Adsorption and Reaction of Formic Acid on the Mo(110) and O/Mo(110) Surfaces

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The adsorption and reaction of formic acid on clean and oxygen-modified Mo(110) surfaces have been studied using temperature programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS). The adsorption of formic acid on Mo(110) and oxygen-modified Mo(110) surfaces is largely irreversible. Only ~30% of an adsorbed monolayer desorbs molecularly from the clean and oxygen-modified surfaces. However, the distribution of the decomposition products and the reaction pathways are significantly different on the two surfaces. Formyl species, monodentate and bridge-bonded, are found on both surfaces, with the monodentate promoted by the presence of oxygen, apparently due to a site-blocking effect. A CO₂− species has been identified for the first time as an intermediate in the decomposition of the formate species on the oxygen-modified Mo(110) surface.

1. Introduction

The adsorption and reaction of formic acid on transition metals have been extensively studied using surface science techniques (refs 1 and 2 and references therein). The results of these studies have been recently reviewed by Columbia and Thiel. It has been shown that the first step in formic acid decomposition occurs through either unimolecular deprotonation or bimolecular dehydrogenation. For both reaction pathways, the formate species has frequently been identified as a surface intermediate. The formate can further decompose either through a unimolecular deprotonation to form H₂ and CO₂ or through a bimolecular hot-hydrogen pathway to form CO and CO₂. It also has been proposed that C−O bond cleavage is the first step in the formate decomposition. The majority of the previous investigations have focused on the later transition metal and their oxygen-modified surfaces. Only two papers have been devoted to the group VIA transition metals. In these papers, the oxygen-modified surfaces. Only two papers have been devoted to the group VIA transition metals. In these papers, the oxygen-modified Mo(110) surface, defined henceforth as O/Mo−(110), using TPD and high-resolution electron energy loss spectroscopy (HREELS). Our study shows a unique behavior of the Mo(110) surface toward formic acid adsorption and reaction and provides new insights into the surface chemistry of this interesting organic acid prototype. This system is of interest both fundamentally and practically, since MoOₓ is one of the most widely used oxidation catalysts, and the formate species has been proposed to be an important intermediate in oxygenate synthesis.3−7

2. Experimental Section

The experiments have been carried out in an ultrahigh-vacuum (UHV) chamber which has been described in detail previously.8 Briefly, the UHV chamber (base pressure < 1 × 10−10 Torr) is equipped with capabilities for HREELS (LK2000), AES, low-energy electron diffraction (LEED), and TPD. HREELS spectra were acquired with a primary beam energy of 3 eV and a typical resolution of 60 cm⁻¹. TPD measurements were carried out with a quadrupole mass spectrometer (QMS) in a line-of-sight configuration with the sample surface and with a linear heating rate of ~5 K/s. It is well-known that electron emission from a QMS can induce damage in a weakly adsorbed layer which, in turn, can introduce extraneous decomposition features into the TPD data. To avoid electron beam damage, the sample was biased at −100 V with respect to the QMS ionization filament during the TPD experiments. The sample could be resistively heated to either 1500 or 2200 K using electron beam heating. The 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 at 1200 K in 2 × 10⁻⁸ Torr of O₂ and subsequently flashing to 2000 K. This procedure was repeated several times until no contaminants could be detected by AES.

Spectroscopic grade formic acid (Aldrich Chemical Company, Inc., 96%) was used after further purification in a vacuum manifold via several freeze−pump−thaw cycles. In the TPD experiments, a directional doser was used to introduce the gas to the crystal surface; for the HREELS measurements the exposure of formic acid was carried out via back-filling the UHV chamber. The exposures are given in units of langmuirs (1 langmuir = 1 × 10⁻⁶ Torr·s) without correction for the dose enhancement and gauge sensitivity. The surface coverage of formic acid is estimated from the TPD data, assuming a unit sticking coefficient for formic acid at 95 K. Coverages are referenced to a monolayer saturation coverage, which is denoted as 1 ML.

The oxygen-precovered surface was prepared by dosing O₂ (99.998% purity) at 100 K and subsequent annealing to 600 K. The saturation coverage was achieved with an exposure of 100 langmuirs, which gives a O(510 eV)/Mo(186 eV) AES ratio of 0.30. At an O/O AES ratio of 0.16, a (2 × 2) LEED pattern has been observed and assigned to correspond to an oxygen coverage of 0.25 ML (referenced to the Mo(110) surface atom density).

