THE ADSORPTION OF NITRIC OXIDE AND NITROGEN DIOXIDE ON POLYCRYSTALLINE PLATINUM

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Received 13 March 1989; accepted for publication 18 July 1989

NO and NO$_2$ adsorption on a polycrystalline platinum surface was studied using temperature programmed desorption (TPD). NO adsorption is irreversible for NO exposures of less than 0.12 L at 120 K yielding only N$_2$ and O$_2$ upon heating. However, when the NO exposure is increased to 0.12 L and above, reversible NO adsorption is observed. Two NO desorption states occur with peaks at 470 and 300 K. No desorption of NO$_2$ resulting from oxidation of NO was observed at any coverage. NO$_2$ adsorption at 120 K is largely irreversible below monolayer saturation coverages. However, a small NO$_2$ desorption peak is observed at 300 K at a monolayer coverage of NO$_2$. NO and O$_2$ TPD spectra following NO$_2$ exposures are quite different from those spectra obtained following NO or O$_2$ exposures. The differences in the NO TPD spectra are due to the influence of coadsorbed O atoms on the adsorption and decomposition of both NO and NO$_2$. Changes in the O$_2$ TPD spectra are due to the very high coverages of adsorbed O atoms that can be obtained from NO$_2$ exposures.

1. Introduction

Fundamental studies of the adsorption and reaction of NO, NO$_2$, and CO on platinum surfaces are becoming increasingly important due to the recent interest in lowering CO and NO$_x$ emissions from automobile exhausts. Numerous studies of reactions between NO$_2$ and NO with CO on polycrystalline platinum surfaces are available in the recent literature [1–7]. For example, we have investigated the steady-state kinetics of NO$_2$ reduction by CO [2], and also performed transient kinetic studies of NO reduction by CO [3]. In order to interpret these results and formulate possible reaction mechanisms, it is necessary to obtain a better understanding of the interaction of the reactants and products with platinum surfaces.

Polycrystalline platinum surfaces are more complex than low miller index single crystal surfaces, and are of practical interest because they expose a variety of reactive sites simultaneously that may be present on commercial catalyst surfaces. Although there are many reports of NO adsorption on

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platinum single crystals [8–14] and stepped surfaces [15–18], there are few studies of NO adsorption on polycrystalline platinum surfaces. Alnot et al. [19] performed NO temperature programmed desorption (TPD) studies in ultrahigh vacuum in which NO exposures were made at 300 K. Previous work also includes studies using high pressure exposures [20] or a temperature ramp in excess of 300 K s\(^{-1}\) [21]. Reports of NO\(_2\) adsorption on platinum single crystals have appeared recently in the literature [22–25], however, no study of NO\(_2\) adsorption on a polycrystalline platinum surface is available. In this paper, we report new adsorption and desorption studies of NO\(_2\) on polycrystalline platinum and also extend previous adsorption studies of NO on this surface.

2. Experimental

The apparatus used for these experiments has been described in detail previously [26]. The UHV chamber is equipped with a quadrupole mass spectrometer with thoriated iridium filaments for TPD and a double pass cylindrical mirror analyzer with a glancing incidence electron gun for Auger electron spectroscopy (AES). The chamber pressure was maintained at 2 \(\times\) \(10^{-10}\) Torr by a 220 \(\ell\) s\(^{-1}\) ion pump and a titanium sublimation pump.

The 0.85 cm\(^2\) (0.91 \(\times\) 0.93 cm) platinum foil sample (99.998% purity) was resistively heated and cooled by contact with a liquid nitrogen reservoir. The sample temperature was controlled with a linear temperature ramp generator using a feedback loop from a chromel–alumel thermocouple spot-welded to the platinum foil. A heating rate of 7.9 K s\(^{-1}\) was employed for all TPD experiments on clean Pt. A heating rate of 4.8 K s\(^{-1}\) was used for the TPD experiments involving NO\(_2\) exposure to an oxygen precovered surface.

An IBM-XT computer, which was interfaced to the mass spectrometer and thermocouple, was used to monitor the pressure of selected gases versus temperature and time during the TPD experiments. Signals corresponding to C and N (12 and 14 amu respectively) were monitored also during the experiments in order to distinguish between N\(_2\) and CO at 28 amu and N\(_2\)O and CO\(_2\) at 44 amu. N\(_2\)O desorption was not detected under any conditions used in this study.

