



# Energetics of adsorbed formate and formic acid on Ni(111) by calorimetry



Wei Zhao<sup>a</sup>, Spencer J. Carey<sup>a</sup>, Sawyer E. Morgan<sup>b</sup>, Charles T. Campbell<sup>a,b,\*</sup>

<sup>a</sup> Department of Chemistry, University of Washington, Seattle, WA 98195, United States

<sup>b</sup> Department of Chemical Engineering, University of Washington, Seattle, WA 98195, United States

## ARTICLE INFO

### Article history:

Received 27 March 2017

Revised 22 May 2017

Accepted 30 May 2017

Available online 23 June 2017

### Keywords:

Nickel

Adsorbed formate

Surface carboxylate

Adsorption calorimetry

Bond energy

Ni(111)

Formic acid

## ABSTRACT

Surface carboxylates are common intermediates in many catalytic reactions and are also used for organo-functionalization of surface. Herein, adsorbed formate, the simplest carboxylate, was produced by dissociative adsorption of formic acid on the Ni(111) surface and the heats of adsorption were measured by single-crystal adsorption calorimetry (SCAC). At 240 K, the integral heat of dissociative adsorption to make adsorbed bidentate formate and adsorbed hydrogen is 117.1 kJ/mol at 1/7 ML. The estimated accuracy of measured heats is within 3 kJ/mol. Therefore, the standard enthalpy of formation of bidentate formate on Ni(111) is derived as  $-449.3$  kJ/mol and the bond enthalpy to the Ni(111) surface is 319.6 kJ/mol. Comparison to our earlier results for Pt(111) shows that bidentate formate is 54 kJ/mol more stable on Ni(111). This is the first experimental measurement of the energy of *any* molecular fragment bonded to *any* Ni surface through metal-oxygen bonds, so it is an important benchmark for validating the accuracy of quantum mechanical calculations of a wide range of adsorbed oxygenates on Ni catalysts. Compared to previous density functional theory (DFT) calculations, we found that DFT calculations systematically underestimate the bond energy of formate to Ni(111), but correctly predict that it is stronger to Ni(111) than to Pt(111). The integral heat of HCOOH adsorption to make molecularly adsorbed formic acid was also measured and found to be 63.2 kJ/mol at 0.45 ML and 120–155 K.

© 2017 Elsevier Inc. All rights reserved.

## 1. Introduction

Adsorbed formate is considered an important intermediate on catalyst surfaces for many catalytic reactions on late transition metal surfaces, including steam reforming of methane, methanol synthesis, and water-gas shift [1–3]. It is a likely intermediate whenever CO<sub>2</sub> with H<sub>2</sub> or water is present above a catalyst, as is true in all oxidation and steam reforming reactions of organic molecules. More complex carbonates (e.g., acetate and longer alkyl carbonates, and various functionalized versions of these) are also frequently suggested as intermediates in catalytic reactions, and since formate is the simplest example of this class of adsorbates, it serves as a prototype for understanding the bonding of this whole class of adsorbates. Moreover, the interactions of organic molecules containing  $-\text{COO}^-$  and  $-\text{COOH}$  groups with surfaces, such as amino acid residues, peptides, and proteins, are also important for the organo-functionalization of surfaces [4], and their use in medical applications [5], medical implants [6], and many other

areas. Thus, characterization of the energetics of adsorbed formate on surfaces is obviously crucial for the fundamental understanding of a wide variety of surface reactions and catalytic processes. However, the heat of formation for surface formate has only been previously measured on one surface, Pt(111), as previously reported by this group [7]. Here we report calorimetric measurements of the heat of formation of adsorbed formate on Ni(111) and find it to be bound 54 kJ/mol more strongly than to Pt(111). Since this is the first experimental measurement of the heat of formation of any adsorbed molecular fragment on any Ni surface whereby it is linked to the surface through O–Ni bonds, this result for bidentate formate will serve as a benchmark for validating the energy accuracy of theoretical estimates of the stability of many oxygenates bound to Ni catalyst surfaces. One of the simplest ways to produce formate is dissociative adsorption of formic acid on the surface as reported on Pt(111) [8], O/Pt(111) [7,9], Ni(111) [10–13], Rh(111) [14], and O/Mo(110) [15]. That is the method used here to produce this formate species. We also report the adsorption enthalpy of molecularly adsorbed formic acid on Ni(111) at 120–155 K.

