doi:10.1246/cl.2012.1004

# Behavior of Formate Adsorbed on Cu(110) When Exposed to Hydrogen Gas

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The behavior of formate adsorbed on Cu(110) surface exposed to hydrogen gas was investigated at 300–330 K. Although an exchange reaction from D–COO(a) to H–COO(a) was observed after exposing a DCOO(a)-covered Ni(110) surface to $H_2$ in a previous report, this did not occur with Cu(110). The preadsorbed DCOO(a) desorbed as DCOOH after accepting a hydrogen atom from a gaseous $H_2$ molecule.

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The observation of adsorbate behavior in the presence of gaseous molecules is indispensable for elucidating the mechanisms of heterogeneous catalysis. To understand the behavior of reactant molecules, the use of well-defined single-crystal surfaces and in situ observation of the adsorbates are helpful. Formate has been observed as an important adsorbate (intermediate) in various heterogeneous catalytic reactions,[1,2] and the reactivity of the formate adsorbed on a metal surface is a subject worthy of careful study.

In a previous study, Yamakata et al. reported that when $H_2$ was introduced on DCOO(a)-covered Ni(110) surface at 300 K, a C–D bond was broken and the D–COO(a) species were exchanged to H–COO(a).[3] In this study, hydrogen was similarly introduced on DCOO(a)-covered Cu(110) surface at 300–330 K, well below the temperature at which the decomposition of formate proceeds, and the behaviors were observed using infrared reflection absorption spectroscopy. The behavior was found to be different from that for formate adsorbed on Ni(110). In addition, we carried out kinetic analysis of the desorption behaviors.

All of the present experiments were carried out in an ultrahigh vacuum chamber equipped with a quadrupole mass analyzer and LEED-AES optics at base pressures below $2 \times 10^{-10}$ Torr (1 Torr = 133.32 Pa), as described previously.[4] In the infrared reflection absorption spectroscopy measurements, a narrow-band mercury–cadmium–telluride detector was used with a Mattson RS-2 spectrometer. A p-polarized infrared beam irradiated the surface at an incident angle of 83° passing through a NaCl window.

The Cu(110) surface was cleaned by $Ar^+$ ion bombardment and annealed at about 780 K. The temperature of the crystal was controlled to within ±0.1 K using a programmable temperature controller and was measured by a chromel–alumel thermocouple spot-welded onto the back of the crystal. The formic acid DCOOD was dried completely by anhydrous copper sulfate and purified by vacuum distillation and freeze–pump–thaw cycles.

Observations of DCOO(a)-covered Cu(110) surface exposed to gaseous $H_2$ were carried out using infrared reflection absorption spectroscopy in the following manner. The Cu(110) surface was sufficiently exposed to DCOOD gas until it was fully covered with DCOO(a) at 300 K. Using about 10 L (Langmuir) of formic acid, a fully covered surface of formate was obtained. After evacuation of the chamber to below $1 \times 10^{-9}$ Torr, hydrogen $H_2$ gas was introduced into the chamber, and infrared reflection absorption spectra were obtained. The resolution was set to 4 cm$^{-1}$, and 1024 scans were averaged to obtain each spectrum. These measurements were made at several surface temperatures in the range of 300–330 K and several pressures in the range of $2.5 \times 10^{-6}$–$1.0 \times 10^{-5}$ Torr. In the temperature-programmed desorption measurements, the formate was adsorbed on Cu(110) at 300 K, and decomposition products were monitored by rising temperature.

Figure 1a shows an infrared reflection absorption spectrum of fully covered formate DCOO(a) on a Cu(110) surface at 300 K under vacuum. The peaks at 2173 and 1329 cm$^{-1}$ were

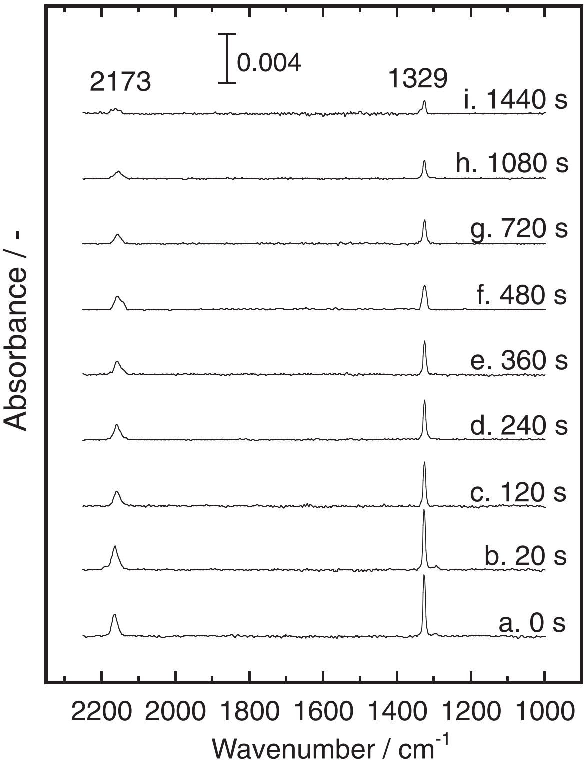

**Figure 1.** Infrared reflection absorption spectra of formate DCOO(a) with $H_2$ gas at 300 K, and at a pressure of $5 \times 10^{-6}$ Torr.

assigned to the $\nu$(C–D) and $\nu_s$(OCO) bands of DCOO(a), respectively.[3,4] Note that peaks of the in-plane and out-of-plane C–D deformation modes and $\nu_{as}$(OCO) of DCOO(a), which were expected at 1000–1800 $cm^{-1}$, were not observed. Considering the surface selection rules of infrared reflection absorption spectroscopy, the absence of these deformation modes and the asymmetric stretching mode in the spectrum indicates that the C–D bond is perpendicular to the surface.[3]

