Adsorption and Reaction of Formic Acid on a Pseudomorphic Palladium Monolayer on Mo(110)

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The adsorption and reaction of formic acid, HCOOH, on monolayer and multilayer palladium supported on a Mo(110) surface have been studied using temperature-programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS). On multilayer palladium, formic acid adsorbs molecularly at 100 K and desorbs primarily intact upon heating to 200 K. A small amount of the adsorbed formic acid in the first adsorbed layer undergoes decomposition to form CO, H2O, and H2. No other surface reaction intermediates were identified using HREELS. In contrast to multilayer palladium, monolayer palladium exhibits a higher reactivity toward the decomposition of formic acid to form a surface formate species, as verified with HREELS. However, monolayer palladium shows a relatively low reactivity toward formate decomposition. The formate species is stable on the surface up to 350 K and exhibits an activation energy and preexponential factor for decomposition of 125 kJ/mol and 4.7 × 1018, respectively. Increasing the Pd thickness to three layers restores the bulk Pd surface chemistry of formic acid.

1. Introduction

The chemistry of monolayer palladium dispersed on a dissimilar substrate has attracted wide attention recently due to its strongly modified properties in comparison to its bulk counterpart. However, most investigations of monolayer Pd systems have been limited to CO and H2. Recently, Koel with the previous results using CO and H2 as probe molecules, multilayer.

2. Experimental Section

The experiments were carried out in an ultrahigh vacuum (UHV) chamber which has been described in detail previously. Briefly, the UHV chamber (base pressure < 1 × 10−10 Torr) was equipped with capabilities for HREELS (LK2000), Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and TPD. HREELS spectra were acquired with a primary energy of 3 eV and a typical resolution of 60 cm−1. TPD measurements were made using a line-of-sight quadrupole mass spectrometer (QMS) and a linear heating rate of ∼5 K/s. It is well-known that electron emission from the QMS can seriously damage weakly adsorbed molecular layers and introduce artifactual decomposition products into the TPD spectra. To avoid such damage, the sample was biased at 100 V when carrying out the TPD experiments. The sample, whose temperature was measured using a W5% Re/W26% Re thermocouple spot-welded onto the sample’s edge, could be heated resistively to 1500 or to 2200 K via an e-beam assembly. The Mo(110) crystal was cleaned by annealing in O2 at 1200 K, with a subsequent flash to 2000 K. This procedure was repeated several times until no impurities could be detected via AES.

The source used for Pd 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. The Pd source was extensively outgassed prior to use; the pressure while evacuating never exceeded 3 × 10−10 Torr. The Pd coverage was calibrated using both TPD and AES, while the Pd evaporation rate was typically ∼1 ML/min (ML = monolayer). The growth and annealing behavior of Pd on Mo(110) has been studied by Park et al. using AES, XPS, LEED, and work function changes. At a coverage of one monolayer or less, Pd forms a pseudomorphic monolayer with no indication of alloy formation. At higher coverages and at 300 K, Pd grows in a layer-by-layer or Frank van der Merwe mode. At elevated temperatures, Pd grows in a layer-by-layer mode within the first layer followed by 3D clustering or a Stranski–Krastanow mode in subsequent layers. Annealing a Pd-covered surface from 300 to 600 K causes the Pd multilayer to agglomerate as well. Significant alloying of
several freeze
96%) was used after further purification in the manifold via Mo(110) and Pd(111)/Mo(110) surfaces in this paper. (HREELS measurements were carried out via backfilling the crystal surface, while the exposures of formic acid for the a directional gas doser was used to introduce the molecules to 12 monolayers, annealing to temperatures as high as 900 K will not cause coalescence, likely due to kinetic considerations. The thick Pd layer shows a sharp hexagonal LEED pattern indicating epitaxial growth and the formation of a Pd(111) surface. Both monolayer and multilayer (>20 ML) Pd with sharp LEED patterns have been utilized in our studies. For brevity, the Pd monolayer on Mo(110) and the epitaxially grown Pd multilayer on Mo(110) will be referred to as the Pd1ML/Mo(110) and Pd(111)/Mo(110) surfaces in this paper.