3. Results

3.1. Temperature Programmed Desorption. TPD spectra monitoring H₂ (mass 2), H₂O (mass 18), CO (mass 28), CO₂ (mass 44), and HCOOH (mass 29 and 46) desorption after dosing formic acid to the Mo(110) surface at 95 K are shown.
A low temperature desorption peak at 165 K has been observed for all masses. This feature, which does not saturate and shifts to higher desorption temperature with increasing formic acid exposures, corresponds to desorption from multilayer formic acid. A second feature at 235 K is observed for masses 46, 44, 29, and 18 and can be assigned to desorption from the first chemisorbed layer of formic acid. Molecular desorption is not observed at a formic acid coverage below $\sim 0.7$ monolayer, where $\text{H}_2$, $\text{CO}$, and $\text{H}_2\text{O}$ are the only desorption products detected. According to the TPD data, approximately 30% percent of the formic acid in the first adsorbed layer undergoes molecular desorption. The temperature of the molecular desorption peak corresponds to a desorption activation energy of 14 kcal/mol using a Redhead analysis, assuming first-order desorption kinetics and a preexponential factor of $1 \times 10^{13} \text{s}^{-1}$. The $\text{H}_2\text{TPD}$ spectrum shows two desorption peaks at 360 and 495 K, which are due to recombinative desorption of atomic hydrogen formed from formic acid decomposition. The CO desorption spectrum shows two intense desorption peaks at 315 and 990 K. The high-temperature peak exhibits a lower temperature shoulder at 880 K and is very characteristic of the recombinative desorption of CO from atomic carbon and oxygen. The peak at 315 K can be unambiguously assigned to the desorption of molecular CO formed from formic acid decomposition. The TPD spectrum of $\text{H}_2\text{O}$ also shows a two peak structure, most likely due to the cracking of formic acid in the QMS. However, the two peaks at 165 and 235 K are not well-resolved as in the case for mass 29 and 44, indicating a second feature between these two peaks. This third peak, which is seen most clearly on the oxygen-modified surface (see Figure 3), can be assigned to the desorption of water formed on the surface. Also seen for mass 18 is a tail extending from 250 to 450 K, which is probably due to recombinative $\text{H}_2\text{O}$ desorption.

The effect of a preadsorbed oxygen layer also has been studied using TPD. TPD spectra of $\text{H}_2$, $\text{H}_2\text{O}$, CO, CO$_2$, and HCOOH on an oxygen-saturated Mo(110) surface is shown in Figure 2. Similar to the clean Mo(110) surface, molecular desorption on the O/Mo(110) surface shows two desorption peaks at 160 and 255 K, which can be assigned to desorption from the multilayer and the first chemisorbed layer, respectively. In contrast to the clean surface, no hydrogen desorption peak was observed on the O/Mo(110) surface. Instead, extensive water desorption was seen. In addition to the two cracking peaks of molecularly desorbing formic acid, $\text{H}_2\text{O}$ desorption peaks were also observed at 200, 350, and 440 K.

The CO TPD also shows two desorption peaks at 310 and 925 K. The peak at 925 K is due to the recombinative desorption of CO. The peak at 310 K, which can be assigned to molecular CO desorption, exhibits a shoulder on the low-temperature side. In contrast to the clean surface, a very broad CO$_2$ desorption peak is observed between 500 and 1000 K. This peak likely arises from recombinative desorption due to the relatively high atomic oxygen coverage on the surface. The difference between clean and oxygen-modified Mo(110) surfaces is seen clearly in Figures 3 and 4, where the $\text{H}_2$, $\text{H}_2\text{O}$, CO, and HCOOH TPD spectra are compared for the clean and oxygen-covered surfaces. It is apparent in Figure 3 that the $\text{H}_2$ desorption decreases dramatically with increasing oxygen coverage. On the oxygen-saturated surface (O/Mo AES ratio = 3.0), essentially no $\text{H}_2$ desorption is observed. The small feature at 425 K is probably due to the displacement of hydrogen from the chamber walls by water (see below). The $\text{H}_2\text{O}$ desorption
spectra, on the other hand, are quite different. Precovering the surface with oxygen leads to an enhancement of the water desorption feature at 200 K and a new desorption peak at 425 K. These results indicate that surface oxygen reacts with hydrogen to form water. The desorption feature of water at 200 K, however, is most likely due to desorption of molecularly adsorbed water formed directly from formic acid decomposition.

The presence of surface oxygen also stabilizes formic acid adsorption, as is apparent in Figure 4. The peak desorption temperature for molecular formic acid shifts from 235 to 255 K going from the clean to the oxygen-modified surface. This change in desorption temperature corresponds to an increase in binding energy of ~1 kcal/mol based on a simple Redhead analysis. However, the quantity of molecular desorption increases only slightly, indicating a similar reactivity of the clean and oxygen-modified surfaces with respect to formic acid decomposition. The CO desorption features decrease in intensity significantly in going from the clean to the oxygen-modified surface. This is consistent with the result that appreciable carbon desorbs from the oxygen-modified surface in the form of CO₂.

