage provides a point that is common to each uptake curve. These desorption spectra show in Figure 3 the manner in which the energetics of the desorption states for NO_2 change as a function of oxygen atom precoverage. No desorption of NO_2 is seen on the clean Pt(111) surface from an NO_2 exposure of 0.35 langmuir.[1] When θ_O = 0.3 ML, some reversible adsorption of NO_2 is observed at 310 K. This corresponds to an activation energy for desorption of 19 kcal/mol and is similar to that observed for NO_2 exposures of 1.5 langmuir and greater on clean Pt(111). At 0.4 ML of oxygen atoms, a greater amount of NO_2 is reversibly adsorbed with a decrease in the activation energy for desorption. By 0.5 ML of oxygen atoms however, the amount of NO_2 that desorbs from this state is diminished, and desorption from a new state is seen at 180 K. When the surface is saturated with oxygen atoms at θ_O = 0.75 ML, the high-temperature desorption state of NO_2 is absent and the low-temperature desorption state is populated to a greater extent. It is saturated by 1.1 langmuir of NO_2. Desorption from this state takes place with first-order kinetics and E_a = 11 kcal/mol. The high-temperature tail for this desorption may be the result of the low degree of order of the oxygen-saturated Pt(111) surface and/or some interconversion of the two NO_2 states.

Directly associated with these changes in the desorption kinetics for molecular NO_2 is the reduction in the amount of NO_2 that is dissociated to oxygen atoms and NO upon warming. This can be seen in Figure 3 from the decrease in the amount of NO that desorbs as the oxygen atom precoverage increases. When θ_O = 0.75 ML, no NO desorbs, signifying that all NO_2 adsorption is reversible. The energy of activation for the first-order desorption of NO shown in Figure 3 decreases continuously with increasing oxygen atom coverage in a similar way to that seen previously for NO desorbing from Pt(111) when coadsorbed with other electronegative coadsorbates.[1,7,8]

When the surface saturated with oxygen atoms is given further exposures to NO_2, two more low-temperature NO_2 desorption states are populated. HREELS spectra show that these states are populated by an N_2O_4 physisorbed species. The vibrational spectra are discussed in the next

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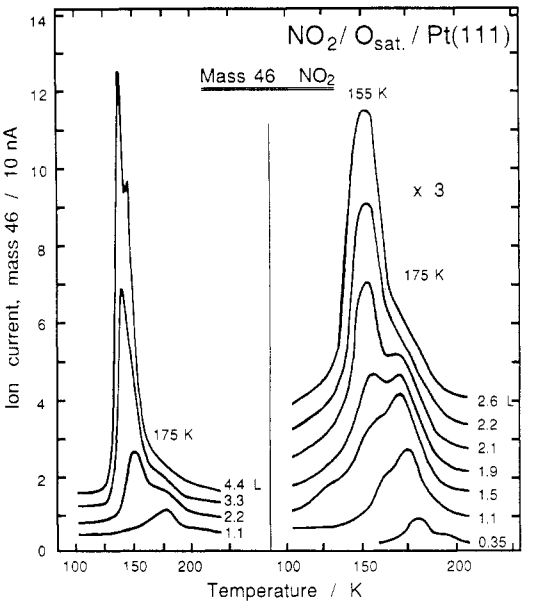

Figure 4. NO_2 desorption spectra from oxygen atom saturated Pt(111) for several NO_2 exposures at 100 K. By 3.3 langmuirs, the zero-order desorption of NO_2 from an N_2O_4 multilayer begins with an onset at 120 K. Exposures less than this are associated with first-order desorption from a physisorbed state with a peak maximum at 155 K that is distinctly different from the chemisorbed state at 175 K.