Spectroscopic grade formic acid (Aldrich Chemical Co., Inc., 96%) was used after further purification in the manifold via several freeze–pump–thaw cycles. In the TPD experiments, a directional gas doser was used to introduce the molecules to the crystal surface, while the exposures of formic acid for the HREELS measurements were carried out via backfilling the UHV chamber. The exposures are given in units of langmuir (=1 × 10−6 Torr s) without correction for the directed dose enhancement or the ionization gauge sensitivity. The surface coverage of formic acid was estimated using TPD and assuming a unit sticking coefficient of formic acid at 95 K; the coverage is referenced to a monolayer saturation coverage, denoted as 1 ML.

3. Results

3.1. TPD. TPD spectra monitoring H2, H2O, CO, CO2, and HCOOH desorption after a formic acid exposure greater than saturation on Pd1ML/Mo(110) at 95 K are shown in Figure 1. The Pd1ML/Mo(110) surface was prepared by evaporating 2.0 ML Pd and subsequently annealing the sample to 1250 K to remove the excess Pd. This procedure can be used for this system since multilayer and monolayer Pd show distinctly different desorption temperatures from the Mo(110) surface and since no alloying between Pd and Mo occurs in the monolayer regime. This procedure yields a Mo(110) surface fully covered with a monolayer of Pd. Our TPD and HREELS results also show essentially the same chemistry with respect to formic acid between the annealed and the as-deposited Pd monolayer.

A low-temperature peak at 175 K is seen for masses 2, 18, 28, 44, and 46. This peak does not saturate with increasing exposure and thus correlates with the desorption of multilayer formic acid. The molecular desorption of formic acid exhibits two additional broad desorption peaks at 220 and 270 K, which are due to desorption from the first adsorbed layer. While the peak at 220 K is due to molecularly adsorbed formic acid, the peak at 270 K is likely a product of recombinative desorption of the dissociatively adsorbed formic acid. It is noteworthy that both peaks are very weak and have been amplified by a factor of 5.

In addition to the low-temperature peak, mass 44 (CO2) exhibits an intense high-temperature desorption feature at 350 K. Since this temperature is well above the typical temperature for CO2 desorption from transition metal surfaces, the 350 K feature is probably due to a reaction-limited process in which CO2 is formed and immediately desorbed from the surface. As the following HREELS results will show, the 350 K feature arises from surface formate decomposition, the only species present on the surface within this temperature range. To gain additional information regarding the decomposition kinetics and related activation energies, plots of \( \ln(r) - n \ln(\theta) \) vs \( 1/T \) were constructed for the CO2 TPD peak at 350 K and are shown in Figure 2. The term \( \gamma \) represents the decomposition rate and is proportional to the CO2 formation rate whereas \( n \) corresponds to the reaction order. The coverage, \( \theta \), can be computed from the integrated TPD areas from time \( t \) to infinity. The absolute coverage need not be known, but rather the relative coverage for the determination of the activation energy. However, the absolute coverage is required in order to determine the preexponential factor for a reaction with order other than 1. As pointed out by Parker et al., this method makes use of the full desorption peak and yields the activation energy without knowledge of the preexponential factor. In Figure 2, plots are provided for reaction orders, \( n \), equal to 0.5, 1, 1.5, and 2. As one can see, only \( n = 1 \) yields a straight line. These results indicate that the decomposition of formate to form CO2 is first order in the surface formate concentration and that the decomposition is a unimolecular process. The slope gives an activation energy of 125 kJ/mol for the formate decomposition. Because the decomposition kinetics is first order, from the intercept a preexponential factor of \( 4.7 \times 10^{19} \) can be obtained without knowing the absolute coverage.

Mass 28 (CO) shows two peaks at 295 and 350 K. The peak at 295 K is very characteristic for desorption of molecularly adsorbed CO on the Pd1ML/Mo(110) surface and is therefore
assumed to adsorbed CO formed from formic acid decomposition. The high-temperature feature at 350 K tracks precisely the CO₂ desorption and therefore can be attributed to the cracking of CO₂ in the QMS. It is important to point out there is no CO desorption above 800 K where desorption of recombinative CO is typically found for the Mo(110) surface. This result, combined with the observed CO desorption feature at 295 K, verifies that the Pd₁ML/Mo(110) surface is fully covered with Pd.

