A Comparative Study of the Coadsorption of CO and NO on Pd(100), Pd(111), and Silica-Supported Palladium Particles with Infrared Reflection–Absorption Spectroscopy

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The coadsorption of nitric oxide and carbon monoxide on Pd(100), Pd(111), and a model silica-supported palladium catalyst has been investigated with infrared reflection–absorption spectroscopy (IRAS) in the temperature range 100-500 K. The palladium surfaces were in equilibrium with a 1 x 10^-4 Torr equimolar mixture of CO and NO during the FT-IRAS studies. The structure and coverage of the adsorbed layers strongly depend on the surface temperature and crystal orientation. On all surfaces, CO and NO form molecularly mixed overlayers, and the CO/NO coverage ratio increases with a decrease in surface temperature. On Pd(100), both CO and NO adsorb at the 2-fold bridging sites at all temperatures. The coverage for CO and NO is similar at temperatures above 400 K, whereas at 100 K the CO/NO ratio is ~5. On Pd(111), the majority surface species is NO, which adsorbs at the 3-fold hollow sites at >400 K. At lower temperatures, CO adsorbs at the bridging sites and the NO at the hollow sites converts to atop NO. At <200 K the overlayer consists of ~0.25 monolayer of NO on the atop sites and ~0.5 monolayer of CO on the nearby bridging sites. The adsorption behavior of a CO/NO mixture on the palladium particles is compared with that of pure CO and NO adlayers on palladium single crystal surfaces on the basis of the presence of (111) and (100) facets.

Introduction

The structure and energetics of adsorbates play a key role in determining surface catalytic reactivity. During the past two decades, numerous studies have been carried out to elucidate the structures of simple adsorbates such as carbon monoxide and nitric oxide on well-defined single crystal surfaces at ultrahigh-vacuum (UHV) conditions. However, adsorbate structures at elevated pressures have received little attention. Adsorbate structures at elevated pressures are most relevant to catalytic processes of technological interest and may be different than those at UHV conditions. Furthermore, most heterogeneous reactions involve at least two gas phase components; therefore, the structures of coadsorbates on different crystal orientation are particularly significant. The structures of multicomponent adsorbates have been less frequently investigated, especially at elevated pressure conditions.

In this paper, we present a comparative study of the adsorption of a carbon monoxide (CO) and nitric oxide (NO) mixture on Pd(100), Pd(111), and model silica-supported palladium catalysts by infrared reflection–absorption spectroscopy (IRAS) at a total pressure of 1 x 10^-4 Torr. Carbon monoxide and nitric oxide have similar electronic structures and similar binding energies on most transition metal surfaces, and both generally adsorb molecularly on noble metals. The structure and interactions of coadsorbed CO and NO is of particular interest with respect to CO–NO reactions.

This study is aimed at providing insight into the mechanisms of nitric oxide reduction by carbon monoxide. The practical importance of this study is that nitric oxide is one of the major air pollutants from automobiles and power stations, while palladium is known to catalyze the CO–NO reaction. Although the reaction of NO and CO on palladium catalysts has been studied in the past, the details of the reaction still remain poorly understood.

The adsorption of CO and NO on single crystal palladium surfaces has been individually investigated by a number of surface spectroscopic techniques; however, only a limited number of these studies have focused on the coadsorption of CO and NO. By far the largest body of information regarding specific adsorption site(s) is derived from vibrational spectroscopies. Although quite successful in many cases, exceptions to the vibrationally assigned sites do exist that indicate ambiguities, or even erroneous assignments can result when independent confirmation of the assignments from structural analysis is lacking. With this cautionary note in mind, we intend to use this technique throughout this work only as a general guide in assigning the observed vibrational bands.

