Adsorption of Ammonia and Its Influence on Coadsorbed Carbon Monoxide on Monolayer and Multilayer Palladium Epitaxially Grown on Mo(110)

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Received: February 11, 1998; In Final Form: March 30, 1998

The adsorption of ammonia on a monolayer of Pd on Mo(110), Pd(1ML)/Mo(110), and multilayer Pd(111)/Mo(110) surfaces has been studied using low-energy electron diffraction (LEED), temperature-programmed desorption (TPD), and high-resolution electron energy loss spectroscopy (HREELS). A diffuse (2 × 2) LEED pattern has been observed for ammonia on the Pd(1ML)/Mo(110) surface. TPD measurements indicate a shift of the desorption peak maximum of ammonia to a lower temperature for monolayer palladium compared to multilayer palladium. However, both surfaces display virtually identical HREELS spectra with the symmetric deformation (umbrella mode) being the dominating feature, indicating an upright adsorption geometry on both surfaces. The coadsorption of NH3 and CO has been also studied with HREELS over a wide coverage range on both surfaces. A strong interaction between adsorbed NH3 and CO is indicated by the red shift of the CO stretching vibrational mode (as large as 400 cm\(^{-1}\)) and a blue shift of the NH3 symmetric deformation (up to 100 cm\(^{-1}\)). On Pd(1ML)/Mo(110), the coadsorption of NH3 induces a CO adsorption site change from the atop site to the three-hollow site. Evidence has been also found for a significantly inclined NH3 molecule in the coadsorbed layer with a relatively high CO coverage.

1. Introduction

The chemistry of bimetallic surfaces has received considerable attention in recent years due to the novel properties exhibited by these systems relative to their single-component counterparts.\(^1\)\(^\text{-}^5\) Palladium monolayers supported on early transition metals are the most studied systems of this kind.\(^1\)\(^\text{-}^17\) It has been found that a palladium monolayer has a reduced ability to adsorb CO, H\(_2\), and C\(_2\)H\(_4\) compared to bulk palladium.\(^6\)\(^\text{-}^8\) There is some controversy in the literature regarding the origin of the modified properties of supported monolayer transition metals on dissimilar metals. Systematic studies have been carried out to address the correlation between the adsorption behavior of a supported metal overlayer toward CO and its electronic structure.\(^1\)\(^,\)\(^4\)\(^,\)\(^5\) The change in the binding energy of CO on a number of supported metal monolayers has been correlated with the XPS core level shifts of the metal overlayer as well as work function changes.\(^4\)\(^,\)\(^5\) A simple model has been advanced to explain the reduced binding energy of a Pd monolayer on early transition metal: the depletion of 4d electron density through charge polarization from Pd toward the metal substrate and the rehybridization of the Pd(4d,5s,5p) levels.\(^1\)\(^,\)\(^5\)

Unlike CO, NH3 is a weak donor ligand, which adsorbs on the surface through the nitrogen lone pair electrons in a single dative bond. It is instructive to compare these two different bonding mechanisms, especially multilayer palladium relative to monolayer palladium. The adsorption of NH3 on transition-metal surfaces is also of considerable interest because of its relevance to ammonia synthesis. In recent years, the catalytic de-NO\(_x\) process using NH3 has also received considerable attention. The interaction of ammonia with NH\(_3\)-synthesis-relevant surfaces, such as Fe and Ru, has been extensively characterized using a number of surface science techniques (refs 19–21 and references therein). These studies have been extended to other surfaces including Pt(111),\(^22\)\(^\text{-}^24\) Ni(111),\(^25\)\(^\text{-}^28\) Ni(110),\(^29\)\(^\text{-}^30\) Ag(111),\(^31\) Al(111),\(^32\) and NiO(100).\(^34\) However, no studies have been carried out on palladium surfaces or any ultrathin metal overlayers. In this paper, we report on our recent studies of adsorption of NH3 on palladium monolayers supported on the Mo(110) surface and a Pd(111) surface epitaxially grown on the Mo(110) surface.

The second focus of this paper is the coadsorption of NH3 with CO on these surfaces. The coadsorption of NH3 and CO has been studied previously on Ni(111),\(^35\)\(^\text{-}^38\) Ni(110),\(^36\)\(^,\)\(^37\) Ru-(001),\(^39\)\(^,\)\(^40\) Re(0001),\(^41\) and Cu(110)\(^42\) surfaces. Using metastable quenching spectroscopy (MQS), Tochihara et al.\(^35\) have studied the coadsorption of NH3 and CO on Ni(111). These authors found that NH3 on top of a CO layer leads to an increase in the back-donation from the metal substrate into the 2π* orbital of CO. The adsorption of NH3 on top of CO chemisorbed on Ni-(111) and Ni(110) has been studied by Dresser et al.\(^34\) and Lanzillotto et al.,\(^37\) using electron-stimulated desorption ion angular distribution (ESDIAD) and temperature-programmed desorption (TPD). A short-range CO–NH3 interaction was found on Ni(111) with the C3z axis of NH3 inclined away from the surface normal. Erley\(^38\) has studied the coadsorption of NH3 and CO on Ni(111) using infrared spectroscopy. Zhou et al.\(^39\)\(^,\)\(^40\) and Sakaki et al.\(^40\) studied NH3 and CO coadsorption on Ru-(001) using high-resolution electron energy loss spectroscopy (HREELS), low-energy electron diffraction (LEED), and TPD, and they showed that CO coadsorbed with NH3 induces a red shift in the C–O stretching vibrational mode. Mijoule et al.\(^43\) have carried out density functional calculations of the vibrational stretching mode of CO coadsorbed with NH3 on Pd clusters. Their calculations showed that the C–O stretching frequency, the CO bond length, and the magnitude of the d–π* back-donation are modified similarly whether NH3 is added explicitly or electrons are simply added to the cluster. However, the
metal–CO vibration, the metal–CO bond length, and the magnitude of the s–d donation are all altered in the opposite direction. Therefore, these authors concluded that the effects of the coadsorption of NH3 with CO cannot arise simply from electron transfer from NH3 to CO through the metal. Other more subtle effects must also be involved.