TPD monitoring water desorption (mass 18) shows an intense feature at 225 K, corresponding to the desorption of water formed via the dehydration of formic acid. TPD of H₂ (mass 2) shows a sharp feature at 360 K, corresponding to the desorption of H₂ formed from the decomposition of a formate intermediate; this formate species is a product of formic acid decomposition. Since H₂ desorbs within a similar temperature range following a hydrogen exposure, the hydrogen formed in the early stages of formic acid decomposition to formate could contribute as well to the peak at 360 K. A feature at 190 K is also apparent in the H₂ TPD spectrum. This feature probably corresponds to a combination of cracking products of formic acid and water in the QMS as well as contributions from the sample holder and crystal backside. An alternative explanation for the 190 K mass 2 feature, although less likely, is that a portion of the hydrogen formed from formic acid decomposition cannot be accommodated on the surface due to the absence of adsorption sites and, therefore, desorbs into the gas phase.

In order to compare monolayer Pd on Mo(110) with bulk Pd, the adsorption of formic acid on multilayer Pd epitaxy grown on the Mo(110) surface was studied. The TPD results following formic acid adsorption on Pd(111)/Mo(110) are presented in Figure 3. Masses 2, 18, 28, 29, 44, and 46 were recorded during the TPD measurements. Masses 2, 18, 28, and 44 correspond to the desorption of H₂, H₂O, CO, and CO₂, while masses 29 and 46 together follow the desorption of molecular formic acid. It is readily apparent from Figure 3, in contrast to the Pd₁ML/Mo(110) surface, that molecular desorption of formic acid is dominant on the Pd(111)/Mo(110) surface. All masses, with the exception of mass 2, show two desorption features at 175 and 200 K. The peak at 175 K is clearly due to desorption from multilayer formic acid. The feature at 200 K corresponds to desorption from the first adsorbed layer. It is noteworthy that masses 29 and 18 exhibit a different intensity ratio between the 175 and 200 K features (higher intensity in feature at 175 K) than mass 28, 44, and 46 (higher intensity in feature at 200 K). These results suggest the presence of different forms of adsorbed formic acid. Since multilayer formic acid is likely present in a polymeric form (see below), the desorbing molecules are likely dimeric. Cracking in the QMS occurs via the elimination of water (mass 18) and HCO (mass 29 plus others). With increasing temperature, the hydrogen bond between adjacent formic acid molecules is broken, and thus significant amounts of formic acid desorb as the monomer. Cracking in the QMS for the monomer occurs via a different pathway thus leading to a different array of products compared to the dimeric form of formic acid. The presence of both monomer and dimer formic acid has been previously observed on the Pt(111)²² and Au(111) surfaces.²³

In addition to the lower temperature desorption features, CO TPD also exhibits a desorption feature at 475 K. This feature can be unambiguously assigned to correspond to the desorption of molecularly adsorbed CO. A broad desorption feature centered at 300 K is also observed in the TPD of hydrogen. The water TPD feature at 200 K also shows a shoulder at 190 K, a shoulder consistently observed in all the mass 18 TPD spectra. The presence of H₂, H₂O, and CO TPD features indicates that a small amount of formic acid decomposes via a bimolecular dehydration pathway.

The marked difference between monolayer Pd on Mo(110) and multilayer Pd toward formic acid adsorption and decomposition can be readily seen in Figure 4, where the TPD spectra of formic acid and CO₂ are compared from both surfaces. It is apparent that the molecular desorption peak at 200 K is strongly attenuated going from multilayer Pd to monolayer Pd. Rather than a sharp feature at 200 K, two broad features are observed at higher desorption temperatures on the Pd₁ML/Mo(110) surface. Integration of the peak intensities indicated that molecular desorption from Pd₁ML/Mo(110) is approximately 65% of that from Pd(111)/Mo(110). At the expense of molecular desorption, a high-temperature feature from CO₂ formation is observed. This result indicates that monolayer Pd has a high reactivity toward formic acid decomposition in comparison to multilayer Pd that is, the formation of a formate species is promoted on Pd₁ML/Mo(110).