3.2. High-Resolution Electron Energy Loss Spectroscopy. 3.2.1. Mo(110). Figure 5 shows HREELS spectra acquired after dosing approximately 5.0 ML formic acid to the surface and subsequently annealing to the indicated temperature. The spectrum acquired at 90 K is very characteristic of a condensed formic acid layer. Features at 260, 700, 950, 1400, 1720, and 2960 cm⁻¹ have been observed and can be readily assigned to the lattice, δ(OCO), π(OH), π(CH), ν(CO), δ(CH), ν(C=O), and ν(CH) vibrational mode. The C=O stretching vibrational mode at 1720 cm⁻¹ exhibits a shoulder at 1640 cm⁻¹. It has been shown previously that the C=O stretching vibrational mode can be used to identify the structure of a condensed formic acid layer. The presence of the doublet features in the C=O stretching region indicates that formic acid is condensed on the Mo(110) surface in the α-polymorphic form. Due to strong hydrogen bonding in the condensed phase, the O−H stretching mode shifts downward below 3000 cm⁻¹ and is in Fermi resonance with a number of combination modes, yielding features between 2500 and 3000 cm⁻¹.

Annealing to 190 K causes a dramatic change in the HREELS spectrum. The π(OH) vibrational mode at 950 cm⁻¹ disappears completely, while the intensity of the lattice vibration at 260 cm⁻¹ falls sharply and shifts to 220 cm⁻¹. Other peaks related to multilayer formic acid show a similar reduction in spectral intensity. These changes correlate with the desorption of multilayer formic acid, in good agreement with the TPD results which indicate a multilayer desorption temperature of 165 K.

The spectrum acquired after annealing to 190 K shows features at 220, 360, 570, 775, 1020, 1255, 1360, 1720, 1860, and 2945 cm⁻¹. Further annealing to 250 K results in the disappearance of the features at 220, 1255, and 1720 cm⁻¹, with the appearance of new features at 1280 and 1750 cm⁻¹. Also apparent is that the peaks at 1020 and 1860 cm⁻¹ gain intensity and shift to 1000 and 1940 cm⁻¹, respectively. The features at 220, 1255, and 1720 cm⁻¹ can be assigned to correspond to the Mo−O, C−O, and C=O stretching vibrations, respectively, of molecularly adsorbed formic acid. The disappearance of these modes in the HREELS spectrum upon annealing to 250 K correlates well with the molecular desorption peak at 235 K observed in the TPD experiments. An alternative assignment of the feature at 220 cm⁻¹ is to the lattice vibration of formic acid in a long chain, where the hydroxyl oxygen atom and its associated hydrogen move above the molecular plane and the carbon atom and its associated hydrogen move below the molecular plane. The feature at 1860 cm⁻¹ has a much higher frequency than any carbonyl vibrational mode of formate or formic acid and is also not in the range of any modes for CO adsorbed normal to this particular surface. Therefore, this peak is assigned to the formyl (HCO) species formed via formic acid decomposition. The most convincing evidence for this assignment, however, comes from the temperature dependency of this peak. Upon annealing to 250 K, the formyl species decomposes to form CO and adsorbed hydrogen, as indicated by the increase in the intensity of the features at 1940 (ν(OCO)) and 980 cm⁻¹ (ν(Mo−H)) (see below).

The surface was further annealed to 300 K, resulting in a concomitant decrease in the intensity of the features at 360, 775, and 1360 cm⁻¹, indicating that the source of these three peaks is a single species. This species is identified as a formate product of formic acid decomposition, and the features at 360, 775, and 1360 cm⁻¹ are assigned to correspond to the Mo−O vibration, the OCO deformation, and symmetric stretching modes, respectively. The frequency of these three modes is very typical for a bridge-bonded formate in a C₂v configuration. An alternative assignment of the peak at 1360 cm⁻¹ is to the C=O vibrational mode of molecularly adsorbed CO in a “lying down” configuration. Chen et al. have studied the adsorption of CO on Mo(110) and O/Mo(110) surfaces. Depending upon...
the CO_{ads} and O_{ads} coverage and the annealing temperature, features at 1130, 1345, 1465–1535, and 1950 cm\(^{-1}\) have been observed and assigned to molecularly adsorbed CO in various configurations. These authors showed that the feature at 1345 cm\(^{-1}\) could be converted to the feature at 1130 cm\(^{-1}\) upon annealing. In the work here the feature at 1360 cm\(^{-1}\) shows an entirely different behavior toward annealing, behavior that could be correlated with the changes in the feature at 775 cm\(^{-1}\). Therefore, the contribution of molecularly adsorbed CO to the feature at 1360 cm\(^{-1}\) is believed to be small, if any. A feature at 1280 cm\(^{-1}\) is also visible in the spectrum. Since this peak gains intensity on the oxygen-precovered surface (see below), it is assigned to the formate, modified by coadsorbed oxygen.