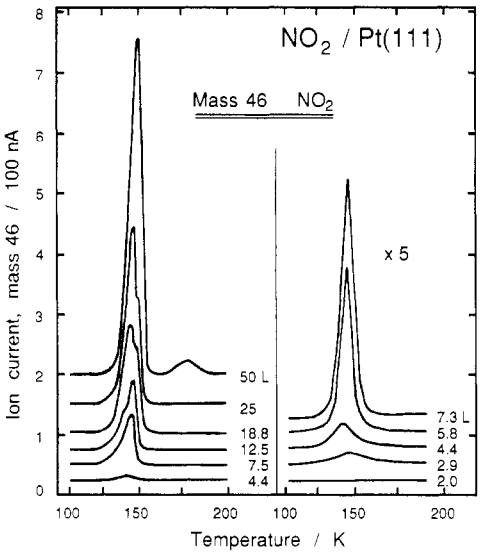

Figure 5. NO_2 desorption spectra from several N_2O_4 multilayer coverages on bridge-bonded NO_2-saturated Pt(111). Saturation of a zero-order desorption state at 12.5 langmuirs is followed by desorption from a different zero-order desorption state.

subsection. The first state is populated by NO_2 exposures greater than 1.1 langmuirs. The desorption of NO_2 from this state at 155 K follows first-order kinetics and is shown in detail on the right-hand side of Figure 4. The left-hand side of Figure 4 shows that this state is saturated by approximately 3.3 langmuirs of NO_2. At this exposure a second NO_2 desorption state begins to form. The desorption takes place with zero-order kinetics with an onset of 120 K. The double peak seen in the desorption spectrum that corresponds to the 4.4-langmuir exposure is reproducible and suggests the possibility that the two physisorption states may become populated competitively at this coverage. Considering that the chemisorbed state is saturated by 1.1 langmuirs and that the multilayer begins at an exposure of approximately 3.3 langmuirs, the NO_2 exposure difference of 2.2 langmuirs is required to saturate the 155 K first-order desorption state. Since the NO_2 sticking coefficient is unity, this exposure indicates

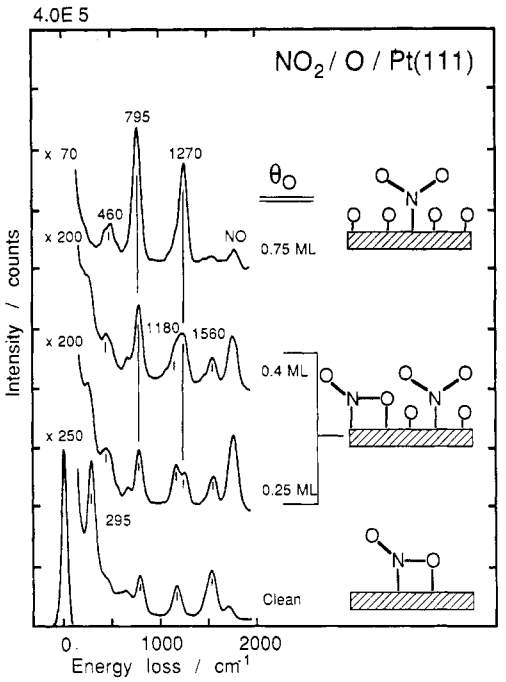

Figure 6. HREELS spectra for NO_2 adsorbed at 170 K with increasing amounts of oxygen atoms on Pt(111).

that an N_2O_4 coverage on the order of 0.25 ML is associated with this desorption state.

The desorption spectra of NO_2 from N_2O_4 on oxygen atom saturated Pt(111) are uniquely different from the desorption spectra of NO_2 from N_2O_4 observed on the bridge-bonded NO_2-saturated Pt(111) surface (in the absence of coadsorbed oxygen atoms) that are shown in Figure 5. This difference may be due to the existence of metastable NO_3. In Figure 5, two physisorbed NO_2 desorption states other than the NO_2 chemisorbed state can also be populated. However, neither of these desorbs with first-order kinetics. The right-hand side of Figure 5 shows that the first of these states begins to be populated by 2.6 langmuirs of NO_2 with an onset of 125 K. The overlap of the leading edges of the desorption curves from greater coverages of NO_2 make it clear that desorption of NO_2 from this state is governed by zero-order kinetics. As shown on the left side of Figure 5, saturation is reached at about 12.5 langmuirs. The NO_2 exposure difference of 9.6 langmuirs that is necessary for saturation implies that approximately 1 ML of N_2O_4 populates this state. At this point the zero-order desorption of NO_2 from a second state begins at an onset of 120 K. This multilayer of N_2O_4 can be populated without limit with greater exposures of NO_2. The desorption of NO_2 at 180 K has been noted previously,[1] but the origin of this state is not understood.