To examine the transition from monolayer Pd to multilayer Pd, the adsorption and reaction of formic acid on Pd/Mo(110) with increasing Pd thickness was studied. Since the Pd multilayer agglomerates into 3D clusters upon annealing to 600 K, the Pd/Mo(110) surfaces in these experiments were prepared by evaporating the Pd at 300 K and subsequently annealing to only 500 K. The TPD spectra monitoring CO (mass 28), CO₂ (mass 44), and formic acid (mass 29) desorption after dosing...
Pd1ML/Mo(110) prepared in this manner are identical to those shown in Figure 5. The TPD spectra for Mo(110) surfaces are dominated by molecular desorption at 200 K and is essentially the same as that for multilayer Pd. The one exception is that no CO desorption feature is observed at ∼295 K. Instead, a CO desorption peak is observed at 880 K, probably due to the recombinative desorption of carbon and oxygen, suggesting the presence of some uncovered Mo on the surface. In going to the Pd2ML/Mo(110) surface, some interesting changes are observed in the TPD spectra. First, the CO2 desorption temperature, which correlates with the activation energy for formate decomposition, decreases from 350 to 325 K. This indicates a higher reactivity of formate on the Pd2ML/Mo(110) surface compared with the Pd1ML/Mo(110) surface. At the expense of formate formation, molecular desorption at 200 K increases. Also apparent is a decrease in the intensity of the high-temperature desorption feature of formic acid. These results indicate a reduced reactivity of the thicker Pd surfaces toward formic acid decomposition, yet an increased reactivity with respect to formate decomposition with increasing Pd thickness. On the Pd3ML/Mo(110) surface, the TPD spectra are dominated by molecular desorption at 200 K and is essentially the same as that for multilayer Pd.

3.2. HREELS. The HREELS spectra taken with increasing formic acid exposures at 95 K on the Pd3ML/Mo(110) surface are shown in Figure 6. From bottom to top, the exposures were 0.1, 0.5, 1.5, and 3 langmuirs, respectively. According to the TPD data (not shown), the surface is saturated with monolayer formic acid at 1.5 langmuirs. At 0.1 langmuir, peaks at 200, 650, 935, 1350, 1660, and 1800 cm−1 are discernible. The peaks at 650, 935, 1055, 1350, and 1680 cm−1 are assigned to the CO2 stretching vibration. Since 1800 cm−1 is well above the ν(C=O) stretching frequency of any formic acid or formate species and below that of molecularly adsorbed CO on this surface, this feature is assigned to the ν(C=O) of a formyl species (HCO).

The peak at 1350 cm−1 can be assigned either to a symmetric OCO stretching vibration of a formate species or the C–H deformation of formic acid. The relatively high intensity of this peak indicates the presence of a formate species on the surface even at small formic acid exposures. The peak at 2030 cm−1 is due to the ν(C=O) of molecular adsorbed CO and the peak at 1800 cm−1 clearly correlates with the carbonyl stretching vibration. Since 1800 cm−1 is well above the ν(C=O) stretching frequency of any formic acid or formate species and below that of molecularly adsorbed CO on this surface, this feature is assigned to the ν(C=O) of a formyl species (HCO).

Upon increasing the formic acid exposures from 0.1 to 3 langmuir, the peak at 200 and 935 cm−1 is enhanced dramatically with the former shifting to 235 cm−1. These features now become the dominant features in the spectra. With increasing exposure, the features at 650, 1055, 1350, 1650, and 2940 cm−1 are also enhanced with an upward shift of the features at 650 to 700, 1350 to 1365, and 1650 to 1700 cm−1. In addition, a sharp feature at 1210 cm−1 begins to develop at an exposure of 0.5 langmuir. This peak can be assigned unambiguously to the C–O stretching vibrational mode of molecular adsorbed formic acid. The spectra acquired following a formic acid exposure of 3 langmuir, which corresponds to a coverage of approximately two monolayers (based on the TPD data), is very characteristic of solid formic acid. The assignments of these features are summarized in Table 1.

The HREELS spectrum at one monolayer (1.5 langmuir) with the one at 2 ML (3 langmuir) shows clearly that the adsorption of HCOOH onto Pd1ML/Mo(110), Pd2ML/Mo(110) and Pd3ML/Mo(110) surfaces is mostly molecular on the Pd1ML/Mo(110) surface at 100 K. The HREELS spectrum at one monolayer (1.5 langmuir) with the one at 2 ML (3 langmuir) shows clearly that the adsorption of formic acid is mostly molecular on the Pd1ML/Mo(110) surface at 100 K.