2. Experimental Section

The experiments have been carried out in a ultrahigh-vacuum (UHV) chamber which has been described in detail previously and whose base pressure was $< 1 \times 10^{-10}$ Torr. Briefly, the UHV chamber is equipped with capabilities for HREELS, Auger electron spectroscopy (AES), LEED, and TPD. HREEL spectra were acquired with a primary energy of 3 eV and a typical resolution of 50–60 cm$^{-1}$. TPD measurements were made with the QMS in line-of-sight with the sample and with a linear heating rate of ~5 K/s. To avoid electron beam damage, the sample was biased at −100 V during the TPD experiments. The sample could be resistively heated to 1500 K or heated to 2200 K using an electron beam assembly. The sample temperature was measured using a W–5% Re/W–26% Re thermocouple spot-welded to the sample's edge. The Mo(110) crystal was cleaned by annealing in 2–6 Torr of O2 at 1200 K, with a subsequent flash to 2000 K. This procedure was repeated several times until no contaminations could be detected via AES.

The palladium source used for deposition was a 0.25 mm Pd wire (99.997%, Johnson Matthey Chemical Limited) wrapped around a tungsten filament. A line-of-sight mass spectrometer was used to monitor the Pd flux which typically corresponded to approximately one monolayer (ML) per minute. The Pd source has been extensively outgassed before use; the pressure during evaporation never exceeded 3 × $10^{-10}$ Torr. The Pd coverage was calibrated using TPD and AES. The growth and annealing behavior of Pd on Mo(110) was studied by Park et al., using AES, XPS, LEED, and the change in work function. At monolayer or less coverage, Pd forms a pseudomorphic monolayer with no indication of alloy formation. At higher coverages, Pd grows in a layer-by-layer or Frank–van der Merwe mode at room temperature. At elevated temperatures, Pd grows layer-by-layer in the first layer followed by three-dimensional (3D) clustering or a Straniski–Krastanov mechanism. Annealing the Mo(110) surface exposes to Pd vapor at room temperature to 600 K will also cause the Pd multilayer to agglomerate. Significant alloying of Pd with Mo via diffusion of Mo into Pd occurs; however, even with the alloying, the surface is still covered by a monolayer of Pd. If the Pd multilayer grown at room temperature exceeds 12 ML, annealing to temperatures as high as 900 K will not cause coalescence, apparently due to kinetic considerations. The thick Pd layer shows a sharp hexagonal LEED pattern, indicating epitaxial growth and the formation of a Pd(111) overlayer structure. Only monolayer palladium and multilayer (>15 ML) Pd structures with sharp LEED patterns have been utilized in the present studies. For brevity, the Pd monolayer on Mo(110) and the epitaxially grown Pd multilayer on Mo(110) will be referred to as the Pd$_{1\text{ML}}$/Mo(110) and Pd(111)/Mo(110) surfaces in the following sections.

The ammonia (Matheson, 99.99%) was used after several freeze–pump–thaw cycles in the gas manifold. Carbon monoxide (Matheson, 99.99%) was used as received without further purification. The gases were introduced via a directional gas doser to the surface for TPD measurements, while the exposures for the HREELS experiments were carried out via backfilling the UHV chamber. The exposures are given in langmuirs, equal to $1 \times 10^{-6}$ Torr s, without correction for the dose enhancement and ion gauge sensitivity. For low coverages, the exposures have been converted in certain cases to coverage using LEED and HREELS results and assuming a constant sticking coefficient.

3. Results

3.1. NH3 Adsorption. 3.1.1. LEED and TPD. The adsorption of NH3 was first studied using TPD with masses 2, 17, 18, 28, and 32 routinely monitored. On both Pd$_{1\text{ML}}$/Mo(110) and Pd(111)/Mo(110) surfaces, molecular NH3 desorption is the only product found in the gas phase. Consistently, AES after TPD experiments showed a surface free of nitrogen, indicating that NH3 adsors molecularly and that the adsorption is completely reversible. Figures 1 and 2 show two series of TPD spectra acquired after increasing exposures of NH3 to Pd$_{1\text{ML}}$/Mo(110) and Pd(111)/Mo(110) surfaces, respectively. The TPD spectra of Figure 1 for the Pd$_{1\text{ML}}$/Mo(110) surface show desorption features between 140 and 350 K for low exposures of NH3. Three broad and significantly overlapping peaks centered at 160,
225, and 280 K are apparent. With increasing NH3 exposures, the features between 150 and 350 K become more intense, and two new features at 100 and 130 K begin to develop. The feature at 100 K does not saturate but shifts gradually to higher desorption temperatures with increasing NH3 dose. This feature is assigned to desorption of NH3 from the multilayer. The feature at 130 K, with a desorption temperature between the multilayer and the first chemisorbed layer, is assigned to second-layer desorption. The Pd(111)/Mo(110) surface displays very similar TPD behavior as shown in Figure 2. Two desorption features between 90 and 150 K are observed, again attributed to desorption from the condensed and second layers, respectively. The chemisorbed layer, however, shows a slightly larger proportion of the high-temperature desorption state on the Pd-1ML/Mo(110) surface compared to the Pd1ML/Mo(110) surface. From Figure 3 one can conclude that a significant fraction of the desorption feature near 270 K is assigned to desorption of NH3 from the multilayer. The (2×2) LEED pattern after annealing to 180 K after dosing with approximately 3 ML of NH3 exhibits a (2×2) LEED pattern after annealing to 180 K after dosing with approximately 3 ML of NH3. This temperature is sufficient to remove both multilayer and second-layer ammonia, leaving a surface covered with only a chemisorbed layer of ammonia. The LEED pattern is very sensitive to the electron beam and can be observed only for a relatively short time period, indicating a high cross section of electron-induced desorption for NH3 on the Pd1ML/Mo(110) surface. This is consistent with the relative weak bonding of NH3 on this surface. The (2×2) LEED pattern observed here has been previously observed by Benndorf and Madey46 for NH3 on the Ru(001) surface and not be confirmed by Sasaki et al.40