High-Resolution Electron Energy Loss Spectroscopy. The dependence of the chemisorbed NO_2 bonding geometry on oxygen atom coverage was explored in a series of HREELS experiments. The population of physisorption states was avoided by carrying out the NO_2 exposures at 170 K. The spectra are shown in Figure 6. Energy losses at 460 cm^{-1} are due to the Pt–O stretch for preadsorbed oxygen atoms.[5,9]

On the clean Pt(111) surface in Figure 6, losses are seen that are due to a Pt(111) μ-N,O-nitrito surface complex possessing C_s symmetry (bridge-bonded NO_2) that has been reported previously.[1] The ONO asymmetric stretch occurs at 1560 cm^{-1}, the ONO symmetric stretch at 1180 cm^{-1}, the ONO bend at 795 cm^{-1}, and the Pt-molecule stretch at 295 cm^{-1}. The high-frequency loss at 1740 cm^{-1} is due to the stretch of a top-site bonded coadsorbed NO impurity. The loss due to this impurity is present in each of the spectra and shifts to a higher frequency with increasing amounts of coadsorbed oxygen atoms.[8] The frequency of the Pt–NO stretch when NO is coadsorbed with oxygen atoms is at 265 cm^{-1}.

When NO_2 is adsorbed with an increasing amount of oxygen atoms on Pt(111), a loss due to a new species grows in at 1270 cm^{-1} while the losses due to bridge-bonded NO_2 become less intense. At intermediate oxygen atom coverages, therefore, two NO_2 adsorption isomers are present at the same time. On the surface saturated with oxygen atoms at θ_O = 0.75 ML, energy losses having the frequencies associated with the ONO asymmetric and symmetric stretches of bridge-bonded NO_2 are present with only minimal intensity. The HREELS spectrum of this surface indicates that NO_2 is adsorbed in a geometry that is distinctly different from that found on the clean Pt(111) surface. This is consistent with the TPD results which show that NO_2 is only reversibly adsorbed on the oxygen-saturated surface. The energy loss at 1270 cm^{-1} is in the frequency range seen for the ONO symmetric stretch in a number of transition-metal NO_2 coordination compounds[10] and is of a similar frequency at the same mode for NO_2 adsorbed in a nitro configuration with C_{2v} symmetry on Ru(001).[2] These vibrational frequencies are given in Table I for comparison.

All of the peaks were attenuated in off-specular scans, and no other modes were observed. Therefore, all of the

Table I. Vibrational Frequencies (cm^{-1}) of Nitro-Bonded NO_2 on O-Saturated Pt(111) Compared to Gas-Phase NO_2,[16] the Free Nitrite Ion Found in $NaNO_2$,[10] and Nitro-Bonded NO_2 in a Pt Coordination Compound[10]

mode	NO_2/O/ Pt(111)[a]	NO_2(g)	NO_2^-	$Pt(NO_2)_4^{2-}$	NO_2/ Ru(001)[b]
δ NO_2 (bend)	795	750	830	838–845	780
ν_s ONO (sym stretch)	1270	1318	1335	1344–1392	1300
ν_a ONO (asym stretch)		1618	1250	1415–1440	

[a] This work. [b] NO_2 coadsorbed with NO and O on Ru(001).[2]