Figure 7 shows a series of HREELS spectra acquired after dosing approximately one monolayer of formic acid onto the Pd1ML/Mo(110) surface and subsequently annealing this surface to the indicated temperature. As discussed above, the spectrum at 100 K is dominated by molecularly adsorbed formic acid with an indication of small amounts of the adsorbed species, formate, formyl, and CO.
Annealing the sample to 170 K leads to a dramatic change in the HREELS spectrum. All the features related to molecularly adsorbed formic acid, with the exception of the feature at 210 cm$^{-1}$, show a decrease in intensity. The feature at 935 cm$^{-1}$, which can be correlated with the O–H bending mode of formic acid, dramatically loses intensity and shifts to 950 cm$^{-1}$. The feature at 1210 cm$^{-1}$, which relates to the C–O stretching vibration of molecularly adsorbed formic acid, essentially disappears. The feature at 1700 cm$^{-1}$, which corresponds to the C=O stretching mode, also loses intensity and shifts to lower wavenumber. Since no desorption occurs upon heating to this temperature, these changes in the HREELS spectra indicate the partial decomposition of formic acid on the surface. At the expense of the features corresponding to molecularly adsorbed formic acid, the features corresponding to the formate species (760 and 1335 cm$^{-1}$) and the formyl species (1835 cm$^{-1}$) gain intensity. Also apparent in this temperature range is that the feature at 660 cm$^{-1}$ gains intensity and becomes broader with the peak maximum shifting toward a higher wavenumber. The broadening of this feature is due partially to the appearance of the librational mode of water formed from formic acid dehydration on the surface during annealing. The presence of formate, water, and formyl species on the surface indicate that formic acid decomposes via a bimolecular dehydration pathway. However, some molecular formic acid is still present on the surface as indicated by the features at 210 and 950 cm$^{-1}$.

Annealing to 190 K leads to a further increase in intensity of the features at 760 and 1335 cm$^{-1}$, indicating the gradual formation of a formate species on the surface. It is noteworthy that the feature at 1695 cm$^{-1}$ decreases in intensity after annealing to 170 K, yet increases in intensity following further anneal to 190 K and shifts to 1650 cm$^{-1}$. The initial decrease is probably due to the decomposition of molecularly adsorbed formic acid, while the increase in intensity upon heating from 170 to 190 K likely corresponds to the formation of the formate species. Therefore, the feature at 1680 cm$^{-1}$ is assigned, in part, to the OCO asymmetric stretching mode of formate. The appearance of the OCO asymmetric stretching mode indicates that the formate species is adsorbed in a configuration with a symmetry lower than $C_{3v}$. Accompanying the formation of the formate species is the shifting of the peak at 210 to 270 cm$^{-1}$. This shift can be correlated with the appearance of the ν(Pd–O) of an adsorbed formate species.

Also noteworthy is that the feature at 1055 cm$^{-1}$ is not reduced in intensity even after heating to 190 K, but does shift to 1080 cm$^{-1}$. This behavior is similar to that of the feature at 1890 cm$^{-1}$ toward annealing. Accordingly, the feature at 1080 cm$^{-1}$ is assigned to correspond to the C–H bending vibration of the formyl species (HCO).

To completely remove molecularly adsorbed formic acid, the surface must be annealed to 270 K. Four intense peaks at 320, 760, 1335, and 2080 cm$^{-1}$ are observed in the spectrum acquired after annealing to 270 K. The features at 760 and 1335 cm$^{-1}$ can be assigned to the δ(OCO) and ν(OCO) vibrational modes of the formate species, and the feature at 2080 cm$^{-1}$ can be assigned to molecularly adsorbed CO. The feature at 320 cm$^{-1}$ consists of contributions from the ν(Pd–O) mode of the formate species and the ν(Pd–C) mode of molecularly adsorbed CO. The features corresponding to the formyl species have now disappeared. At the expense of the formyl features, the CO feature at 2080 cm$^{-1}$ is enhanced. Further annealing to 350 K leads to the desorption of CO and the decomposition of the formate species.

The adsorption of formic acid on the Pd(111)/Mo(110) surface also has been studied using HREELS. In Figure 8, the spectra acquired after dosing a monolayer of formic acid at 95 K to Pd(111)/Mo(110) followed by an anneal to the indicated temperature are shown. The spectrum at 95 K is very characteristic of molecularly adsorbed formic acid with features at 210, 650, 935, 1060, 1205, 1390, 1680, and 2940 cm$^{-1}$. These features can be assigned to correspond to the molecular lattice vibration, the O–H out-of-plane bending, the C–H out-of-plane bending, the C–O stretching, the C–H in-plane deformation, the C=O stretching and the C–H stretching modes, respectively.$^{22,24}$ A peak at 1835 cm$^{-1}$ is also observed and can be correlated with the C=O vibrational mode either due to molecularly adsorbed CO or to the formyl (HCO) species.