The adsorption of CO and NO, individually, on Pd(111) and Pd(100) at elevated pressures has been studied in this laboratory. When equilibrated with gas phase CO, adsorption occurs on the 3-fold hollow sites of Pd(111) at temperatures >400 K, changes to the 2-fold bridging sites during cooling, and forms a (2 x 2) compressed overlayer structure with 0.5 monolayer CO on the hollow sites and 0.25 monolayer on the atop sites at temperatures <200 K. NO on Pd(111) is similar to CO in that the adsorption site changes from a 3-fold hollow to a 2-fold bridging site and then to an atop site with decreasing surface temperature. At low temperatures (<220 K), NO forms a (2 x 2) superlattice, where all of the NO is in the atop sites, reaching a saturation coverage of 0.75 monolayer. On Pd(100), CO adsorbs on the 2-fold bridging sites at all temperatures, whereas NO adsorbs on the bridging sites at high temperatures on both atop and 2-fold bridging sites at low temperatures (<200 K).

Experimental Section

The experiments were carried out in two separate ultrahigh-vacuum (UHV) chambers each equipped with a Mattson Cygnus 100 FTIR spectrometer for IRAS studies, as well as other standard surface characterization techniques such as temperature-programmed desorption (TPD), Auger electron spectroscopy (AES), and low-energy electron diffraction (LEED). The details of the chamber are described elsewhere. Pd(100) and Pd(111) were cleaned with argon ion sputtering and cycles of oxidation at 900 K and annealing at 1200 K in vacuo. The cleanliness was monitored with AES, LEED, and oxygen TPD. Oxygen TPD is particularly sensitive to the carbon contamination; a trace amount of carbon in the near surface region will produce detectable amounts of carbon monoxide and carbon dioxide during TPD following oxygen adsorption.

Coadsorption of CO and NO on Pd Catalysts

The model silica-supported palladium catalysts were prepared by evaporating palladium onto a silica thin film (100 Å) which was supported on a Mo(110) surface. The surface was at either 100 or 300 K during palladium evaporation and was subsequently annealed to 900 K. The resulting Pd particle size and dispersion depend on the initial Pd coverage. The particles were typically in the range 50–500 Å in diameter and consist mainly of the (111) and (100) facets. This Pd/silica system has been shown to be an excellent model for a supported palladium catalyst. Furthermore, this kind of model system facilitates the study of supported metal catalysts with UHV spectroscopies and IRAS.

Results

Figures 1–3 show the infrared reflection–absorption spectra of a CO/NO mixture adsorbed on Pd(100), Pd(111), and supported palladium particles as a function of surface temperature. The adsorbates were in equilibrium with 1 × 10^-6 Torr of an equimolar CO/NO mixture during data acquisition. The data were collected while cooling and warming the surface, with identical results. The reaction of NO and CO was insignificant below 500 K over the time period of the data collection.

On Pd(100), two bands are observed at ∼1650 and ∼1950 cm^-1 for CO/NO coadsorption at temperatures between 100 and 500 K (Figure 1). These two bands are unequivocally assigned to NO and CO adsorption on the 2-fold bridging sites based on a comparison of CO and NO adsorption on Pd(100) at identical conditions of 1 × 10^-6 Torr. Carbon monoxide adsorbs only on the 2-fold bridging sites of Pd(100), exhibiting stretch frequencies of 1940–1995 cm^-1. The stretch frequency increases with the CO coverage, reaching 1995 cm^-1 at a saturation coverage of 0.8 monolayer (ML).

Nitric oxide adsorbs on the 2-fold bridging sites at temperatures above 275 K, with stretch frequencies between 1530 and 1580 cm^-1. The NO frequency also increases with coverage, due to the well-known dipole coupling effect.