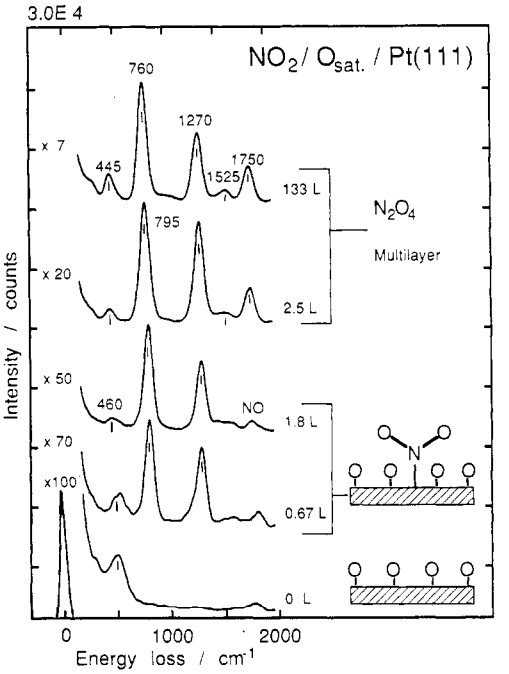

Figure 7. HREELS spectra for increasing NO_2 exposures to oxygen atom saturated Pt(111) at 100 K.

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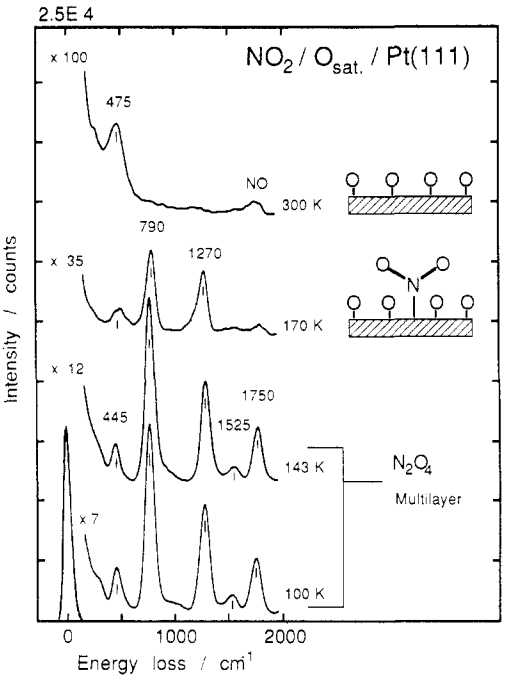
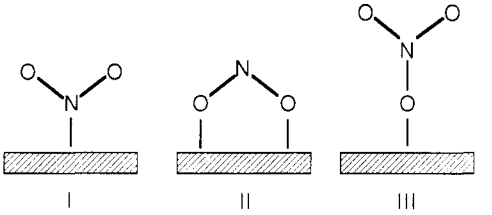


Figure 8. HREELS warm-up experiments for the oxygen atom saturated Pt(111) surface after a 133-langmuir NO_2 exposure at 100 K.

observed losses in Figure 6 are due to dipole scattering. In accordance with the surface dipole-selection rule,[11,12] the disappearance of the asymmetric ONO stretching mode is associated with the adsorption of NO_2 in a geometry of higher symmetry than C_s. NO_2 bonded to the surface with C_{2v} symmetry would be consistent with this and would allow only the ONO bend and symmetric stretch to be observed with on-specular HREELS. Interestingly, the frequency of the NO_2 bending mode is typically insensitive to the NO_2 bonding geometry.[10] A constant value of 795 cm^{-1} seen in Figure 6 is in close agreement with the bending mode of NO_2 found on other surfaces.[1-3,13]

The vibrational spectra in Figure 6 combined with the desorption spectra in Figure 3 at similar oxygen atom precoverages show that decomposition of NO_2 to NO and oxygen atoms only occurs when NO_2 is adsorbed in a bridge-bonded geometry. On the oxygen atom saturated surface, where NO_2 is bonded to the surface exclusively in a nitro configuration, NO_2 decomposition does not occur. This further confirms that bridge-bonded NO_2 is the required precursor to NO_2 dissociation.