Heating the surface gradually from 95 to 190 K causes a slight decrease in the intensity of those features related to molecularly adsorbed formic acid, a shift of peak at 650 to 710 cm$^{-1}$. The spectrum taken after annealing to 190 K is almost identical to the spectrum at 95 K, indicating that the first absorbed formic acid layer remains intact up to 190 K. These results contrast with the results for the Pd$_{3ML}$/Mo(110) surface, where a dramatic change occurs in the HREELS data upon annealing from 100
TABLE 2: Vibrational Frequencies (cm$^{-1}$) and Assignments for the Formyl Species on Pd$_{111}$/Mo(110)

<table>
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<th>Species</th>
<th>ν($\text{C}=\text{O}$)</th>
<th>ν($\text{C}=$H)</th>
<th>δ($\text{C}=$H)</th>
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<td>31</td>
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<td>2943</td>
<td>1032</td>
<td>32</td>
</tr>
<tr>
<td>Pd$_\text{1ML}$/Mo(110)</td>
<td>1870</td>
<td>1080</td>
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to 170 K. These differences indicate that the Pd$_{111}$/Mo(110) surface is much more reactive than Pd(111)/Mo(110) with respect to formic acid decomposition. Also apparent in the temperature range 95–190 K is a small increase in the intensity of features at 1390 and 1835 cm$^{-1}$, consistent with decomposition of a small amount of formic acid with annealing to 190 K. Further annealing to 200 K results in a dramatic decrease in intensity or the disappearance of the features at 210, 710, 935, 1060, 1205, 1390, 1680, and 2940 cm$^{-1}$, indicating desorption of molecularly adsorbed formic acid. This behavior is consistent with the formic acid desorption temperature found in the TPD experiments. The spectrum acquired following the 200 K anneal shows only weak features at 210, 935, 1390, and 1680 cm$^{-1}$, which correspond to traces of molecularly adsorbed formic acid remaining on the surface. The 200 K spectrum is dominated by the molecularly adsorbed CO feature at 1835 cm$^{-1}$. Annealing to 600 K leads to the desorption of molecularly adsorbed CO. The small features at 210 and 935 cm$^{-1}$ are likely due to the readesorption of trace amounts of formic acid from the background.

4. Discussion

The adsorption of formic acid on the Pd$_{111}$/Mo(110) surface at 100 K is primarily molecular. Only small amounts of formic acid undergo decomposition, likely through a bimolecular dehydration pathway as indicated by the presence of HREELS features due to the formyl and formate species. Upon annealing to 190 K, the majority of the formic acid decomposes to form formate, formyl, and water on the surface, indicating a bimolecular dehydration reaction pathway. A bimolecular dehydration pathway has been suggested previously for formic acid on Ru(100),$^{25}$ Ni(111),$^{26}$ Ni(100)$^{27}$ and Ni(110)$^{28,29}$ surfaces. However, a formyl species has not been identified in the previous studies by vibrational spectroscopy; only formate and water on the surface, consistent with the lowering of the bonding symmetry arising from hydrogen bonding between coadsorbed formate and formic acid. Upon annealing to 230 K, the molecularly adsorbed formic acid desorbs, leaving the formate in a C$_2$ bonding configuration.

The formate species is stable at the Pd$_{111}$/Mo(110) surface up to 350 K and then decomposes to form CO$_2$ and hydrogen, via first-order kinetics. This behavior clearly indicates that the C–H bond cleavage is the first step in the formate decomposition. A small portion of the formate species recombines with coadsorbed hydrogen, yielding the molecular formic acid desorption features at 270 K.

