

## IDENTIFICATION OF THE INTERMEDIATES IN THE DEHYDRATION OF FORMIC ACID ON Ni(110) BY HIGH RESOLUTION ELECTRON ENERGY LOSS VIBRATIONAL SPECTROSCOPY

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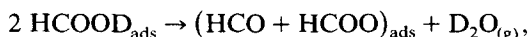
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High resolution electron energy loss vibrational spectroscopy was used to study the intermediate formed in the dehydration reaction for formic acid on Ni(110) and Ni(110)(4×5)C. On the carbided surface only the formate was observed. The frequencies of the asymmetric and symmetric O-C-O stretch indicated a monodentate configuration. On the clean surface a mixed adlayer of CO and HCOO formed. No losses expected for formic anhydride were observed. Lateral interactions between CO and HCOO appear to be responsible for the autocatalytic decomposition of the formate.

### 1. Introduction

The reactions of formic acid have been studied previously on Fe(100) [1], W(100) [2], Ru(1010) [3], Cu(110) [4], Cu(100) [5], Ni(100) [6], Ni(110) [7-9], Ag(110) [10,11], Pt(111) [12], Pt(111) [13], and a Cu/Ni(110) [14] alloy of varying surface composition. On all surfaces except Ni and Ru, dehydrogenation proceeds via cleavage of the O-H bond to form a surface formate. On Pt, Ag and Cu the formate subsequently decomposes with high selectivity to form CO<sub>2</sub> and H<sub>2</sub>, whereas on Fe(100) and W(100) the formate also oxidizes the surface upon decomposition, leading to the production of CO, CO<sub>2</sub>, H<sub>2</sub>, and minor amounts of H<sub>2</sub>O from the reduction of surface oxygen by adsorbed

hydrogen. On nickel, however, a bimolecular dehydration reaction occurs



as shown by isotopic labeling experiments on the Ni(110) [9] surface; the same reaction occurs on Ru(1010). Further, on Ni(110) CO, CO<sub>2</sub> and H<sub>2</sub> were evolved in 1:1:1 [7] ratios. Additionally, since gaseous CO<sub>2</sub> and H<sub>2</sub> were formed in a single, narrow temperature programmed reaction (TPR) peak, it was reasoned that adsorbed HCO and HCOO reacted to form a single adsorbed intermediate, formic hydride.

Two features of the experiment made this deduction uncertain, however. First, the evolution of CO was desorption-limited in TPR experiments so that it could not be ascertained whether the adsorbed CO was formed at the same time as the reaction-limited gaseous H<sub>2</sub> and CO<sub>2</sub> products. Second, in subsequent work the sharp TPR peak was explained by attractive interactions in the adsorbed layer, which produce an increase in the activation energy for decomposition with increasing surface concentration [6]. Under such circumstances, once the reaction is begun at a given initial coverage, it accelerates autocatalytically and differences in rates of decomposition of various hydrogen-containing intermediates can be masked. Effectively, the species are clearly strongly coupled, but they are not necessarily chemically bonded.

The advent of surface vibrational spectroscopy using high resolution electron energy loss measurements has made possible the direct observation of surface reaction intermediates. Surface formates have been studied in this way adsorbed on Cu(100) [5] and Ag(110) [11] after their existence was established by TPRS [4,10]. The purpose of this study was to clarify the nature of the intermediate in the dehydration reaction on Ni(110) using EELS.

## 2. Experimental

These studies were performed in a stainless steel vacuum system equipped with two 127° cylindrical sector analyzers for high resolution electron energy loss spectroscopy (HREELS), Auger electron spectroscopy, low energy diffraction (LEED) and a multiplexed mass spectrometer for thermal desorption spectroscopy (TDS). The formic acid was dried using boric acid anhydride, and vacuum distilled into a glass container. Residual dissolved gases were removed by several freeze-pump-thaw cycles prior to use. Formic acid was adsorbed onto the front surface of the sample using a capillary array approximately 1 cm from the surface. The purity of the formic acid was confirmed using mass spectrometry. In particular, no water impurity was observed. All EELS spectra were recorded near 100 K in the specular direction with beam kinetic energies between 2 and 5 eV.