Figure 7 shows the results of a set of HREELS experiments that were performed as a function of NO_2 exposure on oxygen atom saturated (θ_O = 0.75 ML) Pt(111) at 100 K. Initially, only the Pt–O stretch at 460 cm^{-1} is observed. As in Figure 6, 0.67 langmuir of NO_2 at 100 K on the oxygen-saturated surface gives energy losses that can be assigned to C_{2v} NO_2. At 1.8 langmuirs, an exposure that is sufficient to saturate the chemisorbed state, no changes take place in the spectra except an increase in the intensities of the losses. An exposure of 2.5 langmuirs provides a coverage that corresponds to the first-order desorption state seen at 155 K. The HREELS spectrum has intense losses at frequencies like that seen for N_2O_4 on other surfaces.[1-3] The N_2O_4 losses become much more intense at an NO_2 exposure large enough to populate the zero-order desorption state.



When the N_2O_4 multilayer is warmed up, as shown in Figure 8, there is a decrease in the intensities at 143 K. Other than this, however, there are no changes in the spectra until 170 K. At this temperature, all features of the multilayer are gone, leaving only those of NO_2 chemisorbed with C_{2v} symmetry. There is no detectable conversion to bridge-bonded NO_2 that takes place during the warmup nor does any NO_2 decompose. Consistent with the TPD results, the spectra in Figure 8 show that all of the NO_2 has desorbed from the surface by 300 K.

LEED. LEED observations of adsorbed NO_2 were made under a number of conditions. These used different oxygen atom precoverages for a basis set of experiments in which the exposures of NO_2 were varied and also a thick N_2O_4 multilayer was warmed up. No difference in the surface order of the oxygen atom covered surfaces[5] was detected upon NO_2 coadsorption under any of the conditions studied.

Discussion

Bonding Geometry of NO_2. Although NO_2 can bond to metals in coordination compounds in numerous ways,[10] the C_{2v} symmetry of the adsorbed NO_2 surface complex identified in this study reduces the number of specific bonding configurations that need to be considered to two. The two isomers are nitro (I) and O,O′-nitrito (II) or chelating. A nitrato species (III) with C_{2v} symmetry must also be considered since the high coverages of oxygen atoms present on the surface at the time of NO_2 adsorption present the possibility that an NO_3 species could be formed. However, it would be expected from the vibrational spectra of coordination compounds containing NO_3 that a dipole-active mode at approximately 1000 cm^{-1} due to the MO–NO_2 stretch[14] would be observed if III were formed on the surface. Outka et al.[13] have proposed the existence of III with C_{2v} symmetry on Ag(110) and have assigned an HREELS energy loss at 1080 cm^{-1} to the AgO–NO_2 stretch. At no coverage of oxygen atoms and NO_2 is such a vibrational frequency observed in this work.

The vibrational frequencies of C_{2v} NO_2 adsorbed on oxygen atom saturated Pt(111) match those of NO_2 nitro bonded on Ru(001) very well. Both are listed in Table I for comparison. The intensity of the bend relative to the symmetric stretch is also remarkably similar in the two cases. This implies that NO_2 is bonded in the same configuration on both surfaces. To a large extent, then, the discussion put forth by Schwalke et al.[2] that compares the nitro and chelating bonding geometries can be used to argue that NO_2 is also nitro-bonded on oxygen atom saturated Pt(111). Also, the vibrational frequency of the nitro NO_2 symmetric stretch in $Pt(NO_2)_4^{2-}$[10] given in Table I is only 75 cm^{-1} higher than the frequency of C_{2v} NO_2 on Pt(111). However, the typical frequencies of the symmetric stretch for NO_2 bonded as a chelate in transition-metal complexes are close too, having a range 1171–1225 cm^{-1}.[10,15]

In view of the preceding discussion, it is obvious that an identification of the bonding geometry based only on the small frequency differences between the symmetric