Nitric oxide (Scientific Gas Products, C.P. grade, 99% purity) was purified by passing it through a silica gel trap cooled in a methanol/dry ice bath. High purity NO\(_2\) was prepared in our laboratory [22] and dosed with a micro-capillary array doser.

The platinum foil was cleaned by argon ion sputtering at 1000 K for 8 h, and then by exposure to NO\(_2\) at 800 K for 30 min. This procedure provided a surface free from any contamination as determined by AES.
Exposures reported here have been corrected using the measured doser enhancement factors which include ion gauge sensitivities [22]. All of the adsorbate coverages reported in this paper are obtained using the relative TPD areas referenced to the value of $\theta_O = 0.25$ ML (equal to $3.8 \times 10^{14}$ atoms cm$^{-2}$) resulting from the O$_2$ exposures to Pt(111) reported by Gland [27]. The saturation oxygen coverage from O$_2$ exposure for polycrystalline platinum has been reported as $(4 \pm 2) \times 10^{14}$ atoms cm$^{-2}$ [28], which is approximately equal to the value found on Pt(111). The coverages of all other molecules (NO, NO$_2$, and N$_2$) are referenced to the oxygen coverages assuming the appropriate stoichiometry of reaction.

Desorption activation energies reported were estimated using Redhead analysis [29]. For first-order NO desorption kinetics and NO desorption rate-limited processes, a pre-exponential factor of $1 \times 10^{16}$ s$^{-1}$ was assumed as suggested by others in previous studies of NO desorption [9,22,30]. For all other first-order desorption data, the assumption of a pre-exponential factor of $1 \times 10^{13}$ s$^{-1}$ was used [29]. A pre-exponential factor of $1 \times 10^{-2}$ cm$^2$ s$^{-1}$ was assumed in all calculations involving second-order desorption kinetics.

3. Results

3.1. Adsorption of NO

The thermal desorption spectra of N$_2$, O$_2$, and NO after NO exposures at 120 K are shown in figs. 1 and 2. The observation of N$_2$ and O$_2$ desorption is direct evidence that NO decomposition occurs on the Pt polycrystalline surface. The decomposition of NO was not observed on well-annealed Pt(111) [8,9,14], however, it has been reported on Pt(100) [9,11,15], Pt(110) [10,13], and other platinum polycrystalline surfaces [19–21]. At the lowest NO exposure (curve a in fig. 1A), the N$_2$ peak maximum is located at 470 K. The peak shifts to 460 K for the next higher coverage. Thus, the desorption of N$_2$ appears to follow second-order kinetics initially. However, the N$_2$ peak maximum shifts to a higher temperature of 480 K following exposures greater than 0.12 L (curve c in fig. 1A), and exhibits no subsequent shift with increasing coverage, which is characteristic of first-order desorption kinetics. Assuming first-order kinetics, the activation energy for N$_2$ desorption is estimated to be 36 kcal mol$^{-1}$. The N$_2$ TPD spectra following NO exposures greater than 0.75 L are identical to curve f in fig. 1A.

The O$_2$ thermal desorption spectra following NO exposure are shown in fig. 1B. The O$_2$ peak maximum occurs at 820 K following the highest exposures. As in the case of N$_2$ desorption, the oxygen coverage reaches a maximum following an NO exposure of 0.75 L and all O$_2$ TPD curves for higher exposures are identical to curve f in fig. 1B. The activation energy for O$_2$
desorption was estimated to be 47 kcal mol\(^{-1}\) assuming second-order desorption kinetics. This value is lower than that obtained by Mummey et al. [20] following their high pressure, steady-state work, but it is in good agreement with that obtained by Alnot et al. [19] on polycrystalline platinum under UHV conditions.

The NO thermal desorption spectra following NO exposure at 120 K are shown in fig. 2. No NO desorption occurs for exposures of less than 0.12 L, showing that all NO adsorption is irreversible under these conditions. At higher NO exposures, two desorption states are sequentially populated. Beginning with exposures of 0.12 L, the \(\beta_2\) state is observed with a peak maximum at 500 K. At higher coverages, the \(\beta_2\) desorption peak temperature shifts to 470 K. A more weakly bound NO state, \(\beta_1\), is observed when the exposure is increased to 0.50 L. The peak maximum for this state shifts from 360 to 300 K with increasing NO coverage. The \(\beta_1\) and \(\beta_2\) NO states were saturated following a 2.0 L NO exposure (fig. 2, curve g). We assume that both \(\beta_1\) and \(\beta_2\) states desorb according to first-order kinetics and that the peak shifts are caused by coverage dependent desorption activation energies or the presence of a precursor state [9]. The activation energies for desorption of the \(\beta_1\) and \(\beta_2\) states range from 27 to 22 kcal mol\(^{-1}\) and 38 to 35 kcal mol\(^{-1}\), respectively.