### 3. Results

Reference spectra were first obtained for CO adsorbed on the Ni(110) surface. The surface was initially saturated with CO at 100 K and this CO was partially desorbed by heating to progressively higher temperatures. The EELS and temperature programmed desorption (TPD) are shown in fig. 1. Two CO desorption peaks were observed as expected from previous work [15–17]. At 100 K the saturated CO layer showed loss features at 550 and 1990  $\text{cm}^{-1}$ . After the surface was heated to 335 K to desorb the low temperature state, the low frequency peak shifted downward to 470  $\text{cm}^{-1}$ , and the high frequency peak split into peaks at 1940 and 2060  $\text{cm}^{-1}$ . Further heating led to little change in the spectrum, though additional loss features below 460  $\text{cm}^{-1}$  may be present following the heating to 365 K. The primarily loss features are normally associated with the metal–carbon stretch (400–500  $\text{cm}^{-1}$ ) and bridged

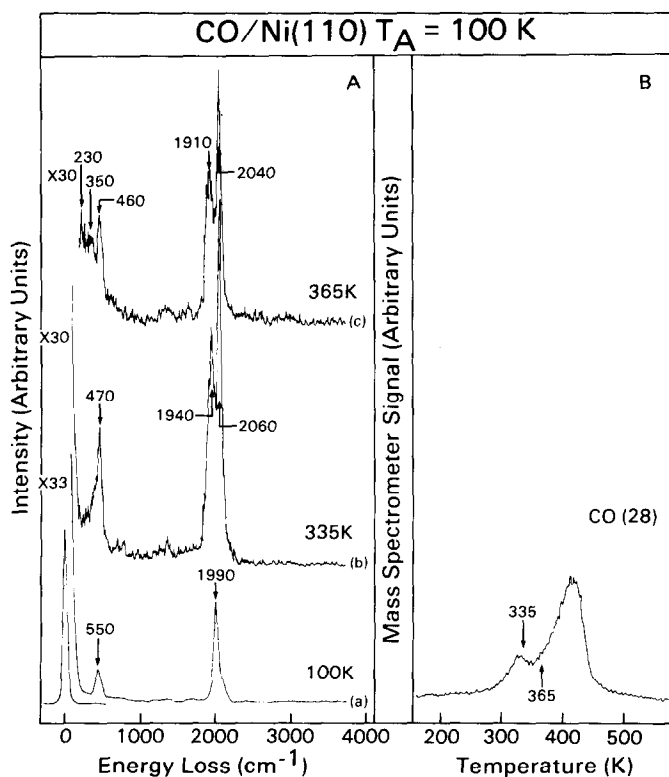


Fig. 1. (A) EELS spectra of (a) saturation CO coverage at 100 K, (b) is (a) heated to 335 K, (c) is (b) heated to 365 K. (B) TPD spectrum following CO saturation at 100 K.

(1940  $\text{cm}^{-1}$ ) and linear (2060  $\text{cm}^{-1}$ ) forms of CO, respectively.

Spectra for formic acid adsorbed on Ni(110)(4 × 5)C at 310 K indicated the sole presence of the formate intermediate, in agreement with previous TPRS results [19]. The spectrum shown in fig. 2 agrees well with spectra previously published for adsorbed formate on the Cu(100) and Ag(110) surface. The loss features are assigned to  $\nu(\text{CH})$  at 2950  $\text{cm}^{-1}$ ,  $\nu_a(\text{OCO})$  at 1670  $\text{cm}^{-1}$ ,  $\nu_s(\text{OCO})$  at 1370  $\text{cm}^{-1}$ ,  $\delta(\text{OCO})$  at 780  $\text{cm}^{-1}$  and  $\nu(\text{Ni-C})$  at 430  $\text{cm}^{-1}$ . No adsorbed CO was detected, and the CO observed in the TPRS profile corresponds to the amount expected due to cracking of  $\text{CO}_2$  in the mass spectrometer. The presence of the  $\nu_a(\text{OCO})$  mode suggests that the formate is inclined relative to the surface plane with the two oxygens in inequivalent binding sites. Similar observations have been made on the Cu(100) and Ag(110) surface. On Cu(100) a reversible conversion between this asymmetric form and an orientation in which the oxygen atoms are equivalently bonded occurred below 400 K [5]. Only the asymmetric form is observed following the formation of the formate at low temperature on silver [11].

