Adsorption and reaction of formic acid on NiO(100) films on Mo(100): Temperature programmed desorption and high resolution electron energy loss spectroscopy studies

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Adsorption and reaction of formic acid on well-defined NiO(100) films prepared on Mo(100) have been investigated using combined temperature programmed desorption (TPD)/high resolution electron energy loss spectroscopy (HREELS). A novel approach to HREELS of oxide materials is utilized to acquire spectral data. This approach enables the direct observation of weak loss features due to the excitation of adsorbates without serious interference from intense multiple surface optical phonon losses associated with oxide materials. The results indicate that formic acid initially adsorbs associatively on NiO(100) surfaces at 90 K and undergoes heterolytic dissociation upon heating to > 200 K to form a formate intermediate. The adsorbed formate species is proposed to bond to a cation site via one of the oxygen atoms of the formate in a monodentate configuration. The presence of a dimeric formic acid species is also indicated and a bonding configuration for this species has been proposed.

I. INTRODUCTION

The investigation of relatively complex organic species chemisorbed on insulating metal oxides has recently received considerable attention due to the importance of these species in heterogeneous catalysis. To date, extensive work on the chemisorptive properties of oxide materials has been carried out; however, information regarding the adsorption geometries and bonding configurations of adsorbed species on oxide surfaces is generally lacking. The principal reason for this deficiency is that these studies have been carried out primarily on powdered samples. Accordingly, the information obtained necessarily represents an average of the various crystal faces exposed plus a variety of defects most surely present on the polycrystalline powdered samples. On the other hand, studies of well-characterized single-crystal metal oxide surfaces using surface science techniques have encountered difficulties associated with surface charging, sample heating, and cleaning due to the highly insulating nature of these materials. It is only recently that several adsorption studies of relatively complex organic molecules on well-characterized single-crystal oxide surfaces have been carried out.1-11

In this article, we present a study of formic acid chemisorbed on the transition metal monoxide NiO(100) using a new approach to study oxides. Our approach consists of preparing well-defined, ultrathin nickel oxide films on a single-crystal dissimilar metal surface, followed by studies utilizing temperature programmed desorption (TPD)/high resolution electron energy loss spectroscopy (HREELS) to determine the adsorption geometry of formic acid on the NiO(100) thin film.

The production of thin oxide films on conducting metal substrates circumvents the difficulties associated with surface charging during charged particle measurements due to the insulating nature of oxide materials. Studies of thin oxide films have another advantage over their bulk counterparts in that a temperature gradient while heating, caused by poor thermal conductivity of oxides, is avoided. This feature allows precise temperature control during thermal desorption studies.

The preparation of ultrathin metal oxide films for surface science studies has been carried out traditionally by oxidizing a metal substrate to form a thin oxide film. However, it is often difficult to control the stoichiometry and thickness of the oxide layer and, accordingly, metal oxide films synthesized using this method are usually highly disordered. Growth and nucleation of the oxide layers at defects can produce a highly nonuniform film. In the present studies, a new method has been employed for the synthesis of highly ordered, uniform NiO(100) films. The approach consists of depositing Ni metal onto Mo(100) in a controlled oxygen atmosphere. Compositional and surface structural studies have shown that the NiO films are essentially stoichiometric and grow epitaxially with their (100) faces oriented parallel to the Mo(100) substrate.

In the application of HREELS to adsorbates on ionic substrates, however, a great difficulty encountered is that the accompanying vibrational spectra are dominated by losses due to excitation of surface optical phonons. Since the intense multiple phonon losses generally extend over a wide vibrational frequency range of the HREELS spectra, it is not practical to observe directly adsorbate losses (which are several orders of magnitude smaller in intensity than the phonon losses) in the 0–4000 cm⁻¹ spectral range. In recent studies,12,13 we have developed a new approach to acquiring HREELS data in order to circumvent the difficulties associated with these phonon losses. By utilizing a high-energy incident electron beam, this new approach enables the direct observation of weak loss features due to the excitation of adsorbates without serious inter-
Truong, Wu, and Goodman: Formic acid on NiO(100)

The adsorption geometries and bonding configurations of formic acid adsorbed on the (100) face of NiO have been examined using this approach. The results indicate that initially formic acid adsorbs associatively on NiO(100) at 90 K and then undergoes heterolytic dissociation upon heating to > 200 K. The adsorbed surface formate species is bonded to a cation site via one of the oxygen atoms of the formate in a monodentate configuration. The presence of a dimeric formic acid species on NiO(100) surfaces is also indicated and a bonding configuration for this species has been proposed.