Our NO TPD results differ from the previous study by Alnot et al. [19]. In their work, the \(\beta_1\) NO state is observed at 400 K and does not shift in
temperature with increasing coverage. In addition, the population of the $\beta_1$ state is much lower relative to the $\beta_2$ state than we observed. However, their report of the behavior of the $\beta_2$ NO state with coverage is in good agreement with our results. The results of Mummey et al. [20] and Ivanov et al. [21] also differ from our results. Their studies were performed, however, under significantly different experimental conditions compared to those used here.

In fig. 3, the coverages of N (■), O (▲), and NO (○) are plotted as a function of NO exposure at 120 K. The total amount of NO adsorbed (▲) is also shown. The conversion of the oxygen TPD area to coverage was accomplished by comparison of the relative O$_2$ TPD areas resulting from O$_2$ and NO exposure, using $\theta_O = 0.25$ ML from O$_2$ exposure [27] as a reference. The absorbed N coverage was set equal to the adsorbed O coverage, since only these products were formed when NO decomposed. The conversion of NO TPD peak area to coverage comes from NO$_2$ TPD results and is discussed in section 3.2. Fig. 3 shows that the maximum coverages for adsorbed O and NO are 0.06 and 0.50 ML, respectively. NO desorption begins at $\theta_O = 0.03$ ML.
but NO decomposition continues up to $\theta_O = 0.06$ ML. At the saturation exposures of NO, approximately 80% of the NO which adsorbs onto the surface is reversibly adsorbed. The slope of the uptake curve does not change with increasing coverage up to $\theta_{NO} = 0.50$ ML, which indicates that the NO sticking coefficient remains constant up to this coverage. This behavior is generally attributed to the presence of a weakly bound, precursor state of NO which controls the adsorption kinetics.

3.2. Adsorption of NO$_2$

Figs. 4–7 show thermal desorption spectra of N$_2$, O$_2$, NO, and NO$_2$ following exposure to NO$_2$ at 120 K. N$_2$ desorption occurs after the lowest NO$_2$ exposures only, as shown in fig. 4. N$_2$ desorption is not observed following exposures greater than 0.41 L. The small N$_2$ signal seen in curves e and f of fig. 4 are due to background effects. This observation is in contrast to the N$_2$ desorption from NO exposure (see fig. 1A), where a constant amount of N$_2$ desorption ($\theta_N = 0.06$ ML) occurred following all NO exposures greater than 0.75 L. Fig. 4 shows that for cases where N$_2$ desorption is observed, the spectra are similar to those obtained following NO exposure. The N$_2$ TPD peak maxima occur at 480 K and do not shift with increasing NO$_2$ exposure.
The activation energy for this process is estimated to be 36 kcal mol$^{-1}$ assuming first-order kinetics.

Fig. 5 shows the O$_2$ TPD spectra following exposure to NO$_2$. Two desorption features are observed. First, a high temperature state is present with a peak maximum near 800 K which we assume follows second-order desorption kinetics. The activation energy for desorption from this state is estimated to be 46 kcal mol$^{-1}$. A second state is populated with a peak maximum at approximately 680 K for exposures greater than 0.41 L. The O$_2$ peak area in TPD is saturated following NO$_2$ exposures of greater than 2.0 L. The peak maximum for the low temperature state does not shift with increasing coverage, suggesting that O$_2$ desorbing from this state follows pseudo first-order kinetics. These results are similar to other results reported for O$_2$ desorption following NO$_2$ exposure on Pt(111) [22–24,31]. In all of these cases, exposure to NO$_2$ generated a high coverage of oxygen atoms resulting in a low temperature O$_2$ desorption peak which was not present following exposure to
Fig. 5. O₂ TPD spectra resulting from NO₂ exposures at 120 K. The NO₂ exposures are: (a) 0.042 L, (b) 0.10 L, (c) 0.20 L, (d) 0.41 L, (e) 0.80 L, (f) 1.2 L, (g) 2.0 L.