The peak at 1940 cm\(^{-1}\) can be unambiguously assigned to the C=O vibrational mode of molecularly adsorbed CO formed from the decomposition of the formyl species. Heating to 350 K results in the disappearance of this feature, which correlates with the desorption of CO at 315 K in the TPD experiments. The spectrum acquired after annealing to 350 K is dominated by features at 400, 600, and 980 cm\(^{-1}\). The peak at 980 cm\(^{-1}\) is stable even after annealing to 450 K, but disappears upon annealing to 650 K. The two features at 400 and 600 cm\(^{-1}\) are stable up to 800 K and then begin to decrease in intensity, with the peak at 600 cm\(^{-1}\) shifting to 550 cm\(^{-1}\) and the peak at 400 cm\(^{-1}\) disappearing at 1200 K (not shown). These features have been observed previously by Colaianni et al., after dosing O\(_2\) onto the surface, and have been assigned to the M–O stretching and bending modes, respectively. As one can see from Figure 5, the peak near 600 cm\(^{-1}\) is already apparent in the spectrum acquired after annealing to 190 K. This indicates that decomposition of a fraction of the formic acid to atomic oxygen has occurred at 190 K.

The peak at 1000 cm\(^{-1}\) shows clearly two components during the annealing sequence, one component desorbing between 250 and 350 K (1020 cm\(^{-1}\)) and a second component apparently stable up to 450 K (980 cm\(^{-1}\)). The disappearance of the high temperature peak correlates with hydrogen desorption at 500 K in the TPD. This feature, therefore, is assigned to the Mo–H vibration of atomically adsorbed hydrogen. A similar vibrational frequency has been observed previously for hydrogen adsorbed on Mo(100). The decrease in intensity of this feature between 250 and 350 K is accompanied by the disappearance of the feature at 1750 cm\(^{-1}\). These two peaks are assigned to the C–O and C=O stretching vibrational mode of the formate species bonded to the surface in a monodentate configuration. Stronger evidence for this assignment can be found in the HREELS spectra of formic acid adsorbed on an oxygen-precovered surface (see below).

It is also noteworthy that the C–H stretching vibrational feature at 2945 cm\(^{-1}\) shows a constant intensity between 250 and 350 K and disappears only after annealing to 400 K, well after the disappearance of the C=O and C–O related stretching vibrations. These results indicate that a C\(_2\)H\(_3\) species is formed from formic acid decomposition and dehydrogenates completely at 450 K.

The chemistry of submonolayer formic acid on the Mo(110) surface also has been studied. Figure 6 shows HREELS spectra taken after dosing 0.3 ML of formic acid to the Mo(110) surface and annealing to the indicated temperature.

Further annealing to 250 K results in the concerted disappearance of the features at 760 and 1340 cm\(^{-1}\). As is the case with a saturation formic acid coverage, these two peaks are assigned to the OCO deformation and the OCO symmetric stretching vibration of the formate species in a bridge-bonded configuration. Also visible in this temperature range is the increase in peak intensity at 1850 cm\(^{-1}\) and its shift to 1900 cm\(^{-1}\). These changes correlate with the decomposition of a formyl species to produce CO_{ads}. The appearance of a peak at 1900 cm\(^{-1}\) is accompanied by a feature at 230 cm\(^{-1}\). Both peaks disappear after annealing to 390 K and can be assigned to the Mo–CO and C–O stretching vibrational modes of molecularly adsorbed CO, respectively.

The peak at 1100 cm\(^{-1}\), which was not observed at saturation formic acid coverage, can also be assigned to molecularly adsorbed CO. This molecularly adsorbed CO is a precursor to dissociation and reacts to form oxygen and carbon upon annealing to 290 K.

The most interesting feature at low formic acid coverages is the peak at 3575 cm\(^{-1}\), which is not observed for formic acid coverages larger than 0.7 monolayer. This peak clearly corresponds to the O–H stretching vibrational mode of a hydroxyl group.