The results obtained for the reaction of formic acid on the clean Ni(110) surface were unexpected. Even though the temperature programmed reaction results were identical to those observed previously [7–9], the vibrational spectra obtained following adsorption of  $\text{HCOOH}$  at 310 K (fig. 3) clearly indicated the presence of coadsorbed CO and formate. The formate appears to be symmetrically bonded. Moreover, vibrational bands expected for adsorbed anhydride species were never observed. In particular, one would expect to observe anhydride C–O stretches from 1700–1800  $\text{cm}^{-1}$  which are clearly

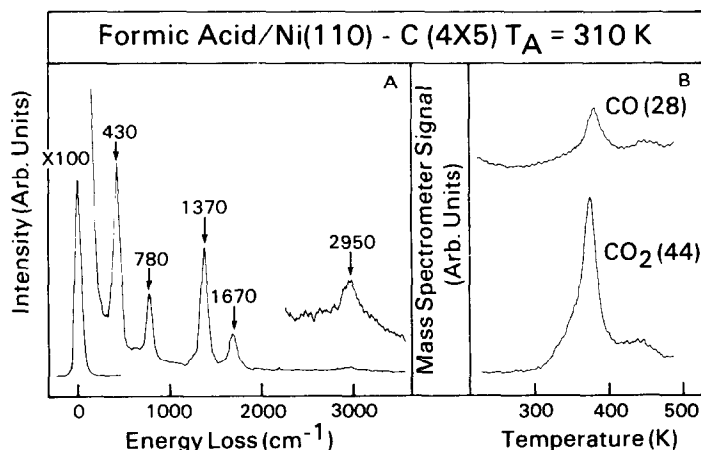


Fig. 2. (A) EELS spectrum following adsorption of formic acid on Ni(110)(4 × 5)C at 310 K. (B) TPD spectrum following adsorption on the (4 × 5)C at 310 K and cooling to 100 K.