O₂. Parker et al. [31] point out that the desorption kinetics of these oxygen coverages are complex, and that activation energies for O₂ desorption from high coverages of adsorbed oxygen can range from 28 to 51 kcal mol⁻¹.

Fig. 6 shows the NO desorption spectra following exposure to NO₂. NO desorption is not observed for NO₂ exposures less than 0.10 L. Following a 0.10 L NO₂ exposure, the β₂ NO desorption state is observed at 490 K. When the NO₂ exposure is increased to 0.80 L, a low temperature desorption state, β₁, is observed with the peak maximum at 360 K. Increasing the NO₂ exposure to 2.0 L causes a shift of both desorption states to lower temperatures. The β₂ shifts from 490 to 430 K, while the β₁ states shifts from 360 to 330 K. The relative populations of the β₁ and β₂ NO desorption states after NO₂ exposures are not identical to those obtained after NO exposure. Fig. 2 shows that the populations of the β₁ and β₂ states are approximately equal following saturation NO exposure. However, fig. 6 shows the population of the β₁ state is significantly greater than that of β₂ state following saturation NO₂ ex-
Fig. 6. NO TPD spectra resulting from NO$_2$ exposures at 120 K. The NO$_2$ exposures are: (a) 0.042 L, (b) 0.10 L, (c) 0.20 L, (d) 0.41 L, (e) 0.80 L, (f) 1.2 L, (g) 2.0 L.

As the NO$_2$ exposures are increased above 2.0 L, the NO desorption curves are unchanged and therefore are not included in this figure.

We assume that both NO desorption states in Fig. 6 follow first-order kinetics and that the observed peak shifts with increasing coverage are due to coverage dependent desorption activation energies (as was assumed for NO desorption from NO exposure). The activation energy for desorption from the β$_{1}$ state ranges from 22 to 20 kcal mol$^{-1}$. However, we believe that this value is not equal to the heat of adsorption of NO because NO desorption is not rate-limiting for this state. This point will be considered in more detail in the discussion section.

The β$_{1}$ NO desorption state shown in fig. 6 is in general agreement with other reports of NO desorption from Pt(111) resulting from NO$_2$ exposure [22,24]. Bartram et al. [22] observed a NO desorption state on Pt(111) showing first-order kinetics with a peak maximum that shifted from 400 to 320 K with increasing NO$_2$ exposures. The β$_{2}$ state observed here was not seen on Pt(111).
Fig. 7. NO₂ TPD spectra resulting from NO₂ exposures at 120 K. The NO₂ exposures are: (a) 0.80 L, (b) 1.2 L, (c) 2.0 L, (d) 4.2 L, (e) 8.3 L, (f) 12 L.

Figs. 4–6 indicate that NO₂ readily decomposes on the clean platinum polycrystalline surface into coadsorbed NO and O. Fig. 7 shows that a small amount of NO₂ can be reversibly adsorbed at near monolayer coverages. A very small NO₂ desorption peak is observed at 300 K following an exposure of 1.2 L. Curve a in fig. 7 represents a NO₂ exposure equivalent to those seen in the (e) curves of figs. 4–6. The activation energy for desorption of chemisorbed NO₂ is 18 kcal mol⁻¹ assuming first-order desorption kinetics. An additional desorption peak appears near 140 K at higher exposures. Desorption from this state exhibits zero order kinetics and is attributed to the decomposition of a multilayer of N₂O₄, as was observed on Pt(111) [22].

The NO₂ uptake curve is shown in fig. 8. This figure shows the coverages of O (●), NO (△), reversibly chemisorbed NO₂ (○), total chemisorbed NO₂ (×), physisorbed NO₂ from the N₂O₄ multilayer state (■), and the total adsorbed NO₂ (□) as a function of NO₂ exposures at 120 K. The oxygen coverage is determined by the same method as discussed previously in section 3.1. NO
Fig. 8. NO$_2$ uptake curve on Pt(poly) at 120 K. The plot is coverage (ML) versus NO$_2$ exposure for NO$_2$ exposures of up to 8.3 L for: NO (△), O (●), reversibly chemisorbed NO$_2$ (○), total chemisorbed NO$_2$ including reversibly and irreversibly adsorbed (×), multilayer NO$_2$ from N$_2$O$_4$ (▪), and total adsorbed NO$_2$ (□).