On Pd(111), the coadsorption of CO and NO produces infrared absorption bands at ∼1550, 1750, 1900, and 2070 cm^-1 (Figure 2). The 1550 cm^-1 band, observed at temperatures above 300 K, is attributed to nitric oxide adsorption on the 3-fold hollow sites of Pd(111). The 1750 cm^-1 band, which is observed at temperatures below 300 K, is assigned to NO adsorption on the atop Pd(111) sites. These assignments are based on our recent study of NO on Pd(111) with IRAS and LEED. At high coverages (∼0.75 ML) and low temperatures, NO forms a (2 × 2) structure in which NO only occupies the atop sites with a corresponding stretch frequency of 1758 cm^-1. At lower coverages (<0.5 ML), NO occupies the 2-fold bridging and 3-fold hollow sites with stretch frequencies between 1530 and 1580 cm^-1.
The most important finding of the IRAS studies on the model silica-supported palladium catalyst (Figure 3) is that all the spectral features of coadsorbed CO and NO can be reproduced with a combination of spectral features from the Pd(100) and Pd(111) adsorption systems (Figures 1 and 2). An analogous behavior has been found for the single adsorbate, CO.12 Our current work extends these investigations to the simple binary adsorption system CO/NO. At 500 K, two bands are observed at 1630 and 1520-1550 cm\(^{-1}\); these two bands are attributed to NO adsorption at the 2-fold bridging sites of Pd(100) facets and the 3-fold sites of Pd(111) facets, respectively. A slight decrease in temperature to 450 K increases the intensities of both bands. At 400 K, small features due to CO adsorption appear at 2060 cm\(^{-1}\) (atop sites) and 1900 cm\(^{-1}\) (bridging sites). Below 250 K, relatively sharp NO and CO bands are observed at 1735 and 1970 cm\(^{-1}\), respectively. These sharp bands are attributed to NO adsorption at the atop sites of (111) facets (1735 cm\(^{-1}\)) and to CO adsorption on the bridging sites of (100) facets (1970 cm\(^{-1}\)).

Figure 4 shows the integrated infrared absorbance of equilibrium CO and NO on Pd(100) and Pd(111) as a function of surface temperature. On Pd(100), CO and NO adsorb exclusively on the 2-fold bridging sites. Both the CO and NO intensities increase with a decrease in the surface temperature from 500 to 400 K (Figure 4a). However, the intensity of the CO and NO bands decreases during cooling from 400 to 350 K. With further cooling from 350 to 200 K, the intensity for the CO band increases with a concomitant decrease in the NO band intensity. Below 200 K, the intensities of the CO and NO bands remain essentially the same. On Pd(111), NO adsorption at the atop and bridging/hollow sites is observed during CO/NO coadsorption. At 550 K, the majority surface species is NO adsorbed at bridging/hollow sites along with minor amounts of bridging CO. Both bands gain intensity between 550 and 400 K. With cooling from 400 to 300 K, the intensity of the bridging CO band increases with a concomitant decrease of the bridging/hollow NO band. With further cooling from 300 K, the bridging/hollow NO band decreases in intensity, whereas the intensity of the atop NO band increases and the bridging CO band remains largely unchanged. At temperatures below 200 K no significant change in the relative intensities of each band is apparent.

**Discussion**

CO + NO on Pd(100). Carbon monoxide and nitric oxide adsorb exclusively at the 2-fold bridging sites on Pd(100) when equilibrated with a gas phase mixture of CO and NO in the temperature (100-500 K) and pressure (10^{-9}-10^{-6} Torr) ranges studied. At the higher temperatures (>400 K), the CO and NO band intensities are comparable, indicating similar surface coverages of CO and NO on Pd(100). However, due to competition for the same type of adsorption sites, the coverage of either CO or NO, when coadsorbed, is lower than the corresponding coverage under the same pure gas partial pressure. This competitive adsorption can be described by a Langmuir adsorption model, in which the equilibrium coverage is determined by \( K_1 P_1/(1 + K_1 P_1) \) for a pure gas and by \( K_1 P_1/(1 + K_1 P_1 + K_2 P_2) \) for a gas mixture. Here the \( K_1 \)'s and \( P_1 \)'s are the equilibrium constants and partial pressures for the respective gases. The equilibrium constant is largely determined by the heats of adsorption, \( \Delta H \). Similar CO and NO coverages suggest that the heats of adsorption for CO and NO on Pd(100) during coadsorption are approximately the same, especially at the low coverages. Both the CO and NO coverage increase with decreasing surface temperature, and their stretch frequencies shift to higher values due to dipole coupling. At temperatures above 400 K, CO, NO randomly adsorb at bridging sites on Pd(100) without forming any ordered structures.