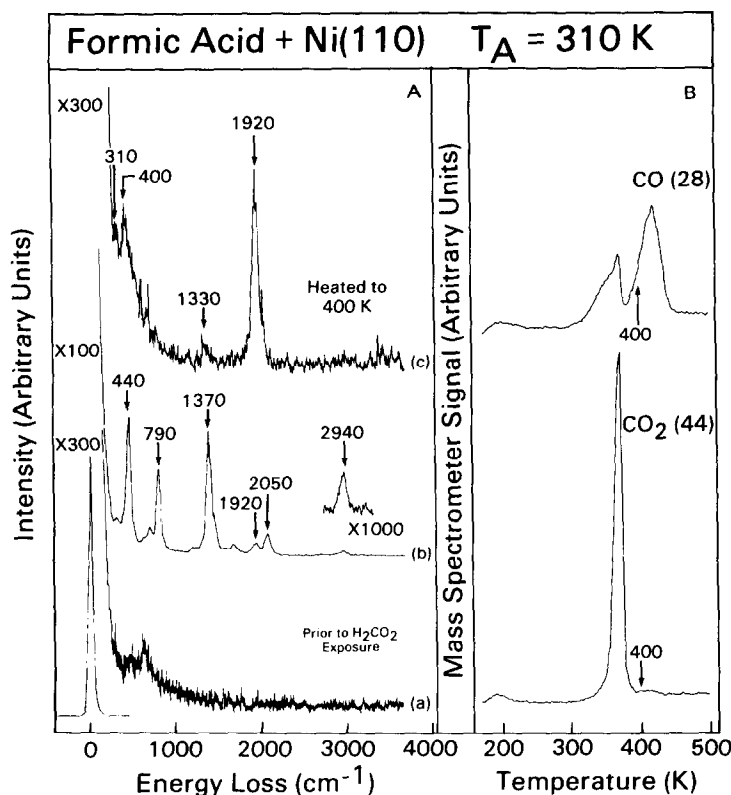


Fig. 3. (A) (a) Ni(110) prior to adsorption, (b) EELS spectrum following adsorption of formic acid at 310 K, (c) is (b) heated to 400 K. (B) TPRS for the condition of spectrum (b) after cooling to 100 K.

absent [20]. When the surface was heated above 335 K to desorb CO<sub>2</sub> and H<sub>2</sub>, only adsorbed CO was detected by EELS, as expected. It is abundantly clear that though the initial reaction of formic acid on Ni(110) is dehydration, the adsorbed formyl species formed dehydrogenates further to form adsorbed CO. The fate of the hydrogen from HCO decomposition is not clear, however, since adsorbed hydrogen atoms could not be detected by EELS during these experiments. For comparison the vibrational loss spectra for CO and HCOOH on Ni(110)(4 × 5) and Ni(110) are shown in fig. 4.

Following small formic acid exposures only one CO<sub>2</sub> peak was observed by TPRS, this peak was of normal width for a first-order reaction. As the exposure to formic acid was increased, this first order CO<sub>2</sub> peak saturated, and the narrow, explosive peak dominated the surface reaction [8,21]. At inter-

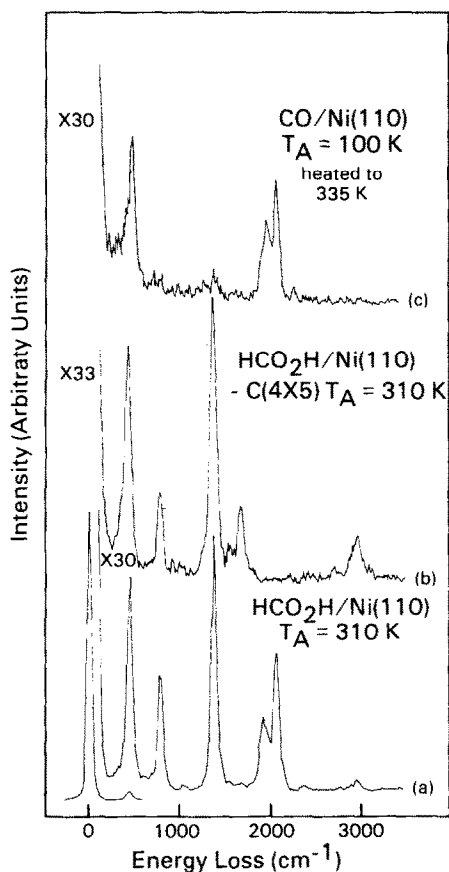


Fig. 4. Comparison of the EELS spectra for (a) formic acid adsorbed on Ni(110) at 310 K, (b) formic acid adsorbed on Ni(110)(4 $\times$ 5)C at 310 K and (c) CO adsorbed on Ni(110) to saturation and heated to 335 K.

mediate exposures, a mixture of the two processes was observed [8]. Coadsorption of CO, following exposure of the surface to formic acid in this intermediate range, converts the normal peak into the autocatalytic peak [8]. This behavior clearly indicates the presence of strong interactions between the CO and the adsorbed formate intermediate. The EELS results reported above make interpretation of this result and the nature of the lateral interactions responsible for the autocatalytic decomposition clearer.