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stretches of nitro and chelating NO_2 ligands in transition-metal coordination compounds cannot be an unambiguous one. From the standpoint of steric hindrance and NO_2 coverage, however, the nitro species is a strong assignment. I certainly takes up less room on the surface than II. The established chemical preference of Pt(111) to adsorb NO_2 in a bridge-bonded geometry[1] suggests that an ensemble of Pt atoms large enough to adsorb II should instead adsorb bridge-bonded NO_2. The adsorption of II would also require the unreasonable "total site" occupancy of greater than 1 ML for the NO_2 saturation coverage of 0.15 ML (effectively 0.3 ML considering the bidentate nature of II) coadsorbed with the oxygen atom saturation coverage of 0.75 ML.

The assignment of nitro-bonded NO_2 is further supported by the intensity of the ONO bend relative to the intensity of the ONO symmetric stretch. The perpendicular displacement of nonbonded oxygen atoms in I during a bending vibration should contribute to a dynamic dipole that is quite large and therefore an energy loss that is more intense than that for II. Of course this argument needs a reference HREELS spectrum of chelating NO_2 bonded to a surface to be convincing. Such a species has recently been identified by us on Au(111).[3] The intensity of the bending mode relative to the symmetric stretch is indeed noticeably less than the same modes of C_{2v} NO_2 adsorbed on oxygen-saturated Pt(111). Also, the symmetric stretching frequency for the chelating species is 1180 cm^{-1}. This is in close agreement with the symmetric stretching frequency of NO_2 coordinated as a chelate in transition-metal complexes.[10,15] Therefore, I and II have unique vibrational spectra that can be used to distinguish one from the other.

No evidence of other vibrational modes due to impact scattering was found in the off-specular HREELS spectra of NO_2 adsorbed on the oxygen atom saturated Pt(111) surface. This implies that the NO_2 asymmetric stretching frequency may be very close to the frequency of the symmetric stretch at 1270 cm^{-1}. The possible near degeneracy of these two modes may be expected since the frequency difference between the two stretching modes of nitro-coordinated NO_2 in transition-metal complexes is typically less than 100 cm^{-1}.[10,15]

Adsorption Kinetics. An important result of this work is the finding that even at high oxygen atom precoverages NO_2 is adsorbed with a high probability and with a reasonably strong chemical bond. The sticking coefficient of unity below 170 K that is insensitive to the coverage of both oxygen atoms and NO_2 suggests the possibility that a metastable NO_3 precursor species may play a role in the efficient uptake of NO_2 on the oxygen-precovered surface. However, this species was not observed with HREELS. The fact that only a small saturation coverage of 0.15 ML of NO_2 can be attained for the chemisorbed state on the oxygen atom precovered surface lends stoichiometric support to the determination that a stable NO_3 is not formed on the surface.

The coverage of irreversibly adsorbed NO_2 is determined by the oxygen atom coverage and decreases linearly as the oxygen coverage goes up. The total chemisorbed NO_2 coverage might have the same dependence on oxygen atom coverage if it was not for the adsorption of NO_2 in a nitro-bonded geometry. This bonding configuration keeps the NO_2 uptake from going to zero on the oxygen atom saturated surface and contributes to the amount of reversibly adsorbed NO_2 being essentially constant with oxygen atom coverage.

Even though the surface bond is weak at 11 kcal/mol, nitro-bonded NO_2 is not incorporated into the multilayer.

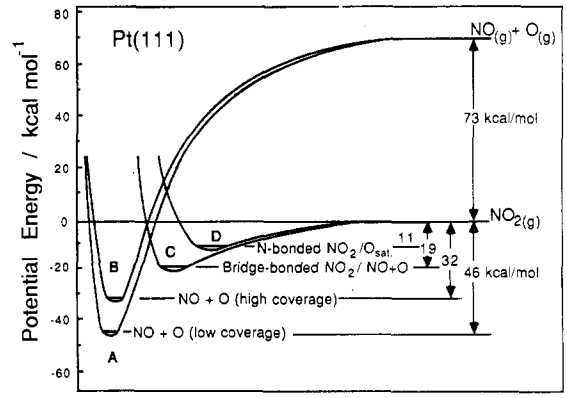

Figure 9. Schematic potential energy curves for the Pt(111) μ-N,O-nitrito surface complex (bridge-bonded NO_2),[1] its decomposition products, and the Pt(111) nitro surface complex (nitro-bonded NO_2) in the presence of oxygen atoms on Pt(111).