Before we can discuss our results for multilayer Pd and compare the monolayer and multilayer Pd systems, it is appropriate to review the previous relevant studies on various Pd surfaces. The adsorption and reaction of formic acid have been previously studied on the Pd(100)$^{37–39}$ and Pd(111)$^{40}$ surfaces and have led to several controversies regarding the reactivity of Pd surfaces toward formic acid decomposition. Jorgensen and Madix studied formic acid desorption on the Pd(100) and O/Pd(110) surface using TPD and HREELS.$^{37}$ On the clean Pd(100) surface, a portion of the formic acid desorbs molecularly at 185 K and a second portion decomposes to form CO and H$_2$; no reaction intermediates were identified via HREELS.$^{37}$ Jorgensen and Madix did not quantify the ratio of molecular desorption vs decomposition; however, only a very small quantity of CO is observed in the corresponding HREELS spectrum. Sander and Erley$^{38}$ have studied the adsorption of formic acid on the Pd(100) surface using TPD and reflection adsorption infrared spectroscopy (RAIRS). These authors’ results are largely consistent with the results obtained by Jorgensen and Madix in that CO and H$_2$ are the only high-temperature desorption products following formic acid adsorption. No other decomposition intermediates were identified by FT-RAIRS. However, the interpretation of Sander and Erley of their results differs somewhat from that of Jorgensen and Madix. These authors simply assume complete decomposition of formic acid in the first adsorbed layer, with no apparent evidence or stated rationale. No mention is made by Sander and Erley that molecular desorption of formic acid was even monitored by TPD. Therefore, the assignment of mass 44 peak at 180 K to the decomposition product CO$_2$ is without basis and misleading. Solymosi and Kovács$^{39}$ in reexamining this system using TPD, EELS, ultraviolet photoelectron spectroscopy (UPS), and work function changes, have shown results that are consistent with the previous studies. Two molecular desorption peaks are observed at 175 and 204 K, with the latter assigned to correspond to desorption from the first adsorbed layer. CO and H$_2$, as observed previously, are the only decomposition products into the gas phase. No reaction intermediates were identified via UPS. Using the TPD peak areas and assuming a CO saturation coverage of 0.66 × 10$^{15}$ molecules/cm$^2$, Solymosi and Kovács estimate that approximately 0.06 × 10$^{15}$ molecules/cm$^2$ undergo decomposition.

Summarizing the previous results, formic acid adsorption on the Pd(100) surface is largely reversible. Only a small portion of the chemisorbed formic acid undergoes decomposition to form CO and H$_2$ at <200 K. Davis and Barteau$^{40}$ have studied the adsorption of formic acid on the Pd(111) surface using TPD and HREELS. After dosing formic acid at 170 K, desorption peaks of molecular formic acid (185 K), CO$_2$ (260 K), H$_2$ (330 K), and CO (490 K) were observed. In this study, formate was and causes the appearance of the asymmetric OCO stretching vibrational mode. On the Pd$_{111}$/Mo(110) surface, the appearance of the OCO asymmetric vibration is also accompanied by molecularly adsorbed formic acid on the surface, consistent with the previous studies. Two molecular desorption peaks of molecular formic acid (185 K), CO$_2$ (260 K), H$_2$ (330 K), and CO (490 K) were observed. In this study, formate was
identified as a decomposition intermediate. These authors estimate that approximately 2/3 of the adsorbed formic acid desorbs molecularly from the surface. The HREELS data show a very low peak intensity related to the formate species, only 15% of the peak intensity of the formate on the (2 × 2)/O/Pd(111) surface. On this latter surface these authors show that all the formic acid is converted to the formate species. In any event, molecular desorption is the dominant process following the adsorption of formic acid on the Pd(111) surface. The Pd(111) surface seems to stabilize the formate reaction intermediate in comparison to the Pd(100) surface.

Our results for the Pd(111)/Mo(110) are very similar to the previous work on Pd(100), yet somewhat different from the Pd(111) surface. The adsorption of formic acid on the Pd(111)/Mo(110) surface is largely molecular in the first adsorbed layer as shown by the TPD and HREELS data. The molecularly adsorbed species is stable on the surface even after annealing to 190 K. In addition to molecular desorption at 200 K, CO, H2, and H2O are observed as the only desorption products and exhibit reaction-limited kinetics. However, only small amounts of CO and H2 were observed in the present experiments. Since the TPD experiments of the present study were carried out with the sample biased at ~100 V, the CO and H2 decomposition products cannot be due to chemistry induced by electrons from the QMS ionizer. Electrons from the ionizer of the QMS have been shown to lead to serious damage in the adsorbed molecular layer and cause spurious results in the TPD spectra. However, it is entirely possible that the CO and H2 decomposition products mainly arise due to various surface defect sites. In the present study, formate was not found following formic acid adsorption on the Pd(111)/Mo(110) surface, in contrast to the Pd(111). The apparent differences between the Pd(111)/Mo(110) and Pd(111) surfaces are not clear.