Though the precise orientation of neither the formate nor CO is known on this surface, it is clear that adsorbed CO and formate have opposing dipole

moments, since both adsorbed species having charge concentrated on the oxygen. Since CO bonds carbon down, and HCOO bonds oxygen down, these dipoles can interact attractively to stabilize the coadsorbed layer with the CO and HCOO dispersed among one another. At low surface coverages only isolated pairs exist which decompose by normal kinetics, whereas at higher coverages islands form which are also stabilized by long range interactions among the adsorbed species. Over the range of coverages for which both decomposition paths exist, coadsorption of more CO stabilizes the isolated formates via dipole interactions, converting the low temperature peak resulting from normal decomposition kinetics into the autocatalytic path [22]. There is

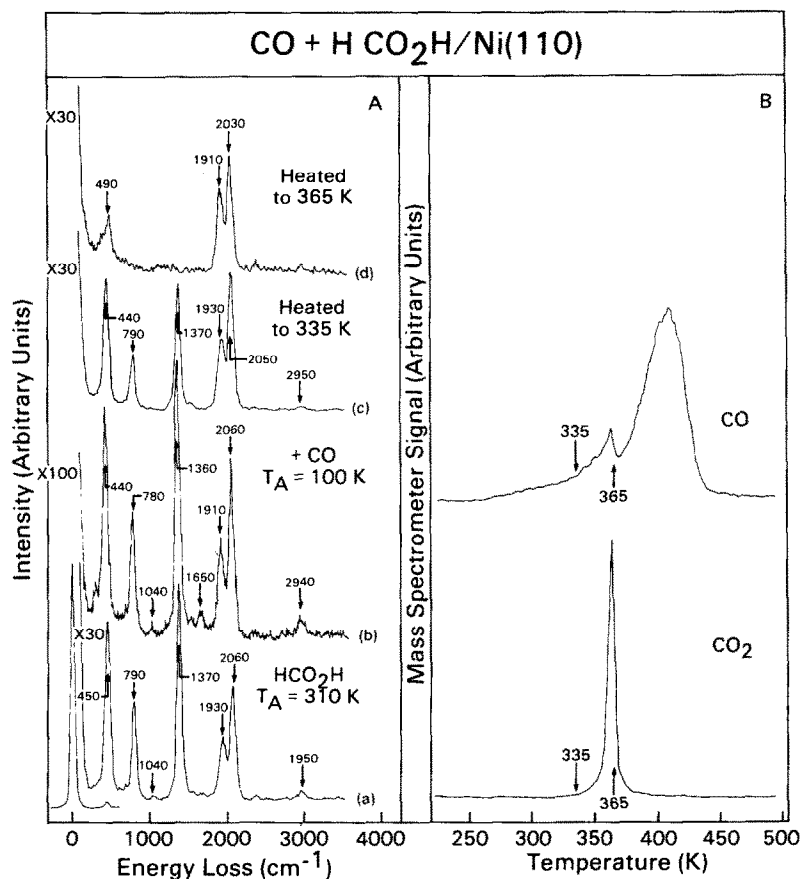


Fig. 5. EELS and TPRS spectra for coadsorption of CO and HCOOH on Ni(110), (A) (a) HCOOH adsorbed at 310 K, (b) CO adsorption saturation, (c) is (b) heated to 335 K, (d) is (c) heated to 365 K. (B) CO and  $\text{CO}_2$  TPRS peaks following EELS spectrum (b).

no direct chemical bonding between adsorbed CO and HCOO. This fact is clearly illustrated by both the spectra in fig. 4 and the spectra obtained following coadsorption of CO, shown in fig. 5; neither the CO nor the HCOO spectra are effected by coadsorption. Due to the analogous behavior of acetic acid and formic acid on Ni(110) [23], the EELS spectra following CH<sub>3</sub>COOH adsorption at 310 K were also briefly examined. In direct analogy with formic acid, the spectra showed the presence of the adsorbed carboxylic (acetate) [24] and CO when the autocatalytic behavior was observed.

In conclusion, on Ni(110) formic acid initially reacts at 300 K via a bimolecular dehydration reaction to form adsorbed HCOO and HCO. The HCO is unstable, decomposing to adsorbed CO and atomic hydrogen. The interactions among the adsorbed intermediates produce abnormal kinetics which lead to an acceleration in rate as the adlayer is depleted.

## Acknowledgements

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