### 3.2.2. Oxygen-Modified Mo(110).

Figure 7 displays a series of HREELS spectra acquired after dosing 0.3 ML of formic acid onto the Mo(110) surface at 100 K with increasing oxygen coverages followed by an anneal to 190 K. With increasing oxygen coverage, the peak at 1100 cm\(^{-1}\), corresponding to molecularly adsorbed CO, disappears. Concomitantly, increases in the features at 340, 755, and 1270 cm\(^{-1}\) are apparent, features corresponding to the Mo–O, OCO deformation, and OCO symmetric stretching vibrations of the formate species in a bridge-bonded configuration. A second symmetric OCO vibrational feature is seen at 1335 cm\(^{-1}\). As previously...
discussed, two bridge-bonded formate species are present on the surface where the one at 1270 cm\(^{-1}\) is modified by the coadsorbed oxygen. Up to an oxygen coverage corresponding to an AES ratio of 0.20, the features at 240, 1070, and 1715 cm\(^{-1}\) grow simultaneously. These three peaks are assigned to Mo–O, C–O, and C\(_d\)–O stretching vibrations, respectively, of a formate species. The large splitting of the two C–O and C\(_d\)–O vibrations and the appearance of a C\(_d\)–O vibrational feature at 1715 cm\(^{-1}\) indicate clearly the presence of a monodentate formate species on the surface.

It is noteworthy that the presence of oxygen on the surface does not promote the formation of hydroxyl groups at this formic acid coverage, as indicated by the decreasing intensity of the peak at 3570 cm\(^{-1}\) with increasing oxygen coverage. These data suggest that a new pathway exists for hydroxyl formation on the clean Mo(110) surface, in contrast to the proton transfer mechanism (from formic acid to coadsorbed oxygen) for the oxygen-modified surface.

The thermal stability of the monodentate formate also has been studied. Figure 8 shows a series of HREELS spectra acquired after dosing 0.3 monolayer of formic acid onto an oxygen-modified surface at 95 K, which was subsequently annealed to the indicated temperature. As is apparent in Figure 8, the spectrum taken at 95 K is predominantly that of the formate species. These data indicate that proton transfer to the surface occurs at 95 K. Upon annealing, the formate is stable on the surface up to 290 K and decomposes completely at 390 K.

The adsorption and reaction of formic acid on the O/Mo-(110) surface at a saturation formic acid coverage also have been studied with HREELS. These results are displayed in Figure 9. The spectrum taken after dosing approximately five layers of formic acid at 90 K is very characteristic of condensed formic acid. To remove the multilayer formic acid, the surface was annealed to 190 K. The spectrum acquired after annealing to 190 K exhibits peaks at 235, 450, 635, 1045, 1250, 1390, 1730, 1860, and 2950 cm\(^{-1}\). The features at 450 and 630 cm\(^{-1}\) can be assigned to the Mo–O vibrations, while the peak at 1860 cm\(^{-1}\) corresponds to the formyl species. The formyl species decomposes during an anneal from 190 to 300 K and forms CO, which subsequently desorbs due to the unavailability of unoccupied adsorption sites. This desorption produces a CO feature between 210 and 280 K in the TPD data of Figures 2 and 4. Both the monodentate formate and molecularly adsorbed formic acid are present as indicated by the C–O stretching vibrational mode at 1045 cm\(^{-1}\) for formate and at 1250 cm\(^{-1}\) for molecularly adsorbed formic acid. The features at 250 cm\(^{-1}\) are assigned to correspond to the lattice vibration of molecularly adsorbed formic acid and the Mo–O vibration of the formate species; the peak at 1730 cm\(^{-1}\) corresponds to the C=O vibration from both species. The features corresponding to molecularly adsorbed formic acid disappear upon annealing to 250 K, consistent with the observed molecular desorption of formic acid at 255 K in the TPD experiments. The spectrum acquired after annealing to 250 K is dominated by the feature
corresponding to the monodentate formate. The peaks at 235, 1045, 1730, and 2950 cm\(^{-1}\) can be assigned to the Mo–O, C–O, C=O, and C–H vibrational modes, respectively, of the formate species in a monodentate configuration. A peak at 3590 cm\(^{-1}\) is also seen and likely corresponds to the \(\nu(OH)\) of the hydroxyl group formed from formic acid decomposition via proton transfer to the adsorbed oxygen. This is in contrast to the clean Mo(110) surface, where no hydroxyl formation is observed at a saturation formic acid coverage. Apparently, the presence of oxygen opens a channel for OH formation on this surface.