3.1.2. HREELS. Figure 4a shows a series of HREEL spectra acquired subsequent to increasing NH3 exposures on the Pd(111)/Mo(110) surface. At an exposure of 0.01 langmuir, two features are seen at 290 and 1100 cm−1, which can be assigned to the Pd−N stretching and symmetric deformation (umbrella) modes of adsorbed NH3, respectively. No features related to the N−H stretching were observed, presumably due to the low cross section for these modes. Upon increasing the NH3 exposure from 0.01 langmuir, the features at 290 and 1100 cm−1 gain intensity until 0.05 langmuir is reached; the 290 cm−1 feature then loses intensity with a further increase in exposure to 0.2 langmuir. Concomitantly, a new feature at 300 cm−1 begins to appear at 0.2 langmuir. The intensity of the peak at 1100 cm−1 is almost constant between 0.05 and 0.1 langmuir and then begins to attenuate with exposures up to 0.2 langmuir. The symmetric deformation mode gradually shifts from 1100 to 1050 cm−1 with increasing NH3 exposures from 0.01 to 0.2 langmuir. At an exposure of 0.025 langmuir, features between 3200 and 3500 cm−1, assigned to N−H stretching modes, begin to develop. With increasing NH3 exposure from 0.2 to 0.5 langmuir, the feature at 1050 cm−1 shifts further to 1005 cm−1 and dramatically loses intensity. Concomitantly, two new features appear at 1100 and 1610 cm−1, while the feature at 300 cm−1 dominates at this coverage. These features collectively can be assigned to bilayer formation. The peaks at 300 and 1610 cm−1 correspond to the NH3 twisting mode and the asymmetric deformation mode, respectively. The NH3 twisting mode is very characteristic of second-layer ammonia on various surfaces and has been used as a fingerprint for the onset of second-layer ammonia adsorption.20 This mode is not visible in the first chemisorbed layer due to free rotation about the N−metal bond.46 In the second ammonia layer, the formation of hydrogen bonds between the amonnias hinders this rotation considerably and shifts its frequency to an accessible frequency in the HREELS measurements. The top spectrum of Figure 4a is that acquired after dosing 2 langmuirs of NH3 (approximately 5–6 monolayers). In this spectrum, features at 420, 1100, and 1625 cm−1 and a doublet at 3360 and 3400 cm−1 are apparent. These features correlate with the formation of the NH3 multilayer phase and can be assigned to the frustrated libration (twisting mode), the symmetric and asymmetric deformation, and the symmetric and asymmetric stretching vibrational modes, respectively.

In Figure 4b, an annealing series after dosing approximately four NH3 layers on the Pd(111)/Mo(110) surface at 90 K is shown. After heating to 120 K to remove the multilayer, the spectrum characteristic of the bilayer is seen, with dominating features at 320 cm−1 due to the NH3 twisting mode and the symmetric and asymmetric deformation mode at 1120 and 1600 cm−1, respectively. Further annealing to 180 K desorbs the second layer with the subsequent spectrum being dominated by the symmetric deformation at 1050 cm−1. Also seen are the
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Pd–N vibrational mode at 300 cm\(^{-1}\) and the asymmetric and symmetric N–H stretching modes at 3260 and 3365 cm\(^{-1}\), respectively. A small feature at 1600 cm\(^{-1}\) is also apparent, which is most likely due to a trace amount of coadsorbed CO. This feature is less likely due to the asymmetric deformation of NH\(_3\) since the asymmetric deformation mode is not observed at a similar coverage in the coverage series of Figure 4a, whereas CO coadsorbed with NH\(_3\) shows a C=O vibrational mode at this frequency (see below). Upon heating the sample to even higher temperatures, the feature at 1050 cm\(^{-1}\) loses intensity and shifts to a higher wavenumber due to desorption of NH\(_3\) from the chemisorbed first layer.

A palladium monolayer supported on Mo(110), Pd\(_{1ML}/\text{Mo-(110)}\), exhibits HREELS spectra analogous to those of the Pd(111)/Mo(110). This can be seen in Figure 5a,b. In Figure 5a, the HREELS spectra acquired after increasing NH\(_3\) exposures are shown, while Figure 5b shows an annealing series. As for Pd(111)/Mo(110), the symmetric NH\(_3\) deformation, which gradually gains intensity and shifts to lower wavenumber with increasing NH\(_3\) coverage, is the dominating feature up to a NH\(_3\) exposure of 0.2 langmuir. The intensity of this feature decreases with further increasing exposure to 0.5 langmuir. The features correlated to the bilayer NH\(_3\) dominate the spectrum at 0.5 langmuir. However, careful inspection of the symmetric deformation shows some differences on the two surfaces that are more evident in Figure 6. On the Pd\(_{1ML}/\text{Mo(110)}\) surface, the features are generally broad and shift more rapidly to lower wavenumbers with increasing NH\(_3\) exposures. The intensity change with increasing NH\(_3\) is more profound for the Pd(111)/Mo(110) surface than the Pd\(_{1ML}/\text{Mo(110)}\) surface. Also, an asymmetric peak shape is apparent for the Pd\(_{1ML}/\text{Mo(110)}\) surface.