During cooling from 400 to 350 K, the absorbance for both CO and NO bands decreases, even though their coverages most surely increase. This observation and that the stretch frequency of CO also undergoes a dramatic increase from 1900 to 1950 cm\(^{-1}\) within this temperature range (Figures 1 and 5) suggest an adsorbate configurational change. For pure CO on Pd(100), a similar blue shift of the CO frequency and a decrease of absorbance with an increase in the CO coverage are observed in the same temperature range with \( P_{CO} = 1 \times 10^{-4} \) Torr. This change corresponds to a commensurate–incommensurate transition of adsorbed CO resulting in a compressed overlayer structure with a coverage >0.5 monolayer.14,15 For pure NO on Pd(100), only a monotonous increase of absorbance and stretch frequency is observed while cooling the sample within this temperature range. Therefore, for CO/NO coadsorption, a compressed overlayer is likely formed while cooling from 400 K at a pressure of 1 \times 10^{-4} \) Torr. The total coverage for the formation of the compressed structure is probably equal to or larger than 0.5 monolayer. The heats of adsorption in the compressed overlayer is reduced from those at low coverages because of repulsive interactions between adsor-
of both CO and NO at the atop and bridging/hollow sites is the surface species is nitric oxide adsorbed at the 3-fold hollow sites. Since the equilibrium coverages are largely controlled by the heats of adsorption, the drop in the heat of adsorption for CO must be less than that for NO with an increasing surface coverage. This implies that the repulsive interaction between NO molecules is stronger than the repulsive interaction between CO molecules. The stronger repulsive interaction experienced by NO can be rationalized by a larger van der Waals radius of the NO molecule.

There are two possible adsorption configurations for a CO and NO mixture on Pd(100) at low temperatures (<200 K). Carbon monoxide and nitric oxide form either large separate domains or molecular mixtures. These two configurations can be differentiated based on the stretch frequencies of CO and NO as a function of temperature and/or coverage. The stretch frequency usually shifts as a function of coverage due to both vibrational dipole coupling and static lateral interactions (either chemical or electrostatic). Particularly, for CO on Pd(100), there is a ~95 cm\(^{-1}\) total blue shift from the zero-coverage limit to the saturation coverage (0.81 monolayer), of which ~35 cm\(^{-1}\) is due to dipole coupling and ~60 cm\(^{-1}\) to a chemical shift. If carbon monoxide were to form large domains during CO/NO coadsorption on Pd(100), the CO stretch frequency should equal the value for pure CO on Pd(100) at identical conditions. At saturation, the CO frequency is 1995 cm\(^{-1}\) for CO/NO coadsorption on Pd(100), 23 cm\(^{-1}\) lower than that for pure CO on Pd(100) (1995 cm\(^{-1}\)). This red shift with respect to CO/Pd(100) is clearly caused by the dilution of the CO overlayer by NO, leading to a reduction in the dipole coupling. In other words, the CO domain size for the CO/NO mixture is significantly smaller than for pure CO on Pd(100) at identical temperatures and gas partial pressures.

On the other hand, the NO stretch frequency increases with decreasing surface temperature (350-100 K), even though the NO coverage decreases based on the IRAS intensity. As discussed in the previous paragraph, the stretch frequency can be affected by both dipole coupling and a chemical shift. For diluted nitric oxide in the CO overlayers, dipole coupling plays only a minor role. Therefore, the blue shift of the NO stretch frequency with an increase in the CO coverage is due primarily to static chemical interactions. At \(\theta_{\text{CO}} \sim 0.1\) ML, a blue shift of ~40 cm\(^{-1}\) is observed for a low CO coverage at 500 K to a high equilibrium CO coverage at 100 K (Figures 1 and 5b). This blue shift can be explained in terms of a "through substrate" chemical interaction between adsorbates. The adsorption of both CO and NO is largely characterized by electron back-donation from the metal substrate into the \(2\sigma^*\) orbitals. An increase in CO coverage reduces the degree of back-donation to NO due to competition for metal electrons, resulting in an increase in the N-O force constant and a blue shift of the NO frequency toward the gas phase value.