Nickel is an important metal catalyst in many chemical applications where formate is an adsorbed intermediate, e.g., steam reforming of hydrocarbons and water-gas shift [16,17]. The (111)

\* Corresponding author at: Department of Chemistry, University of Washington, Seattle, WA 98195, United States.

E-mail address: [charliec@uw.edu](mailto:charliec@uw.edu) (C.T. Campbell).

surface is the most thermodynamically-stable Ni facet and thus it has been widely studied as a well-defined model for Ni-related catalysts.

Previously, the adsorption and dissociation of formic acid on Ni(111) were experimentally studied by temperature-programmed desorption (TPD) [18,19], infrared reflection adsorption spectroscopy (IRAS) [18,20] and time-resolved sum-frequency generation (SFG) spectroscopy [11–13,20]. It has been agreed that formic acid molecularly adsorbs on Ni(111) at low temperatures (<190 K) and that gaseous formic acid monomers dissociatively adsorb to form adsorbed formate and adsorbed hydrogen at elevated temperatures above 225 K. Formate was found stably bonding to the Ni(111) surface in the bidentate configuration (i.e., the two oxygen atoms separately bond to two neighboring Ni atoms) at 250 K, and the monodentate form has not been reported except in one unusual case. Adsorbed bidentate formate was reported to transform transiently into unstable monodentate formate by the rapid laser-induced temperature jump of ~300 K, which was well studied by the time-resolved SFG studies [11–13,20].

Here, we directly measure the heat of molecular adsorption and dissociative adsorption of formic acid monomers onto clean Ni(111) at different temperatures (120–240 K) by calorimetry under ultrahigh vacuum conditions, and extract the enthalpy of formation and the bonding enthalpy of adsorbed bidentate formate on Ni(111). These energetic values not only serve as benchmarks for theoretical studies to improve the accuracy of calculation methods such as DFT, but they also help clarify the energetics of important elementary reaction steps that occur in catalysis on nickel surfaces.

## 2. Experimental

The experiments were performed in an ultrahigh vacuum (UHV) chamber (base pressure <  $2 \times 10^{-10}$  mbar), designed for single-crystal adsorption calorimetry (SCAC) and surface analysis, as described previously [21,22]. Briefly, the chamber is equipped with low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), low-energy ion scattering spectroscopy (LEIS), a quadrupole mass spectrometer (QMS) and a liquid-nitrogen-cooled quartz crystal microbalance (QCM).

The Ni(111) sample used here is a 1  $\mu\text{m}$  thick single-crystal foil, supplied by Jacques Chevallier at Aarhus University in Denmark and the surface was cleaned by cycles of  $\text{Ar}^+$  ion sputtering and annealing. A detailed description of the experimental principles and implementation of the molecular beam flux, sticking probability, and heat measurements can be found elsewhere [21–23]. Briefly, the Ni(111) surface, held at different temperatures, was exposed to a pulsed molecular beam of formic acid and the heat of adsorption and sticking probability were recorded simultaneously. The heat of adsorption was detected using a pyroelectric heat detector pressed against the back of the Ni(111) crystal, and the sticking probability was measured with the QMS. The beam was created by expanding ~2 mbar of formic acid through a microchannel array and then collimated through a series of five liquid nitrogen cooled orifices, and chopped into 102 ms pulses every 5 s with a rotating chopper blade. The microchannel array was heated and kept at 360 K to reduce gas-phase dimerization to less than 1% [24]. We define the coverage of formic acid molecules which adsorb onto the surface irreversibly in units of monolayers (ML) where  $1 \text{ ML} = 1.86 \times 10^{19}$  atoms/ $\text{m}^2$ , which is the surface atom density of Ni(111). A typical dose is 0.007 ML (~ $1.2 \times 10^{12}$  molecules within the beam diameter of ~4 mm) per formic acid pulse.