3.2. Coadsorption of NH\(_3\) with CO. The influence of NH\(_3\) on the vibrational structure of coadsorbed CO on the Pd\(_{1ML}/\text{Mo(110)}\) and Pd(111)/Mo(110) surface has been studied using HREELS over a wide coverage range. In the following sections these results are described and the two surfaces compared at various coverages.

3.2.1. 0.05 langmuir of CO + 0.5 langmuir of NH\(_3\). Figure 7 shows HREEL spectra for the Pd\(_{1ML}/\text{Mo(110)}\) (left) and Pd(111)/Mo(110) (right) systems at a relatively small CO and a relatively large NH\(_3\) coverage. From bottom to top, the spectra acquired after dosing 0.05 langmuir of CO, then 0.5 langmuir of NH\(_3\), and finally an anneal to the indicated temperature are shown. The spectra taken for a 0.05 langmuir CO exposure show features at 350 and 2050 cm\(^{-1}\) on the Pd\(_{1ML}/\text{Mo(110)}\) surface and features at 320 and 1800 cm\(^{-1}\) on the Pd(111)/Mo(110) surface. Dosing 0.5 langmuir of NH\(_3\) on top of these surfaces induces a dramatic red shift of the C=O stretching vibration by 400 cm\(^{-1}\) for Pd\(_{1ML}/\text{Mo(110)}\) and 200 cm\(^{-1}\) for Pd(111)/Mo(110). Concomitantly, the features due to the Pd–CO stretching mode are replaced by the NH\(_3\) twisting mode arising from NH\(_3\) in the second layer. The NH\(_3\) symmetric deformational mode exhibits a doublet at 1010 and 1080 cm\(^{-1}\) for Pd\(_{1ML}/\text{Mo(110)}\) and a single, broad peak at 1030 cm\(^{-1}\) for Pd(111)/Mo(110). Also, the asymmetric and symmetric N–H stretching modes are clearly seen for both surfaces. Since the NH\(_3\) desorbs at a lower temperature than CO, the coadsorption of NH\(_3\) at relatively low coverages with the same CO surface coverage has been studied by annealing the surface to the indicated temperature in Figure 7. The surface
was first annealed to 160 K to remove the NH3 second layer, and as anticipated the peak near 300 cm\(^{-1}\) essentially disappears. Only a small feature, likely relating to the Pd–N stretching mode, remains near 300 cm\(^{-1}\). It should be noted that the Pd–CO stretching mode is not observed for either surface, although this mode has a very high intensity on the NH3-free Pd\(_{1ML}/\text{Mo(110)}\) surface. A small shift (10–15 cm\(^{-1}\)) in both the NH3 symmetric deformational mode and the CO stretching vibrational mode to higher wavenumber is also apparent in this temperature range. On the Pd\(_{1ML}/\text{Mo(110)}\) surface, the doublet near 1050 cm\(^{-1}\) is replaced by a feature at 1010 cm\(^{-1}\) with a shoulder on the low wavenumber side. The HREEL spectra of NH3 alone on the Pd\(_{1ML}/\text{Mo(110)}\) and Pd(111)/Mo(110) surfaces show a NH3 symmetrical, deformational mode for the first chemisorbed layer below 1005 cm\(^{-1}\) and, for the second layer, a feature between 1065 and 1100 cm\(^{-1}\) at 0.5 langmuir of NH3. Comparing the results of coadsorbed NH3 and CO with NH3 alone, it is apparent that the presence of CO on the surface shifts the NH3 symmetrical deformational mode for the first chemisorbed layer of NH3 to a higher frequency. For the Pd(111)/Mo(110) surface, this shift causes the feature for the first chemisorbed layer to collapse into the feature for the second adsorbed layer, resulting in a single NH3 symmetric deformation peak.

To further reduce the NH3 coverage, the sample was heated from 160 to 300 K, and HREEL spectra were acquired after anneals to 230, 250, and 300 K. In this temperature range, the NH3 symmetric deformation and the C–O stretching vibration gradually shift to higher wavenumbers on the Pd(111)/Mo(110) surface. For the Pd\(_{1ML}/\text{Mo(110)}\) surface the C–O stretching mode moves to 2050 cm\(^{-1}\) with a small feature at 1800 cm\(^{-1}\) becoming apparent at 230 K. Also seen is the reappearance of the Pd–CO stretching mode at 350 cm\(^{-1}\) for the Pd\(_{1ML}/\text{Mo(110)}\) surface. The disappearance and reappearance of this peak correlates with the absence and presence of CO adsorbed on the atop site. The cosorption of NH3 shifts the CO adsorption from the atop site to the three-hollow site. The Pd–CO vibrational mode of CO adsorbed on the three-hollow site apparently has a smaller intensity and lower vibrational frequency than does CO adsorbed on the atop site and is obscured by the NH3 twisting mode.

On the Pd\(_{1ML}/\text{Mo(110)}\) surface, the features related to NH3 are greatly reduced upon heating to 250 K after which the C–O stretching mode moves to its position prior to the dosing of NH3. Also, the peak desorption temperature of NH3 is much higher for the Pd(111) surface. Even at 300 K, significant amounts of NH3 remain on the surface, as indicated by the feature at 1170 cm\(^{-1}\). These results show a higher binding energy for NH3 on the Pd(111)/Mo(110) surface than for the Pd\(_{1ML}/\text{Mo(110)}\) surface, even in the presence of CO. Furthermore, by comparing the anneal series with cosorbed NH3 to that acquired on the CO-free surface, it can be concluded that cosorption of NH3 with CO increases the NH3 binding energy. This conclusion is also valid for other CO coverages, as discussed below.