CO + NO on Pd(111). The adsorption of a CO/NO mixture on Pd(111) is much more complex than on Pd(100). Adsorption of both CO and NO at the atop and bridging/hollow sites is observed on Pd(111). Between 400 and 500 K, the majority surface species is nitric oxide adsorbed at the 3-fold hollow sites. The coverage of carbon monoxide is much less than that of NO and also much less than the CO equilibrium coverage when only gas phase CO is present. This arises because the heat of adsorption for NO is ~2 kcal/mol larger than for CO at these coverages. The CO/NO coverage ratio, \(\sim 1:10\) at 450 K, estimated from the difference in the heats of adsorption, agrees with the measured infrared absorbances of the CO and NO bands (Figure 4b).

Upon cooling from 400 to 300 K, the intensity for NO on the bridging/hollow sites decreases with a concurrent increase in the bridging CO band. This displacement of NO by CO is caused by an increase in the lateral repulsive interactions at high coverages which reduces the heat of adsorption for nitric oxide. At the same pressure conditions, NO adsorbs at the 3-fold hollow sites on Pd(111) when equilibrated with pure NO gas at 400 K and transforms to the 2-fold bridging sites when cooled to ~300 K. Carbon monoxide adsorbs at the bridging sites of Pd(111) at these temperatures and pressures. Since the van der Waals radius of NO is larger than that of CO, NO experiences a stronger lateral repulsive interaction, resulting in its displacement by CO.

With further cooling from 300 to 200 K, the infrared absorption spectrum of NO on Pd(111) transforms to the 2-fold bridging sites when cooled to ~300 K, giving rise to a single sharp infrared absorption band at ~2110 cm\(^{-1}\). Likewise, CO is also compressed to form a (2 \(\times\) 2) structure at saturation with 0.5 monolayer on the 3-fold hollow sites and 0.25 monolayer on the atop sites, giving rise to two sharp bands at ~2110 and 1894 cm\(^{-1}\). If separate domains of NO and CO were to form in the CO/NO overlayer, the infrared spectra should be able to be reproduced by a linear combination of the spectra from NO/Pd(111) and CO/Pd(111) under such conditions. Instead, the spectra for the CO/NO mixture lack the sharp band at ~2110 cm\(^{-1}\) characteristic of CO/Pd(111). The infrared spectra for CO/NO on Pd(111) suggest a mixed overlayer primarily consisting of nitric oxide adsorbed at atop sites and carbon monoxide at the modified bridging sites. The relatively narrow atop NO band for CO/NO on Pd(111) suggests a quite homogeneous local environment for nitric oxide. The dominant CO band is centered around bridging CO frequencies with a very broad band at 1850-2000 cm\(^{-1}\), indicating multiple binding environments for the bridging CO species. In addition, intensities at ~2000 cm\(^{-1}\) also suggest the presence of atop-bound CO, although the concentration of the species is rather low.

The preferential atop adsorption for NO and bridging adsorption for CO in a CO/NO overlayer on Pd(111) is not well understood at present. The coadsorption system represents a complex interplay between the energetics of metal-adsorbate bonds at various adsorption sites and adsorbate lateral interactions. The atop CO in a pure (2 \(\times\) 2)CO/Pd(111) overlayer desorbs at ~160 K, whereas the atop NO in a pure (2 \(\times\) 2)NO/Pd(111) overlayer desorbs at ~220 K, suggesting that the atop NO is more stable than atop CO in the pure adsorbate overlayer at 0.75 monolayer. Therefore, configuration favoring atop NO is likely to be more stable than atop CO in the mixed CO/NO overlayer.