This follows a thermodynamic reasoning that has been applied previously to explain the behavior of NO_2 adsorbed on clean Pt(111).[1] Nitro-bonded NO_2 is a true chemisorbed species with a well-defined bonding geometry.

Desorption from the Multilayer. The existence of a metastable, short-lived NO_3 species formed from the decomposition of N_2O_4 to NO_2 on the oxygen-saturated surface when heated during TPD could explain the NO_2 first-order desorption peak at 155 K from a state that has a vibrational spectrum clearly that of N_2O_4. The amount of N_2O_4 associated with this state is about 0.25 ML. More importantly, this means that 0.5 ML of NO_2 would be available from this state. This amount of NO_2 approaches the one-to-one correspondence with the oxygen atom coverage of 0.75 ML that might be expected if the formation of an NO_3 transient was favorable. This is a reasonable possibility in view of NO_2 desorption from the N_2O_4 multilayer present on Pt(111) saturated with bridge-bonded NO_2. For this case, desorption from the initial N_2O_4 monolayer takes place with zero-order kinetics since no oxygen atoms are available and metastable NO_3 cannot be formed. The presence of two zero-order desorption states shown in Figure 5 must be the result of a slight energetic difference between NO_2 desorption from a N_2O_4 layer that is on top of another N_2O_4 layer and NO_2 desorption from a N_2O_4 layer that is on top of a bridge-bonded NO_2 layer.

Adsorption Geometry Requirements for Dissociation. In Figure 9, schematic potential energy diagrams for each of the three states in which NO_2 is known to exist on Pt(111) are placed on the same reaction coordinate with zero energy being referenced to gas-phase NO_2. Although qualitative in shape they are quantitative in depth, using data from this work and ref 1. For the purpose of this discussion, the curves' crossing points adequately illustrate the influence of kinetic barriers on the observed behavior of NO_2 on clean and on oxygen-covered Pt(111). The curves are used to discuss the dependence that NO_2 dissociation has on its adsorption geometry. As such, the role of bridge-bonded NO_2 as the necessary precursor to dissociation on the Pt(111) surface is emphasized.

Previous work[1] has shown that at low coverages molecular adsorption of NO_2 at 100 K on clean Pt(111) is followed by complete dissociation at 170 K to yield oxygen atoms and NO. The potential energy curve for these products has a well depth of 46 kcal/mol and is represented by curve A in Figure 9. The well-depth for oxygen atoms and NO is diminished continuously with increasing NO and oxygen atom coverage until $\theta_{O+NO} = 0.5$ ML. It is at this point that a constant well depth of 32 kcal/mol is reached (curve B) and NO_2 desorption becomes com-

petitive with its decomposition. The potential energy curve for NO_2 under these conditions is represented by curve C and is associated with bridge-bonded NO_2. It has a depth of 19 kcal/mol that is constant over a large range of NO_2, NO, and oxygen atom coverages. The crossing point of B and C, elevated with respect to the crossing point of A and C, qualitatively depicts that when the potential energy curve of the dissociation products NO and oxygen atoms is lifted to 32 kcal/mol, a kinetic barrier is formed that is of sufficient height to allow some reversible adsorption of NO_2 to take place. In further agreement with this representation is the fact that at no coverage up to saturation in the chemisorbed NO_2 monolayer does decomposition cease being competitive with desorption. In addition, the NO_2 that desorbs does so exclusively with first-order kinetics, indicating that the height of the barrier for NO and oxygen atoms to recombine and form NO_2 is higher than the barrier to NO desorption.[1,8]