### 3.2.2. 0.25 langmuir of CO + 0.5 langmuir of NH3

Figure 8 shows two series of HREEL spectra acquired after dosing 0.5 langmuir of NH3 to the Pd\(_{1ML}/\text{Mo(110)}\) and Pd(111)/Mo(110) surfaces, precovered with 0.25 langmuir of CO, and a subsequent anneal of each to the indicated temperature. For reference, the spectra of the surfaces with only CO are shown at the bottom. The peaks at 360 and 2060 cm\(^{-1}\) on the Pd\(_{1ML}/\text{Mo(110)}\) and at 320 and 1830 cm\(^{-1}\) on the Pd(111)/Mo(110) surface can be assigned to the Pd–CO and C–O stretching modes, respectively. The adsorption sites are atop for the Pd\(_{1ML}/\text{Mo(110)}\) and likely three-hollow for the Pd(111)/Mo(110) surface. Dosing 0.5 langmuir of NH3 on top of these surfaces shifts the C–O stretching vibration to lower wavenumber. On the Pd\(_{1ML}/\text{Mo(110)}\) surface, two features corresponding to C–O stretching modes appear at 1705 and 1810 cm\(^{-1}\), while on the Pd(111)/Mo(110) surface a feature at 1750 cm\(^{-1}\) with a shoulder at 1600 cm\(^{-1}\) is seen. As for lower CO coverages, the features corresponding to the Pd–CO stretching modes are not observed. Instead, the NH3 twisting modes are observed in this frequency range. It is noteworthy that this twisting mode is much weaker for the Pd\(_{1ML}/\text{Mo(110)}\) surface compared to the Pd(111)/Mo(110) surface or to the Pd\(_{1ML}/\text{Mo(110)}\) surface with a lower CO coverage. This is probably due to the lower capacity of the Pd\(_{1ML}/\text{Mo(110)}\) surface for the adsorption of CO and NH3. At an exposure of 0.25 langmuir of CO, the amount of NH3 adsorbed in the first chemisorbed layer on the Pd\(_{1ML}/\text{Mo(110)}\) is smaller than on the Pd(111)/Mo(110) surface. The bilayer structure for the Pd\(_{1ML}/\text{Mo(110)}\) is therefore limited to a relatively small part of the surface, suggesting that the twisting mode at 300 cm\(^{-1}\) is characteristic of NH3 on top of NH3. This is consistent with the observation that hydrogen bonding shifts this vibrational feature to an accessible value for detection by HREELS.

To examine the effect of NH3 coverage on CO adsorption at 0.5 langmuir, both surfaces were gradually annealed to 300 K. Following the desorption of the second NH3 layer by annealing to 140 K, the features corresponding to the NH3 twisting mode lose intensity. The NH3 symmetric deformational mode and the C–O stretching mode also show changes in the line shape without a significant shifting of the primary features. No significant shifts were observed for the NH3 symmetric deformational mode even at the higher annealing temperatures. However, the C–O stretching mode shifts from 1750 to 1800 cm\(^{-1}\) for the Pd(111)/Mo(110) surface and from 1705 or 1810 to 2060 cm\(^{-1}\) on the Pd\(_{1ML}/\text{Mo(110)}\) surface. A small feature at 1910 cm\(^{-1}\) is also seen on the Pd\(_{1ML}/\text{Mo(110)}\) surface after annealing the surface to 230 K, which is probably due to CO interacting with small amounts of NH3 remaining on the surface. After desorbing essentially all of the NH3, the Pd–CO stretching mode regains its original intensity.

### 3.2.3. 0.5 langmuir of CO + 0.5 langmuir of NH3

The most striking finding in this coverage range, as shown in Figure 9, is the C–O stretching mode at 1850 cm\(^{-1}\) for Pd\(_{1ML}/\text{Mo(110)}\) and at 1780 cm\(^{-1}\) for Pd(111)/Mo(110). Each of these features...
Figure 9. 9. HREEL spectra after dosing 0.5 langmuir of NH$_3$ onto 0.5 langmuir of CO-precovered (a) Pd$_{3ML}$/Mo(110) and (b) Pd(111)/Mo(110) surfaces and subsequently annealing to the indicated temperature.

Figure 10. 10. HREEL spectra after dosing 0.5 langmuir of NH$_3$ onto 1.0 langmuir of CO-precovered (a) Pd$_{3ML}$/Mo(110) and (b) Pd(111)/Mo(110) surfaces and subsequently annealing to the indicated temperature.

exhibits a foot extending with gradually decreasing intensity to 1500 cm$^{-1}$. These results suggest a long-range interaction between coadsorbed CO and NH$_3$ on both surfaces. Also noteworthy is that the main C$=$O stretching feature does not shift with annealing temperature to 160 K and that the NH$_3$ symmetric deformational mode does not shift during the entire annealing cycle of these experiments.

As for lower CO coverages, the Pd$=$CO vibrational mode is quenched in the presence of NH$_3$, with the NH$_3$ twisting mode becoming apparent. The N$=$H stretching mode is also observed with a relatively high intensity.

3.2.4. High (1.0 langmuir) CO Coverage and 0.5 langmuir of NH$_3$. The influence of NH$_3$ on CO coadsorption at high CO coverage is shown in the HREEL spectra of Figure 10. The spectra of CO on the NH$_3$-free surfaces correspond to CO adsorption on the bridging site of Pd(111)/Mo(110) and both bridging and atop sites on Pd$_{3ML}$/Mo(110). Dosing 0.5 langmuir of NH$_3$ on top of the CO-precovered surface causes again rather dramatic changes in the C$=$O and Pd$=$CO vibrational regions.