Comparison of CO + NO on Pd(100) and Pd(111). On both Pd(100) and Pd(111), initial low coverage adsorption (>400 K) favors NO over CO largely due to the difference in heats of adsorption. With increasing coverage, CO and NO form a molecularly mixed compressed overlayer at <200 K when equilibrated with an equimolar CO/NO gas mixture. One thermodynamic driving force favoring a mixed overlayer rather than separate islands of CO and NO is configurational entropy. A second driving force may be the electrostatic attraction between CO and NO. Based on work function measurements, the dipole moments for CO and NO on palladium surfaces point in opposite directions, thus, an adsorption configuration with alternating
CO and NO dipoles would likely lead to a lower energy configuration. The adsorption sites for CO and NO on Pd(100) and Pd(111) are strongly dependent on the crystal orientation. On Pd(100), CO and NO adsorb on the 2-fold bridging sites at all coverages and temperatures, whereas on Pd(111), adsorption of CO and NO on atop and bridging sites is observed. On Pd(100), CO and NO adsorb on the 2-fold sites with similar coverages at temperatures above 400 K and likely undergo a commensurate—incommensurate transition at 300-400 K to form a compressed structure with a CO/NO ratio of ~5:1 at 100 K. On Pd(111), NO together with a small amount of CO adsorbs on hollow/bridging sites of Pd(111) at high temperatures (>400 K). This NO species is replaced by atop NO and bridging CO at low temperatures (<200 K).

CO + NO on Silica-Supported Palladium. The IRAS spectra of a CO/NO mixture on the supported palladium particles (Figure 3) can be readily reproduced with a combination of spectra for a CO/NO mixture on Pd(100) and Pd(111). These results suggest that, within the range of the particle sizes investigated (50-500 Å), the behavior of the supported palladium particles can be modeled by a combination of low-index planes of palladium single crystal surfaces. Based on the intensity of the most prominent, relatively sharp bands of bridging CO on the (100) facets at 1975 cm⁻¹ and the atop NO on the (111) facets at 1740 cm⁻¹, a useful estimate of the effective surface area ratio of the (100) and (111) facets can be obtained. Here the assumption is made that, at an identical pressure and surface temperature (100 K) conditions, the bridging CO concentration on the (100) facets is the same as that for Pd(100) and the atop NO concentration on the (111) facets is the same as that for Pd(111). By further assuming that the infrared cross section for CO/NO on the palladium particles supported on silica(100 Å)/MgO(110) is the same as that for CO/NO on Pd single crystals, the surface area of a particular facet can be estimated from the CO infrared absorbance. For example, from the data shown in Figure 3 for ~500 Å palladium particles, the overall area ratio of (111) to (100) facets is estimated to be 1.3.

Conclusion

The equilibrium structure and coverage for the adsorption of a CO/NO mixture on palladium surfaces strongly depend on the surface temperature and crystal orientation. On all surfaces, CO and NO form molecularly mixed overlayers, and the CO to NO coverage ratio increases with a decrease in the surface temperature when equilibrated with an equimolar CO/NO gas mixture. On Pd(100), CO and NO adsorb on the 2-fold bridging sites at all temperatures. The coverage for CO and NO is similar at temperatures above 400 K and is ~5:1 at 100 K. On Pd(111), the majority surface species is NO, which adsorbs at bridging/hollow sites at >400 K. At lower temperatures, CO is adsorbed on the bridging sites and the bridging NO converts to atop NO, forming an overlay with ~0.15 ML of NO on the atop sites and ~0.5 ML of CO on the nearby bridging sites. The IRAS spectra of a CO/NO mixture adsorbed on supported palladium particles can be interpreted on the basis of the presence of the (111) and (100) facets. The intensity of the infrared bands can be used to estimate the distribution of (111) and (100) facets. CO adsorption is 0.7 and ~0.3 eV, respectively, indicating that CO and NO have opposite dipole moment on the palladium surface.

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References and Notes

(37) The infrared extinction coefficient is similar for adsorbed CO and NO, since similar integrated absorbance is observed for the same saturation coverage. However, it should be pointed out that the extinction coefficient varies with the coverage and adsorbate structure. The infrared absorbance is only used to compare the surface coverage at similar conditions.
(38) Estimated from the peak temperatures of thermal desorption spectra of CO and NO mixture.
(39) The work function change (ref 40) of CO(100) induced by CO and NO adsorption is 0.7 and ~0.3 eV, respectively, indicating that CO and NO have opposite dipole moment on the palladium surface.