The maximum adsorbed N coverage observed during the NO$_2$ TPD experiments was 0.03 ML following an NO$_2$ exposure of 0.10 L. No N$_2$ desorption is observed at NO$_2$ exposures above 0.41 L. This is due to the inhibition of NO decomposition by coadsorbed oxygen atoms which result from NO$_2$ decomposition. The maximum coverage of adsorbed O (and therefore NO) is 0.41 ML following saturation NO$_2$ exposures at 120 K. This oxygen coverage is significantly larger than the maximum obtained following NO exposure and is 1.6 times greater than that obtained by exposure to O$_2$ under UHV conditions [27]. The maximum NO coverage of 0.41 ML is 0.1 ML lower than the
maximum NO coverage observed following NO exposure. No reversible NO₂ adsorption was observed at exposures below 1.2 L. However, at higher exposures where $\theta_o > 0.2$ ML, the decomposition of NO₂ is inhibited to such a degree that reversible adsorption of NO₂ is observed. The maximum amount of reversibly adsorbed NO₂ is approximately 0.1 ML, or 20% of the total chemisorbed NO₂.

Although NO₂ adsorption was almost completely irreversible for the chemisorbed monolayer on the clean Pt surface, reversible adsorption is favored if oxygen is preadsorbed on the surface. This is illustrated in fig. 9 which shows NO₂ TPD spectra following a constant NO₂ exposure of 2.1 L as a function of oxygen precoverage on the Pt surface. This NO₂ exposure gave a saturation coverage of the chemisorbed layer on the clean Pt surface. Oxygen precoverages ranging from 0 to 0.87 ML were generated by exposing the platinum surface to NO₂ at temperatures ranging from 425 to 700 K to produce the desired oxygen coverage. This procedure produces chemisorbed oxygen
adatoms [31]. The oxygen coverage was monitored by AES with the O(510)/Pt(260) ratio calibrated using O₂ TPD areas.

Fig. 9 shows that at least three additional NO₂ desorption states are observed when preadsorbed oxygen atoms are present on the surface. The dashed line in fig. 9 shows NO₂ desorption resulting from the decomposition of physisorbed N₂O₄. When 0.28 ML of oxygen is preadsorbed onto the surface (curve b in fig. 9), a low temperature β₁ NO₂ state is observed with the desorption peak at 160 K. The β₁ peak is clearly not due to NO₂ desorption from physisorbed species. Two more NO₂ states, denoted as β₂ and β₃, with peak maxima at 175 and 230 K, respectively, are populated when 0.50 ML of oxygen is preadsorbed onto the platinum surface (curve c in fig. 9). The activation energies for NO₂ desorption from the β₁, β₂, and β₃ states are 9.5, 11, and 14 kcal mol⁻¹, respectively, assuming first-order kinetics.

Previous reports have shown that NO₂ is an efficient source of adsorbed oxygen atoms on several single crystal Pt surfaces [22-24,31]. We show here
that this is also the case for platinum polycrystalline surfaces. This is illustrated clearly in fig. 10 which compares the O₂ TPD spectra following saturation exposures of NO, O₃, and NO₂ at 120 K in curves a, b, and c, respectively. The areas under these O₂ TPD curves correspond to oxygen coverages of 0.06, 0.25, and 0.41 ML. The O₂ TPD spectrum following a 2.1 L NO₂ exposure at 425 K is shown in fig. 10, curve d, and corresponds to an oxygen coverage of 0.87 ML. The population of the low temperature oxygen desorption state is greatly enhanced by increasing the NO₂ exposure temperature to 425 K and results in a much larger total oxygen coverage than those generated by exposure to O₂, NO or NO₂ at 120 K. These results agree with previous studies of O₂ TPD from Pt(111) following NO₂ exposure at temperatures between 400 and 500 K which show that the oxygen coverage can be increased three-fold from high temperature NO₂ exposure relative to that generated from O₂ exposure in UHV [22-24,31]. These larger coverages of adsorbed oxygen from NO₂ exposures are due to the large dissociative sticking probability of NO₂ compared to O₂. Thus, the low coverage of chemisorbed oxygen adatoms from O₂ exposure is due to a kinetic limitation rather than a thermodynamic one. Indeed, the maximum value of the oxygen coverage on a polycrystalline Pt surface can be largely enhanced by O₂ exposure at higher temperatures [37] or higher temperatures and pressures [38].