For the Pd$_{3ML}$/Mo(110) surface, the intensity of the C$=$O vibrational mode shifts from a feature corresponding to the atop site to a feature related to the bridging site, with a small shift of both features to lower wavenumber. The peak at 1905 cm$^{-1}$ shows as before a foot with decreasing intensity extending to lower wavenumber. The feature at 330 cm$^{-1}$ corresponding to the Pd$=$CO stretching mode disappears into the shoulder of the feature corresponding to the NH$_3$ twisting mode. Two well-separated features related to the NH$_3$ symmetric deformational modes are observed at 1080 and 1180 cm$^{-1}$. In contrast to the spectra acquired at lower CO coverages, a feature due to the NH$_3$ asymmetric deformational mode is apparent at 1610 cm$^{-1}$. Upon heating to 120 K, the feature at 250 cm$^{-1}$ disappears and the Pd$=$CO vibration at 350 cm$^{-1}$ regains some of the intensity; the latter’s intensity is completely restored by heating to 230 K. The feature at 1080 cm$^{-1}$ loses significant intensity upon heating to 120 K and then disappears completely at 160 K with desorption of the NH$_3$ second layer. This indicates that the large blue shift of the NH$_3$ symmetric deformational mode is due to a surface-mediated interaction rather than a direct through-space interaction between CO and NH$_3$. Otherwise, one would expect to see a large shift as well for NH$_3$ adsorbed in the second layer. It should be noted that the NH$_3$ symmetric deformational mode for the first chemisorbed layer is at a higher wavenumber than that for the second layer. This result contrasts with that for the surfaces covered with only NH$_3$, where the first chemisorbed layer displays a lower vibrational frequency for the NH$_3$ symmetric deformational mode (between 970 and 1010 cm$^{-1}$) than the second adsorbed NH$_3$ layer (between 1065 and 1100 cm$^{-1}$).

The gradual shift of the NH$_3$ symmetric deformational mode to higher wavenumber with increasing CO coverages is the result of two processes. First, the presence of CO on the surface reduces the NH$_3$ density in the first layer, therefore reducing the NH$_3$$-$NH$_3$ repulsive interaction. Second, the attractive interaction between NH$_3$ and CO shifts the NH$_3$ symmetric deformational mode to a higher frequency. Since the NH$_3$ symmetric deformation shows a vibrational frequency of approximately 1100 cm$^{-1}$ at the zero-coverage limit with no CO coadsorbate, well below the vibrational frequency (1180 cm$^{-1}$) with coadsorbed CO, the shift induced by the NH$_3$$-$CO attractive interaction contributes most significantly to the observed shift in the frequency of the NH$_3$ symmetric deformation.

Coadsorption of CO with NH$_3$ slightly shifts the C$=$O stretching vibration to lower frequency from 1940 to 1890 cm$^{-1}$. Two NH$_3$ symmetric deformation features are observed at 1160 and 1210 cm$^{-1}$, with the lower frequency feature disappearing after annealing to 160 K. Both the Pd$=$CO and the NH$_3$ twisting vibrational modes are evident. A new feature at 1480 cm$^{-1}$, which was not observed at lower CO coverages, is apparent and becomes more evident upon annealing the surface to 120 K. This feature is still evident even after heating the sample to 230 K. This feature obviously arises from the relatively high coverage of CO. To confirm this, HREEL spectra were acquired after dosing 0.5 langmuir of NH$_3$ onto a 3 langmuirs CO-precovered Pd(111)/Mo(110) surface. The resulting HREEL spectra are shown in Figure 11. As anticipated, the feature at 1490 cm$^{-1}$ is now even more intense. The low frequency of this feature precludes a CO-related origin. This peak is assigned accordingly to the asymmetric deformation of NH$_3$. The high intensity of this peak suggests that NH$_3$ is no longer present in an upright configuration.

3.2.5. NH$_3$ + CO. The effect of CO on coadsorbed NH$_3$ can be more clearly seen if one doses CO onto an NH$_3$-precovered surface. HREEL spectra acquired after dosing 0.5 langmuir of CO on a 0.4 langmuir NH$_3$-precovered surface are shown in Figure 12. Spectra for NH$_3$ alone are shown at the bottom of (a) and (b). Each surface was covered slightly in excess of 1 ML of NH$_3$, as indicated by the feature at 300 cm$^{-1}$ and the
small shoulder at 1100 cm\(^{-1}\). Coadsorption with CO shifts the feature at 1000 cm\(^{-1}\) to 1140 cm\(^{-1}\). The feature at 300 cm\(^{-1}\) loses some intensity, likely to displacement of NH\(_3\) in the chemisorbed layer by CO. The intensity of the N–H stretching vibrations, however, is enhanced by the present of CO. Two peaks corresponding to C=O stretching modes are seen at 1700 and 1850 cm\(^{-1}\) for Pd\(_{1}\)/Mo(110) and at 1610 and 1720 cm\(^{-1}\) for Pd\(_{1}\)/Mo(110). Upon annealing, the NH\(_3\) symmetric deformational mode loses intensity without shifting significantly, while the C=O stretching modes gradually shift to higher wavenumber.

3.2.6. 0.02 langmuir of CO + 0.02 langmuir of NH\(_3\). The interaction of CO and NH\(_3\) at the zero-coverage limit has also been studied after dosing 0.02 langmuir of CO and 0.02 langmuir of NH\(_3\) on Pd\(_{1}\)/Mo(110) and at 1610 and 1720 cm\(^{-1}\) for Pd\(_{1}\)/Mo(110). Upon annealing, the NH\(_3\) symmetric deformational mode loses intensity without shifting significantly, while the C=O stretching modes gradually shift to higher wavenumber.