A comparison of the present results for the Pd(111)/Mo(110) surface with the results for Pd(100), Pd(111), and Pd(111)/Mo(111) surfaces demonstrates clearly that monolayer Pd shows a strongly modified surface chemistry relative to multilayer Pd with respect to formic acid adsorption and decomposition. First, the monolayer shows a higher reactivity toward formic acid decomposition. This higher reactivity can be attributed either to the reduced activation energy of formic acid decomposition on the monolayer Pd or to an increase in the binding energy of formic acid on monolayer Pd. As the HREELS results show, the decomposition of formic acid occurs already at 170 K on the Pd(111)/Mo(110) surface, while formic acid remains intact on the Pd(111)/Mo(110) surface even after annealing to 190 K. These results illustrate the contrasting kinetics of formic acid decomposition on the Pd(111)/Mo(110) surface relative to bulk Pd. Since the decomposition products, H2 and the formate species, are more weakly bonded to monolayer Pd, the lower activation energy for decomposition of formic acid on the Pd(111)/Mo(110) surface compared to Pd(111)/Mo(110) is likely an initial state effect, and perhaps related to the geometric differences between the two surfaces. Due to the lattice mismatch between Mo and Pd, the Pd–Pd distance is larger in the pseudomorphic Pd monolayer compared to that in bulk Pd, yielding a more open surface for Pd(111)/Mo(110). For formic acid decomposition, the Pd–Pd distance is likely a key parameter with the larger lattice constant of Pd(111)/Mo(110) being more suitable for reaction. This explanation is also consistent with the observed structure sensitivity of formic acid reactivity on various Pd surfaces.

Formate decomposition exhibits a sharply contrasting behavior to formic acid decomposition. On the Pd(111)/Mo(110) surface, formate was found to decompose at 350 K, compared to the Pd(111) and O/Pd(111) surfaces, where the formate species decomposes at 260 and 280 K, respectively. On Pd(100), no formate was detected, however, precooling the surface with oxygen promoted the formation of formate, which subsequently decomposed at 265 K. Since on the Pd(100) surface oxygen combines with hydrogen at 175 K to evolve water, leaving only a formate species on the surface, the decomposition temperature measured in this study is relevant to the present study. Accordingly, monolayer Pd shows a higher decomposition temperature for formate compared to either the Pd(100) or Pd(111) surfaces. It is noteworthy that the decomposition temperature of formate on Pd(111)/Mo(110) is between the formate decomposition temperatures observed for Pd single crystals and that found for group IB metals. For example, on Cu(110) the formate species decomposes at 450 K to form CO2 and H2. The present results are consistent with the previous results showing that monolayer Pd often exhibits a chemical behavior between Pd and group IB metals. This altered chemical behavior in monolayer Pd can be explained by the reduced density of electronic states near the Fermi level compared to bulk Pd.

5. Conclusion

The surface chemistry of formic acid on the Pd(111)/Mo(110) surface has been studied using TPD and HREELS and can be summarized as follows:

\[
\text{HCOOH}(a) \xrightarrow{225 \text{K}} \text{HCOOH}(g)
\]

\[
2\text{HCOOH}(a) \xrightarrow{170-200 \text{K}} \text{HCOO}(a) + \text{H}_2 \text{O} + \text{HCO}(a)
\]

\[
\text{HCO}(a) \xrightarrow{190-270 \text{K}} \text{H}(a) + \text{CO}(a)
\]

\[
\text{HCOO}(a) \xrightarrow{350 \text{K}} \text{CO}_2(g) + \frac{1}{2}\text{H}_2(g)
\]

In comparison to bulk Pd, the Pd(111)/Mo(110) surface shows a higher reactivity toward formic acid decomposition, but a lower reactivity with respect to formate decomposition. The higher reactivity of Pd(111)/Mo(110) toward formic acid is attributed to a geometric effect; that is, the larger lattice constant of the pseudomorphic monolayer Pd leads to enhanced decomposition of formic acid. Electronic differences between the monolayer and multilayer Pd are believed to be responsible for the marked differences in the formate reactivity.

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References and Notes

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