4. Discussion

The discussion of our results is divided into two sections. First, the NO and NO₂ TPD results from the polycrystalline Pt surface are compared to results obtained by us and other investigators on single crystal Pt surfaces. In the second section, the N₂, NO, and O₂ spectra following NO exposure are compared to those obtained from NO₂ exposure on a polycrystalline Pt surface.

4.1. Comparison to single crystal Pt surfaces

Adsorption studies on polycrystalline surfaces are important because these surfaces expose a variety of crystallographic planes and other reactive sites that may be present on commercial catalysts. However, in order to understand these results, it is useful to compare data from these studies to data obtained on single crystals. The goal is to contribute to a fundamental understanding of the relative contribution of the various reactive sites present on the polycrystalline surface.

NO adsorption has been studied previously on Pt(111) and Pt(100) [9] and Pt(110) surfaces [13]. A single NO desorption peak which shifts from 400 to 350 K with increasing NO exposures occurs on Pt(111), three NO desorption
states including a broad peak at 500 K occurs on Pt(100), and a narrow NO desorption peak at 470 K occurs on Pt(110). In addition, Banholzer et al. [32] found that the amount of NO dissociation depended strongly on the crystal face used. After saturation exposures, no dissociation of NO was observed on Pt(111), 5% dissociation was seen on Pt(110), and 50% dissociation was observed on Pt(100). Fig. 2 shows that two NO desorption states exist on the Pt(poly) surface with desorption peak maxima ranging from 300 to 360 K and 470 to 500 K and fig. 3 shows that 20% dissociation of NO occurs on the polycrystalline Pt surface following NO exposure. Thus, NO desorption from a platinum polycrystalline surface can be accounted for very well by a sum of the (111), (100), and (110) platinum planes, with a small concentration of very reactive edge and kink sites. A majority of the polycrystalline surface exists as the the (111) plane.

NO$_2$ has been studied on two Pt single crystal surfaces, Pt(111) [22–24] and Pt(100) [25]. Schwalke et al. [25] studied NO$_2$ on the clean Pt(100) surface and observed a broad NO$_2$ TPD peak which consisted of two desorption states at 260 and 270 K. NO$_2$ desorption was observed to occur in a single peak at 310 K on Pt(111) [22–24] with an activation energy for desorption of 19 kcal mol$^{-1}$. In addition, Bartram et al. [22] concluded that adsorbed NO$_2$ existed as a bridge-bonded $\mu$-N, O–nitrito surface complex with C$_2$ symmetry on Pt(111) and that approximately 20% of the chemisorbed NO$_2$, i.e. 0.1 ML, was adsorbed reversibly. In our work, the NO$_2$ desorption maximum occurs at 300 K with an activation energy for desorption of 18 kcal mol$^{-1}$, which is in good agreement with the results on Pt(111). We did not observe a contribution from the (100) face which would have resulted in NO$_2$ desorption peaks at 260 to 270 K. Our results also indicate that approximately 0.1 ML of NO$_2$ is adsorbed reversibly on the platinum polycrystalline surface. Thus, the behavior of the polycrystalline surface with respect to NO$_2$ adsorption is similar to the Pt(111) surface.

Fig. 9 shows that the relative amount of reversibly chemisorbed NO$_2$ increases with $\theta_O$, as reflected by the appearance of three new molecular NO$_2$ states at 150, 170 and 230 K. This is consistent with observations on Pt(111) where preadsorbed oxygen resulted in the presence of new NO$_2$ TPD states at 180 and 155 K. Using high resolution electron energy loss spectroscopy (HREELS) results, Bartram et al. [33] determined that the desorption state at 180 K was due to a nitro-bonded NO$_2$ species with C$_2$ symmetry and speculated that the state at 155 K resulted from a metastable NO$_3$ species formed during TPD. Based on these comparisons, we conclude that the new NO$_2$ desorption states on O precovered polycrystalline Pt are the result of more weakly bound chemisorbed NO$_2$ states, or possibly NO$_3$ states, on the variety of crystal planes available on Pt(poly). Further work would be required in order to identify the origin of these states conclusively.