The spectrum taken after annealing to 300 K shows a decrease in all formate-related features. At the expense of the formate species, two new features appear at 855 and 1155 cm\(^{-1}\). These two peaks are assigned to correspond to chemisorbed CO\(_2\). The first layer decomposes upon heating. Formic acid decomposes at saturation coverage on the Mo(110) surface apparently to atomic oxygen also occurs to a small extent at relatively low temperatures (below 200 K). At saturation coverage, molecular desorption is observed due to self-poisoning. Based on the TPD data, \(\sim 70\%\) of the formic acid in the first layer decomposes upon heating. Formic acid decomposition at saturation coverage on the Mo(110) surface apparently occurs through a bimolecular pathway:

\[
2\text{HCOOH}_{\text{ad}} \rightarrow \text{HCO}_{\text{ad}} + \text{HCOO}_{\text{ad}} + \text{H}_2\text{O} \quad (1)
\]

Formate and formyl species remain adsorbed on the surface, while the water product can either desorb into the gas phase or remain on the surface, depending upon the reaction temperature. Both the formyl and formate species have been clearly identified in our HREELS spectra. Bimolecular dehydration has been suggested previously for Ru(100),\(^{17}\) Ni(111),\(^{18}\) Ni(100),\(^{19}\) and Ni(110)\(^{20,21}\) surfaces. However, formyl has not been identified via vibrational spectroscopy; only formate and CO have been found.\(^{19,22-23}\) The inability to identify the formyl species has been attributed to its instability on the surface. Bhattacharya\(^4\) has studied the adsorption of formic acid on the W(100) surface using work function measurements and photoemission spectroscopy (PES). On the basis of PES, this author suggested the formyl species as a possible reaction intermediate in addition to formate. Our experiments show that the formyl species is stable on the Mo(110) surface up to 190 K and decomposes upon heating to 250 K, forming CO\(_{\text{ad}}\) and H\(_2\)\(_{\text{ad}}\), as indicated by the simultaneous disappearance of the features at 1860 cm\(^{-1}\) and the growth of the features at 980 (Mo–H) and 1940 cm\(^{-1}\) (C=O) (see Figure 5).

According to coordination chemistry,\(^{23-24}\) the formate species can be bonded to the metal center via a monodentate, a bidentate, or a bridging configuration as illustrated in Figure 10. It has been shown that the splitting, \(\Delta \nu\), between the OCO symmetric and asymmetric stretching vibrations is a good indication of the structure, although exceptions to this trend are known.\(^{24}\) The bidentate configuration shows a very small splitting (\(\Delta \nu < 80\) cm\(^{-1}\)), while a splitting of 200 cm\(^{-1}\) has frequently been found for the bridge-bonded formate. For the monodentate configuration, the coupling between the C–O and C=O bonds is very small, and the splitting is usually larger than 300 cm\(^{-1}\). Using vibrational spectroscopy, the formate species has been identified as a reaction intermediate on various transition metal surfaces including Pt(110),\(^{26}\) Pt(111),\(^{27,28}\) O/Pt(111),\(^{1,28}\) Ni(110),\(^1\),\(^{19}\) O/Pd(100),\(^{29}\) Pd(111),\(^{30}\) O/Pd(111),\(^{30}\) Rh(111),\(^{31}\) O/Rh(111),\(^{31}\) O/Ag(111),\(^{32}\) Cu(100),\(^{33}\) Cu(110),\(^{34}\) and Ru(001).\(^{2,23}\) In most cases, a bridge-bonded formate has been found for transition metal surfaces. A monodentate has been found only on O/Pt(111)\(^{28}\) and Ru(0001)\(^{23}\) surfaces, based on the appearance of the OCO asymmetric vibration. The monodentate species is stable only at relatively low temperatures and is converted to the bridge-bonded formate after heating to 190–200 K. However, as shown by Dubois et al.,\(^{35}\) the coexistence of molecular formic acid, even in trace quantities, causes a tilting of the formate species by forming a hydrogen bond between the formate species and formic acid. This interaction lowers the symmetry of the formate, resulting in the appearance of the asymmetric OCO stretching vibrational mode. On the Mo(110) surface, both the monodentate and bridge-bonded formate species were identified. The corresponding vibrational frequencies of the formate species on the Mo(110) surface are listed in Tables 1 and 2. For comparison, the literature values for formate on various surfaces are also listed. The identification of a bridge-bonded formate species on the Mo(110) and the assignment of its vibrational frequencies are unambiguous; however, a second OCO symmetric peak at 1270 cm\(^{-1}\) was found. The fact that its intensity increases with increasing oxygen coverage suggests a formate species bonded to a surface site next to an adsorbed oxygen atom. The change in the vibrational frequency reflects an electronic modification of the Mo–formate bond by the