## 3. Results

### 3.1. Sticking probability

The short-term ( $S_{102\text{ms}}$ ) and long-term ( $S$ ) sticking probabilities of formic acid on clean Ni(111) were measured at four temperatures, as shown in Fig. 1. The coverage reported here and elsewhere represents the formic acid permanently adsorbed, regardless of the products produced. The long-term sticking probability is the probability that a gas molecule strikes the sample surface, sticks, and remains until the next gas pulse starts ~5 s later, which is used to calculate the adsorbate coverage remaining at the start of the next gas pulse. The short-term sticking probability is the probability that a gas molecule strikes the sample surface, sticks, and remains at least throughout the time window of our heat measurement (i.e., the first 102 ms). This is used to calculate the number of moles of gas-phase reactant that contribute to the measured heat of adsorption. At all temperatures, the initial sticking probabilities are high (>0.8) and slightly increase as more formic acid molecules adsorb, indicating a precursor-mediated adsorption mechanism. At 120 K, the formic acid molecularly adsorbs on the surface and forms a multilayer (see below), with both the long-term and short-term sticking probabilities almost unity even to multilayer coverages. At 155 K, the long-term sticking probability quickly decreases to zero between 0.35 and 0.45 ML, while the short-term sticking probability remains high (>0.85). This indicates that the first adlayer of formic acid on Ni(111) saturates at 0.45 ML, but that formic acid still transiently adsorbs with high probability on that saturated adlayer and desorbs again slowly (but before the next pulse arrives 5 s later). The formic acid is only molecularly adsorbed at 155 K, and does not yet dissociate (see below). For 210 K and 240 K, where formic acid dissociates to make formate and  $\text{H}_{\text{ad}}$  at low coverages (see below), the long-term sticking probabilities decline earlier than at 155 K, with saturation coverages of 0.20 ML for 210 K and 0.14 ML for 240 K, while the short-term sticking probabilities stay high (>0.85), similar to 155 K. Again, this indicates that the formic acid molecules transiently adsorb on the surface after saturation, but desorb again within 5 s before the next pulse.

### 3.2. Heats of adsorption

In this paper, the term heat of adsorption is defined as the negative of the differential standard molar enthalpy change for the

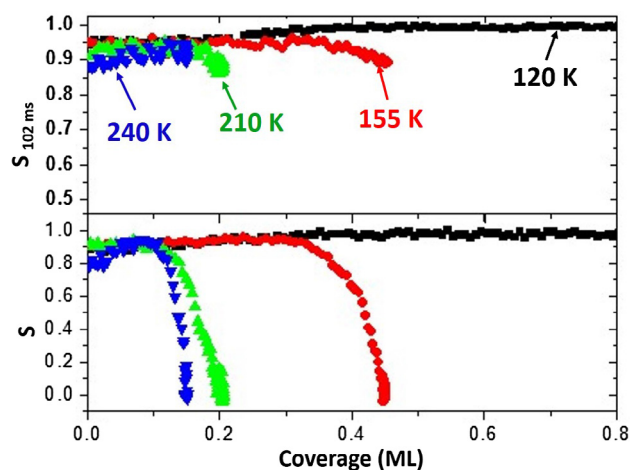


Fig. 1. Short-term (top) and long-term (bottom) sticking probabilities of formic acid on clean Ni(111) at 120, 155, 210, and 240 K as a function of total formic acid coverage that adsorbed irreversibly, irrespective of whether it dissociated.

Download English Version:

<https://daneshyari.com/en/article/6455397>

Download Persian Version:

<https://daneshyari.com/article/6455397>

[Daneshyari.com](https://daneshyari.com)