II. EXPERIMENTAL

These studies were carried out utilizing an ultrahigh vacuum (UHV) system, described elsewhere, with capabilities for HREELS, Auger electron spectroscopy (AES), low energy electron diffraction (LEED), TPD, and sample heating and cooling. The crystal cleaning procedure has also been detailed previously.

The preparation of NiO films consists of depositing Ni onto Mo(100) in a controlled oxygen atmosphere and annealing in oxygen ambient following the film synthesis. Nickel deposition was performed via thermal evaporation of a high-purity ribbon tightly wrapped around a tungsten filament. The flux of Ni evaporation was directly monitored by a mass spectrometer which was mounted in line with the metal sources. The evaporation rate of the metal vapor was determined by a combination of TPD and AES measurements. The detailed studies regarding film synthesis and characterization are described elsewhere. Displayed in Fig. 1 is the Auger spectrum acquired following the film synthesis which shows features essentially identical to those from single-crystal NiO(100). The NiO films prepared using our approach exhibited an excellent (1X1) LEED pattern indicative of long-range order.

The HREELS measurements were carried out in the scattering compartment of a two-tiered chamber. The incident angle of the electron beam was set at 60° with respect to the surface normal. The primary energy of the electron beam of the spectrometer (LK-2000, Larry Kesmodel Technologies) can be varied in the 0-250 eV range. While an elastic peak count rate of 20,000 Hz could be typically obtained from the clean surface using an electron beam with E_e=50 eV at the spectral resolution 80-100 cm^{-1}, adsorption of HCOOH resulted in a more-than-tenfold decrease in count rate.

Because of the low signal levels encountered in our HREELS measurements, an optimal Fourier filtering technique has been utilized to remove high frequency random noises and spikes in the HREELS spectra. All HREELS spectra reported below have been smoothed using this Fourier filtering technique. Figure 2 shows the HREELS spectrum with and without filtering, which demonstrates the effectiveness of the Fourier filtering technique to remove high frequency random noises without distorting the HREELS spectrum.

Spectroscopic grade formic acid (96%) was used in this study. Further purification was achieved in the manifold via freeze-pump-thaw cycles prior to introduction of the reactant into the vacuum chamber. In the TPD experiments, a directional gas doser was used to introduce the molecules to the crystal surface; however, the exposure of formic acid was performed via backfilling the UHV chamber for the HREELS measurements. The formic acid sur-
exhibit a desorption feature with a maximum at 375 K and TPD spectra. The desorption of the parent molecule is shown in Fig. 3. Several mass channels (m/e= 2, 18, 28, 44, 45, and 46) evolve as a function of formic acid coverage has been studied by monitoring the area of the HCOOH-TPD peak assuming that no decomposition of formic acid occurs under UHV conditions. This assumption is supported by the TPD studies in which no evidence for the formation of CO, CO2, and H2O gaseous products was found.

III. RESULTS

A. Temperature programmed desorption spectroscopy

The adsorption of HCOOH on NiO(100) films was carried out at 90 K and has been examined using TPD. The evolution of various desorption features as a function of formic acid coverage has been studied by monitoring several mass channels (m/e=2, 18, 28, 44, 45, and 46). The desorption of the parent molecule is shown in Fig. 3. TPD spectra (m/e=46) at low coverages (θ<0.22 ML) exhibit a desorption feature with a maximum at 375 K and a broad weak feature at ~450 K. Further exposure to formic acid results in the population of the 375 K desorption state and the appearance of two new features at lower temperatures. These desorption states appear to fill in non-sequentially with increasing exposure. While other desorption features remain saturated at θ≥2, the desorption peak at 155 K increases in intensity as θ is increased, indicating that this feature arises from condensed multilayers of formic acid. The peak at 185 K can be interpreted as arising from the desorption of bilayers of the molecules. Assuming the first-order kinetics and a prefactor ν=8×10^16 Hz (Ref. 18), the activation energy of desorption of this bilayer is deduced to be 12.7 kcal/mol for the decomposition of dimeric formic acid. The desorption of monolayer formic acid formed via recomposition of surface formate and surface hydrogen occurs between 300–400 K with a maximum at 375 K. The heterolytic dissociation of HCOOH on NiO(100) upon heating at coverages below one monolayer is indicated by HREELS and is discussed below.