| TABLE 1: Frequencies (cm\(^{-1}\)) and Assignment of a Bidentate or Bridge-Bonded Formate |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | \(\nu(C-H)\) | \(\nu_d(OCO)\) | \(\nu_{as}(OCO)\) | \(\delta(OCO)\) | \(\nu(O-M)\) | ref              |
| Pt(111)         | 2950           | 1340            | 790             | 370             | 27             | 11              |
| O/Pt(111)       | 2920           | 1330            | 780             | 360             | 11             | 28              |
| Pd(111)         | 2915           | 1355            | 800             | 340             | 30             | 30              |
| Ni(110)         | 2940           | 1370            | 790             | 440             | 19             | 24              |
| Ag(110)         | 2900           | 1640            | 1340            | 770             | 280            | 32              |
| Cu(100)         | 2910           | 1640            | 1330            | 760             | 340            | 33              |
| Mo(110)         | 2945           | 1360            | 775             | 360             | 30             | this work        |
| O/Mo(110)       | 2950           | 1270            | 755             | 340             | 34             | this work        |

| TABLE 2: Frequencies (cm\(^{-1}\)) and Assignment of a Monodentate Formate |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | \(\nu(C-H)\) | \(\nu_d(OCO)\) | \(\nu_{as}(OCO)\) | \(\delta(OCO)\) | \(\nu(O-M)\) | ref              |
| Ru(001)         | 2357           | 1681            | 1290            | 780             | 360             | 28              |
| O/Pt(111)       | 2920           | 1620            | 1290            | 780             | 360             | 28              |
| Mo(110)         | 2935           | 1745            | 1010            | 340             | 34             | this work        |
| O/Mo(110)       | 2940           | 1720            | 1025–1070       | 240             | 24             | this work        |

Figure 10. Possible bonding configurations of a formate species.
coadsorbed oxygen. The presence of surface oxygen has been shown to promote the formation of a formate species on various transition metal surfaces. It is noteworthy, however, that the ν(OCO) of formate shows a very similar frequency on most clean and oxygen-modified surfaces, as one can see in Table 1. The larger shift observed on the Mo(110) surface is likely due to the significantly stronger Mo―O bond, comparatively, and therefore a larger electronic influence of the oxygen on the formate.

The strong Mo―O bond is also manifested in the decomposition pathway of the formate species. According to the HREELS data, the decomposition of formate on the Mo(110) occurs between 250 and 350 K; however, the only gas-phase product is CO. Even at a saturation formic acid coverage on the Mo(110) surface, where molecular desorption of formic acid is detected due to the lack of vacant reactive sites, CO is the only carbon-containing product from formate decomposition detected via TPD or HREELS. This result indicates that the decomposition occurs in sequential/concerted steps where one of the two C―O bonds is broken to produce atomic oxygen and CO, with cleavage of the C―H bond to give atomic hydrogen on the surface. This result can be compared to previous results on other transition metals, where CO₂ always has been found as a formate decomposition product in TPD. On Ni(110), Ru(100) and Rh(111), surfaces, CO also has been observed as a formate decomposition product in addition to CO₂. Two mechanisms have been proposed to explain the coexistence of CO and CO₂ as formate decomposition products. Sun and Weinberg have suggested the “hot hydrogen” decomposition mechanism. In this mechanism the decomposition occurs through the C―H bond cleavage producing a “hot” H, which inserts in the C―O bond of a neighboring formate, producing CO and a hydroxyl group. The CO/CO₂ ratio is expected to be unity according to this mechanism. On the Rh(111) surface, two formate decomposition reactions have been proposed: the majority of the formate decomposes via C―H bond cleavage producing CO₂ and atomic hydrogen on the surface, while a much smaller quantity of formate undergoes C―O bond cleavage producing CO, H, and O on the surface. Our results show that C―O bond cleavage is the only pathway for formate decomposition on the Mo(110) surface. This is most surely due to the relatively high strength of the M―O bond.

At small formic acid coverages on the Mo(110) surface, hydroxyl formation is also observed. The hydroxyl group can be formed either as a primary decomposition product of formic acid

\[
\text{HCOOH} \rightarrow \text{HCOO} + \text{OH} \quad (2)
\]

or in a secondary step from H₂O

\[
\text{H}_2\text{O} \rightarrow \text{OH} + \text{H} \quad (3)
\]

which is formed from the bimolecular dehydration of formic acid. Our results do not allow an unambiguous assignment to be made between these two alternatives. However, our results do indicate that the direct decomposition of formic acid is the dominant pathway. First, the peak corresponding to the formyl species is the dominant feature in the HREELS spectrum at the lower formic acid coverages. Second, no Mo―H vibration is observed at low coverages; the decomposition of water would also produce atomic hydrogen on the surface. Third, the presence of oxygen does not promote OH formation. This is not understandable if the reaction 3 is operative and can only be explained through reactive site blocking for reaction 2 by coadsorbed oxygen. The coadsorbed oxygen will, however, facilitate the direct transfer of hydrogen from formic acid to the surface and open a new pathway for the hydroxyl group formation at high oxygen coverages. At high formic acid coverages on the Mo(110) surface, no hydroxyl formation is observed, presumably due to self-poisoning. Precoating the surface with oxygen leads to the production of surface hydroxyl groups even at a saturation formic acid coverage. This is due to direct transfer of hydrogen from formic acid to coadsorbed oxygen.