4. Discussion

4.1. NH\(_3\) Adsorption. The adsorption of NH\(_3\) has been previously studied on various surfaces using TPD.\(^{19-34}\) Consistent with these previous results, the TPD spectra of NH\(_3\) in the present study show a broad desorption peak for the chemisorbed state on both the Pd\(_{1}\)/Mo(110) and Pd\(_{1}\)/Mo(110) surfaces. This is due to the increasing repulsive interaction between the adsorbed NH\(_3\) with increasing coverage. NH\(_3\) adsorbs via a dative bond through the electron lone pair on the N atom, leading to a relatively large dipole between NH\(_3\) and the surface. These dipoles interact repulsively with each other, therefore destabilizing the NH\(_3\). This general picture is consistent with work function measurements of NH\(_3\) adsorbed on Ru(001) by Benndorf and Madey.\(^{46}\) These authors found that the work function initially decreases linearly with increasing NH\(_3\) coverage due to electron donation from NH\(_3\) to the surface but then decreases less rapidly up to 0.15 ML due to depolarization. The other possible explanation for the broad desorption feature observed for chemisorbed NH\(_3\) is the presence of multiple adsorption sites.\(^{23,32}\) However, the single narrow feature observed for the NH\(_3\) symmetric deformational mode for the chemisorbed NH\(_3\) layer on Pd\(_{1}\)/Mo(110) indicates that this is unlikely. In this context it is noteworthy that, in the IR measurements of NH\(_3\) adsorption on Ru(001) by Rodriguez et al.,\(^{19}\) only a single feature for chemisorbed NH\(_3\) is observed.

The adsorption of NH\(_3\) is completely reversible for both Pd\(_{1}\)/Mo(110) and Pd\(_{1}\)/Mo(110); no indication of dissociation is found in the TPD and HREELS data. The adsorption of NH\(_3\) on several of the later transition metals has also been found previously to be largely reversible. These include Ru(001), Pt(111), Ni(111), and Ni(110). Only on Ni-
(110) has a substantial amount of dissociation been found after
dosing NH3 at room temperature.44

HREELS has been used to study NH3 adsorption on Ru(001),
Pt(111), Ni(111), Ni(110), Ag(110), Ag(311), and Fe(110). The
HREELS spectra of chemisorbed NH3 in most of these cases are
dominated by the NH3 asymmetric deformational mode. The
wavenumber of this vibrational feature has been correlated either
to the strength of the NH3-metal bond39 or to the charge density
at the substrate atoms.20 NH3 adsorbed on NiO(110) shows a
very similar TPD spectra as for the transition metal; however,
no shift in the NH3 asymmetric deformational mode with increasing
NH3 coverage is apparent. This is likely due to the
localized nature of the charge in an insulating oxide. Thus,
the shift of the symmetric deformational mode with increasing
NH3 coverage is likely dominated by effects related to the
electron density at the surface. In any event, this shift is a
measure of the ability of the substrate to accept and stabilize
the nitrogen electron lone pair of NH3. This, in turn, correlates
to the density of states near the Fermi level as well as the
electron density within individual orbitals. That this vibration
has exactly the same frequency for both Pd1ML/Mo(110) and
Pd(111)/Mo(110) surfaces at lower NH3 coverage and decreases
to lower frequency at a more rapid rate on the Pd1ML/Mo(110)
surface than on the Pd(111)/Mo(110) surface indicates a slightly
enhanced reduction in the density of states near the Fermi level
for the Pd1ML/Mo(110) surface compared to Pd(111)/Mo(110),
but a very similar electron density of individual orbitals for both
systems. In this respect a slightly reduced high-temperature
state in TPD for NH3 adsorbed on Pd1ML/Mo(110) in comparison
to the Pd(111)/Mo(110) surface has been found.

Previously, a reduced binding energy has been found for CO
bound to a Pd monolayer on a number of substrates, including
transition metals, noble metals, and sp metals such as Al. This
indicates that the reduced reactivity of monolayer Pd is an
intrinsic property. An interaction with the substrate will
certainly further modify the electronic structure of the Pd
monolayer, which accounts for the differences in Pd monolayers
supported on various substrates since the CO reduced binding
energy has been attributed primarily to reduced back-bonding
from the metal. In this study, the reduced ability of a Pd
monolayer to accept electrons has been demonstrated and is
clearly due to a reduced density of states near the Fermi level.
The monolayer presents a transition from an atomiclike structure
with discrete states to a band structure with continuous states.
Angular-resolved ultraviolet photoemission spectroscopy (ARUPS)
of monolayer Pd on Al(111), where the features corresponding
to the Pd monolayer can be clearly distinguished from the
substrate emission, shows that the transition from the atomiclike
structure is not yet complete at a monolayer coverage of Pd.
That is, an atomiclike electronic structure in a Pd monolayer is
retained to a degree. Consequently, the density of states near
the Fermi level for the monolayer is less than bulk Pd, and the
monolayer shows reduced reactivity.

4.2. Coadsorption of NH3 with CO. Coadsorption of CO
and NH3 causes a blue shift of the NH3 symmetric deformation
mode and a red shift of the C=O stretching mode for monolayer
and multilayer Pd. However, each of these shifts occurs to a
significantly larger extent for Pd(111)/Mo(110) than Pd1ML/Mo(110).
This is consistent with a higher binding energy for CO
and NH3 on Pd(111)/Mo(110) compared to Pd1ML/Mo(110) and
indicates that the interaction between CO and NH3 occurs
primarily through the surface.