Fig. 9 also demonstrates that although the Pt polycrystalline surface is
active for NO\textsubscript{2} decomposition, adsorbed O effectively inhibits this process. In a recent steady-state kinetic study of the reaction between CO and NO\textsubscript{2} on a platinum polycrystalline surface \cite{2}, it was proposed that under excess CO conditions, the high coverages of CO inhibited NO\textsubscript{2} decomposition and therefore promoted a bimolecular reaction mechanism between molecularly adsorbed NO\textsubscript{2} and CO. This proposal is supported by the TPD results presented here which demonstrate that the presence of a coadsorbate will stabilize molecular NO\textsubscript{2} on the polycrystalline surface.

4.2. Comparison of N\textsubscript{2}, NO, and O\textsubscript{2} desorption following NO and NO\textsubscript{2} exposure

This study has shown that NO\textsubscript{2} readily decomposes into coadsorbed NO and O on the platinum polycrystalline surface. The primary differences in the N\textsubscript{2} and NO TPD spectra resulting from NO\textsubscript{2} exposure compared to those obtained following NO exposure are due to the presence of coadsorbed oxygen which results from the decomposition of NO\textsubscript{2}. The spectra presented in this study demonstrate that coadsorbed oxygen has a significant effect upon the thermal desorption spectra of both N\textsubscript{2} and NO. The primary difference in the O\textsubscript{2} TPD spectra after NO and NO\textsubscript{2} exposure is due to the difference in coverage of atomic oxygen that results in each case and coverage dependent changes in O\textsubscript{2} TPD spectra.

The N\textsubscript{2} spectra resulting from NO and NO\textsubscript{2} exposures (figs. 1A and 4, respectively) show that N\textsubscript{2} desorbs with the peak maximum located at 480 K exhibiting first-order kinetics. This peak occurs at a higher temperature than is expected, since previous studies of N\textsubscript{2} adsorption on Pt(s)-(9\{111\} × \{111\}), Pt(111), and Pt(100) surfaces \cite{34} have shown that the N\textsubscript{2} desorption peak maximum occurs at 450 K when similar heating rates in TPD are employed. In order to explain these observations, we note that the temperature of the N\textsubscript{2} desorption peak coincides with the desorption maxima of the \( \beta_2 \) NO states shown in figs. 2 and 6. We suggest that N\textsubscript{2} desorption following both NO and NO\textsubscript{2} exposure is rate-limited by NO decomposition, as was proposed by Gorte et al. \cite{9} on Pt(100). However, Mummey et al. determined that the activation energy for NO decomposition is 13.5 kcal mol\textsuperscript{-1} on Pt(poly), which is significantly less than the 36 kcal mol\textsuperscript{-1} deduced from the N\textsubscript{2} desorption activation energy. We have determined that the rate of NO decomposition under similar conditions is limited by the number of available surface sites that are active for this process \cite{3}. Therefore, we suggest that the rate of NO decomposition, or N\textsubscript{2} formation, is limited by NO desorption, a process that generates the sites needed for NO decomposition. This implies that the activation energy for N\textsubscript{2} desorption (36 kcal mol\textsuperscript{-1}) is simply a measure of the activation energy for NO desorption from the \( \beta_2 \) state (reported earlier ranging from 32 to 38 kcal mol\textsuperscript{-1}). The suggestion that N\textsubscript{2} desorption is rate-limited by NO desorption accounts for the first-order N\textsubscript{2} desorption
behavior observed in figs. 1A and 4. In addition, this suggestion also explains the observation that N₂ is not formed following NO₂ exposures greater than 0.41 L, since at these exposures, sites that are active for NO decomposition are occupied by oxygen atoms that result from NO₂ decomposition.

Figs. 2 and 6 show important differences between the NO thermal desorption spectra following exposures to NO and those following exposures to NO₂. The β₂ NO peak maximum is located at 470 K following a saturation NO exposure, while the β₂ peak maximum is observed at 430 K following a saturation NO₂ exposure. This shift of 40 K is easily explained in terms of the relative amounts of oxygen which are adsorbed onto the surface by NO and NO₂ dissociation. The uptake curves in figs. 3 and 8 show that 0.4 ML oxygen results from a monolayer NO₂ exposure at 120 K, while 0.06 ML of oxygen results from a similar NO exposure. Previously, coadsorbed O has been observed to slightly weaken the NO–metal bond which would shift the desorption maximum to a lower temperature [35,36]. Thus, oxygen from NO₂ decomposition is expected to cause a shift in the corresponding NO peak maximum to lower temperature relative to the NO peak maximum from NO exposure. This is consistent with the observed behavior of the β₂ NO desorption state.