The coadsorption of oxygen shows a strong effect on the formic acid adsorption and decomposition on the Mo(110) surface. Coadsorbed oxygen stabilizes the molecular formic acid on the surface, without increasing its reactivity significantly. This indicates that the increase in its binding energy is due to an electronic effect, and the similarity of its reactivity is due to site blocking by the coadsorbed oxygen, which might also alter the formic acid decomposition reaction pathway.

The fact that the chemisorbed formic acid on the O/Mo(110) has a much higher desorption temperature than the multilayer indicates that the formic acid is bonded directly to the Mo via a hydroxyl oxygen, rather than bonded to the coadsorbed oxygen through a hydrogen bond.

At low coverages, formic acid is converted completely to formate even at 95 K. Formic acid decomposition occurs most likely via proton transfer from the formic acid directly to the coadsorbed oxygen, as indicated by the presence of hydroxyl groups and the dominant formate spectral features. However, a small amount of formic acid decomposes via a bimolecular pathway, as indicated by the small quantity of formyl species found in the HREELS data. The formate species has been identified unambiguously as a monodentate on the O/Mo(110) surface. The formate is stable on the surface up to 290 K and decomposes upon heating to 390 K. Since CO is the only carbon-containing product observed in this temperature range in the TPD, the decomposition of formate occurs via C―O bond cleavage.

At high formic acid and oxygen coverages, the decomposition of formate exhibits a different reaction pathway. Upon annealing from 250 to 350 K, a CO₂⁻⁻ species forms on the surface. CO₂⁻⁻ has been identified previously subsequent to dosing CO₂ onto Re(0001), Pd(110), and Ni(110). Table 3 compares the vibrational frequencies of CO₂⁻⁻ on various surfaces.

Concomitant with CO₂⁻⁻ formation, a decrease is observed in the peak intensity corresponding to the C―H vibrational mode of formate and an increase in the peak intensity corresponding to the hydroxyl group. It is also noteworthy that no hydrogen desorption is observed; water is the only hydrogen-containing desorption product found upon heating to 300 K. This clearly shows that the formate species transfers hydrogen to a neighboring coadsorbed oxygen-atom (or OH), forming a CO₂⁻⁻ species and a hydroxyl group (or H₂O). This decomposition pathway is illustrated in Figure 11. The identification of a CO₂⁻⁻ species as a decomposition intermediate of adsorbed formate is the first such observation, to our knowledge, although CO₂ has been observed frequently as a desorption product in TPD. This

<table>
<thead>
<tr>
<th>Surface</th>
<th>ν(M-O) (cm⁻¹)</th>
<th>δ(OCO) (cm⁻¹)</th>
<th>ν(OCO) (cm⁻¹)</th>
<th>ref</th>
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</thead>
<tbody>
<tr>
<td>Re(0001)</td>
<td>650</td>
<td>1230</td>
<td>39.00</td>
<td></td>
</tr>
<tr>
<td>Pd(110)</td>
<td>770</td>
<td>1200</td>
<td>40.00</td>
<td></td>
</tr>
<tr>
<td>Ni(110)</td>
<td>410</td>
<td>750</td>
<td>1130</td>
<td>41</td>
</tr>
<tr>
<td>Mo(110)</td>
<td>855</td>
<td>1155</td>
<td>this work</td>
<td></td>
</tr>
</tbody>
</table>
Adsorption of formic acid occurs dissociative on both Mo(110) and O/Mo(110) surfaces at low formic acid coverages, even at 100 K. At a saturation formic acid coverage, molecular adsorption occurs at 100 K; subsequent heating to 250 K leads to both molecular desorption and decomposition. On the Mo(110) surface, the majority of the formic acid decomposes via a bimolecular pathway, forming a formate and formyl species on the surface. However, on the oxygen-precovered surface unimolecular decomposition via proton abstraction by the coadsorbed oxygen atom is the dominant reaction pathway. At low formic acid coverages on the Mo(110) surface, evidence is also found for the unimolecular process, where the C—O bond is cleaved to form a hydroxyl and a formyl species on the surface. The formyl is stable only to 190 K, decomposing at 250 K. At a saturation formic acid coverage, molecular desorption and decomposition. 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