It is evident in Fig. 3 that population of the bilayer and multilayers of adsorbed formic acid begins prior to completion of the first monolayer. This behavior suggests that the formic acid tends to aggregate via hydrogen bonding. The hydrogen bonding configurations will be discussed in details in the following section.

It is noteworthy that no desorption signal was observed for masses other than the parent peak and its fragments, e.g., m/e=45 or 46, implying that the parent molecules are the only species desorbed from the surface. This behavior contrasts with that found for formic acid adsorbed on a number of transition metal surfaces. The decomposition of formic acid on Cu(100) (Ref. 21) and Pt(111) (Ref. 23), e.g., was reported to yield CO2 and H2 via a dehydrogenation route, whereas formic acid decomposes on Ni(100), Ni(110) (Ref. 24), Ru(1010) (Ref. 18), and Ru(0001) (Ref. 25) not only via C–H bond cleavage, but also by C–O bond cleavage. In each of these cases, deprotonation of the adsorbed formic acid to the adsorbed formate intermediate has been confirmed by HREELS. It has also been reported that formic acid undergoes decomposition on the (0001)-Zn polar surface of ZnO to produce CO, CO2, and H2.

B. Electron energy loss spectroscopy

Adsorption of formic acid on thin NiO(100) films has been further examined using HREELS. Displayed in Fig. 4 is a set of HREELS spectra of formic acid adsorbed on a ~20 ML NiO film at 90 K as a function of exposure. Exposing the sample to HCOOH at 90 K gives rise to a number of distinct loss features in the 750–4000 cm−1 region. At coverages below one monolayer, the losses observed at 1020, 1397, 1672, 2985, and 3466 cm−1 are due to excitations of the C–O stretching [ν(C–O)], the C–H deformation [δ(CH)], the C–O stretching [ν(C–O)], the C–H stretching [ν(CH)], and the O–H stretching [ν(OH)] modes, respectively. The 3466 cm−1 loss shifts to
lower energies and becomes broadened as the coverage exceeds one monolayer. This feature indicates that the O–H stretching frequency of formic acid is altered due to hydrogen bonding in the multilayer phase. Compiled in Table I are vibrational modes for monomeric and dimeric formic acid species, along with various loss energies taken from the literature.26,27

The evolution of the losses as a function of the annealing temperature \( T \) at different coverages is shown in Figs. 5 and 6. All loss features remain essentially un-

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**TABLE I. Compilations of vibrational modes (in \( \text{cm}^{-1} \)) of monomeric and dimeric formic acid species.**

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Monomer NiO(100)* (90 K)</th>
<th>Monomer Monophase (IR)</th>
<th>Dimer/ NiO(100)* (90 K)</th>
<th>Dimer (IR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>v(OH)</td>
<td>3466</td>
<td>3570</td>
<td>2500–3500</td>
<td>2500–3000</td>
</tr>
<tr>
<td>v(CH)</td>
<td>2985</td>
<td>2943</td>
<td>2975</td>
<td>2960</td>
</tr>
<tr>
<td>v(C=O)</td>
<td>1672</td>
<td>1770</td>
<td>1709</td>
<td>1694</td>
</tr>
<tr>
<td>( \delta (\mathrm{C}-\mathrm{H}) )</td>
<td>1397</td>
<td>1387</td>
<td>1387</td>
<td>1395</td>
</tr>
<tr>
<td>( \delta (\mathrm{O-C-H}) )</td>
<td>...</td>
<td>1229</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>v(C=O)</td>
<td>1020</td>
<td>1105</td>
<td>996</td>
<td>1049</td>
</tr>
</tbody>
</table>

*The present work.

Reference 25.

Reference 26.

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changed at \( T < 200 \text{ K} \). However, dramatic changes occur upon annealing to temperatures greater than 200 K—the C=O stretching mode disappears completely and a new loss at 1594 \( \text{cm}^{-1} \) appears. The shape and relative intensity of the losses at 1397 and 1020 \( \text{cm}^{-1} \) also change as the temperature exceeds 200 K. The changes of these vibrational modes clearly indicate the dissociation of formic acid and the formation of a surface formate species.9,11,21,22

The losses observed at 1034, 1377, and 1594 \( \text{cm}^{-1} \) are thus attributed to the out-of-plane C–H deformation [\( \tau (\mathrm{CH}) \)], and the symmetric and asymmetric O–C–O stretching modes, respectively, of the surface formate.9,11,21,22 The in-plane C–H deformation [\( \delta (\mathrm{CH}) \)] mode has a loss energy very near that of the v(C=O) mode; the present energy resolution of the instrument (~80 \( \text{cm}^{-1} \)) prohibits differentiating between these features.