However, this argument does not explain our results for the β₁ NO desorption state. The peak maximum for the β₁ state following NO exposure, where θ₀ = 0.06 ML, occurs at 300 K. The peak maximum following NO₂ exposure, where θ₀ = 0.4 ML, is observed at a higher temperature of 330 K. Thus, the observed behavior of the β₁ state is opposite of that expected from the above discussion. However, the above argument applies only to NO desorption rate-limited processes. If NO desorption following NO₂ exposure is kinetically limited by the rate of NO₂ decomposition, then a direct comparison of the peak maxima of the two β₁ states is not meaningful, since the activation energies governing NO desorption are a reflection of different processes. Since oxygen atoms should have the same effect on the β₁ state as was seen for the β₂ state above, we conclude that the β₁ NO state from NO₂ exposure is NO₂ decomposition rate-limited rather than NO desorption rate-limited. With this in mind, the activation energy for NO desorption from the β₁ state was estimated to range from 20 to 22 kcal mol⁻¹. This value should represent the activation energy for NO₂ dissociation into coadsorbed NO and O. This value is in good agreement with Bartram et al. [22,33] who estimated an NO₂ decomposition barrier of 19 kcal mol⁻¹ on Pt(111).

5. Summary

In this paper we have presented new studies of the adsorption of NO and NO₂ on polycrystalline platinum. NO was found to adsorb completely irre-
versibly at coverages below 0.03 ML. Two NO desorption states were observed at higher coverages with coverage dependent activation energies ranging from 27 to 22 kcal mol\(^{-1}\) and 38 to 35 kcal mol\(^{-1}\). For saturation coverages of NO, approximately 20% the NO adsorbed on the surface decomposes into \(\text{N}_2\) and \(\text{O}_2\) upon heating in TPD.

Most of the \(\text{NO}_2\) adsorption at 120 K was found to be irreversible, with less than 20% adsorbing reversibly. The activation energy for chemisorbed, molecular \(\text{NO}_2\) desorption is 18 kcal mol\(^{-1}\). The desorption of the high temperature NO desorption state following \(\text{NO}_2\) exposure was observed at a lower temperature than that observed from NO exposure. This shift is due to the presence of coadsorbed O atoms for \(\text{NO}_2\) exposure. NO desorption from the low temperature state from \(\text{NO}_2\) exposure is rate-limited by \(\text{NO}_2\) decomposition. The activation energy for this process is 20 to 22 kcal mol\(^{-1}\). The desorption of \(\text{N}_2\) is observed only for the lowest \(\text{NO}_2\) exposures, due to inhibition of NO decomposition by oxygen adatoms resulting from \(\text{NO}_2\) decomposition. Several additional \(\text{NO}_2\) desorption states with desorption activation energies ranging from 9.5 to 14 kcal mol\(^{-1}\) were detected using an oxygen precovered surface. We propose that these states are a result of the formation of weakly chemisorbed species on the variety of crystal planes that are available on the Pt(poly) surface.

A comparison of the NO and \(\text{NO}_2\) TPD data from Pt foil with TPD data from the Pt(111), (100), and (110) surfaces shows that the adsorption and desorption of NO and \(\text{NO}_2\) on polycrystalline Pt can be understood well as a combination of the low-index faces (mainly Pt(111)) and some small amount of reactive edge and kink sites. As observed in previous Pt(111) studies, \(\text{NO}_2\) was found to be a very efficient source of surface oxygen atoms. The coverage of oxygen on polycrystalline Pt following \(\text{NO}_2\) exposure at 425 K is greater than three times the saturation coverage attainable from \(\text{O}_2\) exposure at 300 K under UHV conditions and is estimated to be 0.87 ML.

Acknowledgments

The authors wish to thank Dr. Mike Bartram for helpful and informative discussions regarding work with \(\text{NO}_2\). We would also like to thank Dr. Neil Avery for providing us with unpublished work concerning \(\text{NO}_2\) adsorption on Pt(111) in the early stages of this work. Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. DTW also wishes to thank the Cooperative Institute for Research in Environmental Sciences (CIRES) for providing a Visiting Fellowship.
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