The existence of NO_2 in numerous weakly bound adsorption geometries has been postulated[1] to explain the high sticking coefficient of NO_2 on Pt(111).[1,6] The results reported in this paper make it clear that one of the precursors that could play an important role in adsorption to form bridge-bonded NO_2 may be nitro-bonded NO_2. The kinetic barrier between bridge-bonded NO_2 and nitro-bonded NO_2 is too low on clean Pt(111) for nitro-bonded NO_2 to be stable on the HREELS time scale. However, in a manner consistent with our HREELS observations, the diagrams in Figure 9 show how nitro-bonded NO_2 (curve D) can be stabilized if the possibility for bridge-bonded adsorption (curve C) is removed. By simple steric inhibition, coadsorbed oxygen atoms not only can reduce the amount of NO_2 adsorbed but at a saturation coverage of $\theta_O = 0.75$ ML can also remove any Pt ensembles large enough to allow a bridge-bonded configuration to be achieved. To overcome this, the displacement of at least one oxygen atom on the surface by an oxygen atom from bridge-bonded NO_2 would be required. This would be thermodynamically unreasonable. Therefore, with the bridge-bonded adsorption geometry no longer available, curve C is effectively removed from the diagram in Figure 9, and decomposition of nitro-bonded NO_2 is eliminated by the large barrier represented by the crossing point of curves B and D. Thus, NO_2 coadsorbed with 0.75 ML of oxygen atoms on Pt(111) is restricted to a nitro-bonding geometry, and simultaneous contact between the Pt surface, the oxygen atom, and the nitrogen atom cannot be achieved. As a result, NO_2 cannot dissociate to oxygen atoms and NO. Recently, we have used HREELS and TPD to prove that a true barrier exists for the reverse case by showing that NO coadsorbed with high coverages of oxygen atoms on Pt(111) does not form NO_2.[8]

Summary

The coadsorption of NO_2 and oxygen atoms on Pt(111) has been studied. Changes in the NO_2 coverage, adsorption energy, and the adsorption geometry have been observed as a function of oxygen atom precoverage. When $\theta_O \geq 0.25$ ML, a new chemisorption state for NO_2 is stabilized. NO_2 is bonded directly to a platinum atom via the nitrogen atom in a nitro configuration with C_{2v} symmetry. This is the exclusive bonding geometry for NO_2 when it is coadsorbed with 0.75 ML of oxygen atoms on Pt(111). TPD has been used to determine that this chemisorbed state has a heat of adsorption of 11 kcal/mol and can be populated to a saturation coverage of 0.15 ML of NO_2. NO_2 chemisorption takes place with an initial sticking coefficient of unity at temperatures below 170 K and is completely reversible on the oxygen atom saturated surface. There is no coverage at which a stable NO_3 species is formed from the coadsorption of NO_2 and oxygen atoms on Pt(111) at 100 K. However, a short-lived NO_3 intermediate is proposed to explain the strong precursor adsorption kinetics and a first-order desorption feature in TPD of the first physisorbed N_2O_4 layer.

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Coadsorption of Hydrocarbon Fragments with CO on Ni(100) and Ru(001)†,‡

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The coadsorption of CO with C_2 hydrocarbon fragments was studied on Ni(100) and Ru(001). The hydrocarbon intermediates included vinyl, ethylidyne, acetylinic/vinylidene, and acetylide species. These fragments exhibited greater thermal stability in the presence of high coverages of coadsorbed CO. The stabilization is mainly attributed to a site-blocking effect of CO. The implications of this effect for Fisher-Tropsch synthesis are considered in detail.

Introduction

Under Fisher-Tropsch (F-T) synthesis conditions, various known and postultaed hydrocarbon fragments,[1-4] viz., C, CH_x, and C_nH_m, coexist with a large amount of coadsorbed CO, which nearly saturates the metal surface.[5] Any interaction between CO and the hydrocarbon fragments is expected to influence the mechanistic and kinetic

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