Further support for the presence of a surface formate species upon heating to > 200 K is that while the loss energy of the v(CH) mode remains unchanged, the broad v(OH) band in the 2500–3500 \( \text{cm}^{-1} \) region, which appears to maximize at 3308 \( \text{cm}^{-1} \), shifts to higher loss energies. The shift of the v(OH) band to an energy which corresponds exactly to that of the loss feature identified as an OH species associated with the acidic proton adsorbed on the basic oxygen anion sites (arising from abstracting hy-
HREELS spectra of HCOOH adsorbed on a ~20 ML NiO(100) film at 90 K as a function of annealing temperature: (a) 90 K; (b) 130 K; (c) 220 K. The surface coverage of formic acid is 2.0 ML. The spectra were collected at $E_E=49.8$ eV and at the specularly reflected beam direction. The HREELS spectra have been smoothed using a Fourier filtering technique.

The dependence of the bonding configuration of the surface formate species on the substrate temperature has also been examined. Figure 7 presents HREELS spectra acquired at 298 K following adsorption of formic acid (the adsorption temperature is also 298 K). The spectra exhibit identical features to those displayed in Figs. 4(b) and 5(c) which have been annealed to above 200 K.

IV. DISCUSSION

A. Monomeric/dimeric formic acid species and condensed multilayers on NiO(100) surfaces

Adsorption of formic acid on thin NiO(100) films at 90 K gives rise to a number of distinct loss features which

<table>
<thead>
<tr>
<th>Assignment</th>
<th>NiO(100) HREELS$^a$</th>
<th>MgO(100) HREELS$^b$</th>
<th>MgO powder (IR)$^c$</th>
<th>ZnO(0001) (HREELS)$^d$</th>
<th>ZnO powder (IR)$^e$</th>
<th>Oxidized aluminum film (IETS)$^f$</th>
<th>Aluminum oxide (IETS)$^g$</th>
<th>HCOONa (IR)$^h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$(CH)</td>
<td>2901</td>
<td>2951</td>
<td>2890</td>
<td>2939</td>
<td>2670</td>
<td>2847</td>
<td>2890</td>
<td>2841</td>
</tr>
<tr>
<td>$\nu_2$(CO)</td>
<td>1594</td>
<td>1614</td>
<td>1575</td>
<td>1612</td>
<td>1572</td>
<td>1605</td>
<td>1595</td>
<td>1567</td>
</tr>
<tr>
<td>$\nu_4$(CO)</td>
<td>1377</td>
<td>1349</td>
<td>1348</td>
<td>1387</td>
<td>1374</td>
<td>1379</td>
<td>1373</td>
<td>1366</td>
</tr>
<tr>
<td>$\delta$(CH)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\pi$(CH)</td>
<td>1034</td>
<td>1094</td>
<td>1046</td>
<td>1079</td>
<td>1100</td>
<td>1049</td>
<td>1053</td>
<td>1079</td>
</tr>
</tbody>
</table>

$^a$The present work.  
$^b$Reference 11.  
$^c$Reference 27.  
$^d$Reference 9.  
$^e$Reference 28.  
$^f$Reference 26.  
$^g$Reference 29.  
$^h$Reference 30.
can be assigned unambiguously to the vibrational modes of molecularly adsorbed HCOOH species. In comparison to the IR spectrum of the free molecules in the gas phase (see Table I) the presence of the monomeric species of initially adsorbed formic acid is confirmed. This contrasts with formic acid adsorbed on MgO surfaces,\textsuperscript{32,33} where dissociative adsorption to a stable formate species occurs as low as 90 K. This difference in reactivity between NiO and MgO surfaces can be readily explained in terms of their surface basicity. Magnesium oxide is a typical basic oxide whose surface basicity is stronger than that of nickel oxide.\textsuperscript{34,35} The acid/base interactions between the model MgO surface and various probe molecules with acid strength ranging from those of carboxylic acids and alcohols to alkenes may be superimposed on the S(CH) band as shown in Fig. 4(e). A difference was apparent between the present HREELS spectrum [Fig. 4(e)] and that from previous studies\textsuperscript{21-22} in the frequency region of the O-H stretching vibrations. The present studies showed the O-H band appears in the 2500-3500 cm\(^{-1}\) region with a maximum at 3308 cm\(^{-1}\), whereas the OH band maximum was observed at 2640 cm\(^{-1}\) in the previous work.