The frequency shift to lower wavenumber of the C=O
vibrational mode induced by a coadsorbed electropositive
species such as ammonia or alkali metals has been a subject of
intensive debate. Several mechanisms have been proposed to
explain this red shift. In the chemical shift model, the
coadsorption of an electron donor leads to greater surface
electron density, therefore leading to an enhanced electron
transfer into the 2π* antibonding orbital of the adsorbed CO.
This occurs through either depolarization in the case of a more
localized electron donor such as NH3 or electron transfer into
the substrate in the case of alkali metals. The consequence of
the enhanced back-bonding is that the C=O bond is weakened
while the CO-surface bond is stabilized. Concomitantly, the
C=O stretching mode shifts to lower wavenumber. An
increased binding energy of CO is also observed with the
coadsorption of alkali metals. Since NH3 desorbs well below
CO from transition metals, the influence of coadsorbed NH3
on the CO binding energy cannot be addressed using conven-
tional TPD. However, the above arguments suggest that CO
coadsorbed with NH3 will have a higher binding energy.
In contrast, the electrostatic model argues that adsorbed CO
and NH3 have opposite dipoles with respect to the surface normal.
The dipole-dipole interaction then stabilizes both molecules
on the surface. The blue shift is simply a result of the interaction
of CO with the electrostatic field produced by the coadsorbed
molecules (Stark shift).

In actuality, a combination of both charge transfer and
electrostatic interaction exists. To separate these effects,
Hoffman et al. studied coadsorption of CO with Xe on the Ru-
(001) surface.47 Since Xe is only weakly physisorbed and
charge transfer is negligible, the observed red shift of the C=O
vibrational mode can be assumed to be due solely to an
electrostatic interaction. Yates and co-workers48-50 have re-
cently studied coadsorption of CO with Xe, H2, or O and were
able to correlate the shift of the C=O vibrational mode with the
global work function change. These authors argued that
the shift of the C=O vibrational mode was primarily due to the
alteration of the Fermi level by the coadsorbate. Depending
upon the coadsorbed species, the Fermi level moves either up
or down, resulting in an increase or decrease in the back-bonding
and, therefore, a red or blue shift of the C=O stretching mode.
The dipole-dipole interaction plays only a minor role in the
observed frequency shift.

The present results for Pd1ML/Mo(110) and Pd(111)/Mo(110)
are consistent with both long-range and short-range interactions.
The long-range interaction, likely due to a work function change,
is most clearly seen at lower CO coverages on Pd(111)/Mo-
(110). At 0.05 langmuir CO exposure, a gradual shift of both
the C=O stretching mode and the NH3 symmetric deformation
to higher frequencies with decreasing NH3 coverage is observed.
Desorbing NH3 causes a gradual increase in the work function
and therefore a decrease in the d−π* back-bonding. The NH3
symmetric deformational mode also shifts to higher frequency
due to an attenuated NH3−NH3 interaction. This result can also
be rationalized in terms of the work function change, which
enhances the ability of the substrate to accept electrons from
NH3, thus forming a more stable bond. In any event, it is clearly
a long-range, rather than a short-range, effect. On the Pd1ML/
Mo(110) surface, the interaction between NH3 and CO also
results in a change in the adsorption site at relatively high
annealing temperatures, from the atom site to a likely 3-fold
hollow site. With respect to the 3-fold hollow site, the C=O
vibrational mode gradually shifts from 1680 cm−1 at higher CO
exposures to 1810 cm−1 at a CO exposure of 0.05 langmuir.
This shift (130 cm−1) is somewhere smaller than the corre-
sponding shift (200 cm−1) found for the 3-fold hollow site on
the Pd(111)/Mo(110) surface. This is consistent with CO and NH₃ being more strongly bonded to the Pd(111)/Mo(110) surface compared to the Pd₁ML/Mo(110) surface. The interaction through the substrate is also more significant.

In addition to long-range interactions, short-range interactions are also clearly evident. For instance, the dosing of NH₃ on top of a CO-covered surface converts a single C–O vibration feature to two C–O vibrational features or occasionally a broad peak with a foot extending to lower wavenumbers. These results suggest either a different number of NH₃ neighboring molecules of CO or a reduced density in the NH₃ neighbors. This short-range effect is probably dominated by local charge transfer and, to a lesser degree, dipole–dipole interactions. In a charge-transfer mechanism, NH₃ donates electron density via the nitrogen atom to the substrate, polarizing the substrate electron density such that the d–σ* back-donation is increased.

It is also noteworthy that the presence of NH₃ promotes the occupancy by CO of more highly coordinated sites on the surface, with the Pd monolayer appearing more bulklike with respect to CO adsorption. It has been demonstrated that CO bonded to a 3-fold hollow site is more strongly destabilized relative to the atop site in going from bulk Pd to monolayer Pd. As a result, the atop site is the most stable adsorption site for CO on the supported Pd monolayer, while the three-hollow site is the most stable adsorption site for CO on bulk Pd. The presence of the NH₃ molecule, an electron donor, on the Pd₁ML/Mo(110) surface partially restores the adsorption behavior of bulk Pd with respect to CO. This again is due to electron donation from NH₃ to the surface and implies that the availability of electron density for back-donation in CO bonding to a transition-metal surface is the dominating factor in determining the adsorption site of CO.

Since both CO–CO and NH₃–NH₃ interactions are repulsive and the CO–NH₃ interaction is attractive, coadsorbed CO and NH₃ form mixed, rather than separate, domains. Even at the low coverage limit, a change in the bonding site of CO from atop to the 3-fold hollow, induced by coadsorbed NH₃ molecules, is consistent with the formation of a (CO)₆−(NH₃)₈⁺ complex due to the attractive interaction between CO and NH₃.

5. Conclusion

Using NH₃ as a probe, the Pd monolayer has been shown to have a slightly reduced density of states near the Fermi level and thus is better able to accept electron density from NH₃ compared with the bulk-terminated Pd surface. These results together with previous results obtained for these systems show that monolayer Pd compared with bulk Pd has a more deficient density of state near the Fermi level. The results of NH₃ and CO coadsorption show an attractive interaction between these two molecules, a significantly modified characteristic vibrational mode, and a change in the CO adsorption site on the Pd₁ML/Mo(110) surface.

Acknowledgment. We acknowledge with pleasure the support of this work by the Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences.

References and Notes