\section*{B. Surface formate species on NiO(100) surfaces}

The dissociation of formic acid and the formation of a surface formate species were observed upon heating to above 200 K as shown in Figs. 5 and 6. A comparison to the vibrational frequencies of adsorbed formate on various oxide surfaces (see Table II) leads immediately to the assignment to all loss features observed in Figs. 5(b) and 6(c). The observation of the asymmetric O-C-O stretching mode indicates that the surface formate species on NiO(100) does not have \(C_{2h}\) symmetry.\textsuperscript{21} This type of symmetry was typically found for formate species adsorbed on most transition metals,\textsuperscript{21,23,25} which possess a bridging or bidentate bonding configuration.\textsuperscript{21} In these configurations, the vibrational dipole moment associated with the \(v_s(\text{OCO})\) mode is parallel to the surface and is therefore dipole forbidden. In the present studies, a likely bonding picture for the formate species on NiO(100) surfaces involves bonding of a formate species to the cation sites via one of the oxygen atoms of the formate in a monodentate configuration as shown in Fig. 9.

Displayed in Fig. 7(b) is the spectrum collected at an angle 8° off the specularly reflected beam direction. Acquiring the data at the off-specular direction results in a decrease in the loss intensities of the symmetric and asym-
metric O-C-O stretching modes indicating the dipole nature of these modes, and an increase in the loss intensity of the $\pi$(CH) mode which shows an impact scattering contribution. The $\nu$(CH) mode remained essentially unchanged, exhibiting a strong impact scattering behavior. All these features further support the proposed monodentate bonding configuration of the formate species on NiO(100).

The monodentate bonding configuration for the formate species adsorbed on the (0001)-Zn faces of ZnO and on MgO(100) surfaces have been proposed previously. The main argument for the formate species favoring a monodentate configuration is consideration of the geometric and electronic structures of ZnO and MgO. The distance between the surface cation sites of these oxides greatly exceeds the oxygen–oxygen distance in the free formate ion (2.25 Å). The bridging configuration would then induce significant strain on both the adsorbed formate and the surface and is therefore not likely a viable structural model for the formate species. The bidentate configuration can also be ruled out due to the nature of the cation sites which have only a single dangling bond. This same argument applies to the adsorption system discussed here.

It has been demonstrated that the bonding configuration of the surface formate on Cu(100) varies depending on the substrate temperature. In order to explore the orientational dependence of the formate species on NiO(100) with temperature, the adsorption of formic acid was carried out at 298 K and the corresponding HREELS spectra were acquired at the same temperature, as shown in Fig. 6. The loss features were found to be identical to those shown in Figs. 5(b) and 6(c). This similarity indicates that the bonding configuration of the surface formate on NiO(100) surfaces does not depend on the substrate temperature. This result is not surprising in that the electronic structure of the cation sites of NiO surfaces is rather localized. Therefore the formate species might be expected to bond more tightly to the cation sites than to the Cu surface.

V. CONCLUSIONS

The interaction of formic acid with NiO(100) surfaces has been investigated by means of TPD and HREELS. By preparing well-defined NiO(100) films on a Mo(100) surface, difficulties associated with surface charging due to the insulating nature of this material are circumvented during surface spectroscopic measurements. A novel approach to HREELS of oxide materials is utilized to acquire spectral data. This approach enables the direct observation of weak loss features due to the excitation of adsorbates without serious interference from the intense multiple surface optical phonon losses associated with oxide materials. The TPD and HREELS results indicate that formic acid initially adsorbs associatively on NiO(100) at 90 K and undergoes heterolytic dissociation upon heating to over 200 K. There is no evidence for further decomposition of formate intermediates to yield CO$_2$, CO, and H$_2$ products. The formate species are bonded to the cation sites via one of the oxygen atoms of the formate in a monodentate configuration. The presence of a dimeric formic acid species on NiO(100) surfaces has also been detected and a bonding configuration for this species proposed.

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