Figures 1b–1i show infrared reflection absorption spectra of formate DCOO(a) adsorbed surface exposed to $H_2$ gas at 300 K. When $H_2$ gas at $5 \times 10^{-6}$ Torr was introduced onto the surface, the peak intensities of the $\nu$(C–D) and $\nu_s$(OCO) bands of preadsorbed DCOO(a) decreased with increasing exposure time. As a result of temperature-programmed desorption measurement, the adsorbed DCOO(a) was decomposed into $CO_2$ and $D_2$ around 450 K. This decreasing the peak intensities was observed at a temperature (300 K) well below the decomposition temperature of formate. In addition, no products associated with the decomposition of formic acid, such as CO, $CO_2$, and $D_2$, were observed by the quadrupole mass analyzer. Therefore, the preadsorbed formate was desorbed as formic acid by the transfer of hydrogen atoms from the $H_2$ gas, as given in eq. 1.

$$\mathrm{DCOO(a)} + \frac{1}{2}\mathrm{H_2(g)} \rightarrow \mathrm{DCOOH(g)} \qquad (1)$$

Yamakata et al. reported that the C–D bond was broken and D–COO(a) was exchanged for H–COO(a) when a DCOO(a)-adsorbed Ni(110) surface was exposed to $H_2$ gas.[3] Furthermore, no desorption of adsorbed formate species was observed. On a Cu(110) surface, this exchange reaction was not observed, but the desorption was observed.

In order to investigate the desorption process in more detail, kinetic analysis was performed. The rate of the desorption ($r$) is defined as

$$r = -k\theta^{m}{}_{\mathrm{DCOO}}P^{n}{}_{\mathrm{H_2}} \qquad (2)$$

where $k$, $\theta_{\mathrm{DCOO}}$, and $P_{\mathrm{H_2}}$ are the rate constant, the coverage of DCOO(a), and the hydrogen gas pressure, respectively. The superscripts $m$ and $n$ represent the orders of desorption with respect to the formate coverage and the pressure of $H_2$ gas, respectively.

The desorption order $m$ was determined. The coverage of DCOO(a) was estimated from the peak areas in Figure 1. The total coverage at 0 s (Figure 1a) was normalized to 1 monolayer (ML). A good linear relationship between $\ln \theta_{\mathrm{DCOO}}$ and time was obtained, as shown in Figure 2, confirming that the rate of desorption was first order with respect to formate coverage. The observations ($m = 1$) suggest that the desorption occurs uniformly on the surface.

The order of desorption with respect to hydrogen pressure $n$ was also determined. The parameter $n$ was estimated to be 0.87 at 300 K in the $H_2$ pressure range of $2.5 \times 10^{-6}$ to $1.0 \times 10^{-5}$ Torr, as shown in Figure 3a. If the rate-determining step is the adsorption of hydrogen molecules on the formate-adsorbed surface, the value of $n$ should be unity. The smaller value of 0.87 ($<1$) indicates that the rate-determining step is the reaction between the DCOO(a) and hydrogen adsorbed.

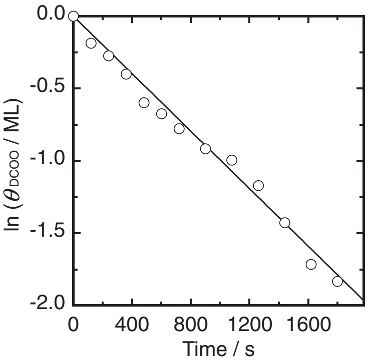

**Figure 2.** Relationship between the coverage and time at 300 K, and at a pressure of $5 \times 10^{-6}$ Torr.

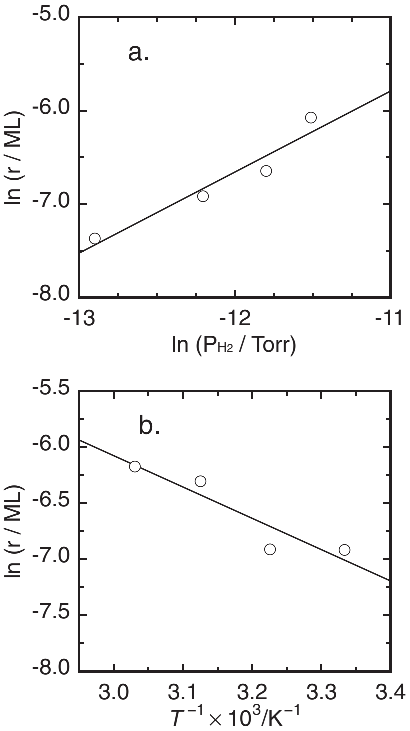

**Figure 3.** Dependence of desorption rate on pressure of $H_2$ gas at 300 K (a), Arrhenius plot at a pressure of $5 \times 10^{-6}$ Torr (b).

The activation energy of the desorption was determined by measuring the rate of desorption at a fixed $H_2$ pressure of $5.0 \times 10^{-6}$ Torr while varying the temperature between 300 and 330 K. The Arrhenius plot is shown in Figure 3b, and the activation energy was estimated to be 23 kJ $mol^{-1}$.

The difference in the behavior of adsorbed formate on Cu(110) and Ni(110) depends on the factors such as the adsorption structure on the surface, the interaction between formate and metal surface. Around 10 L of formic acid was required to fully cover the clean Cu(110) surface, mentioned earlier. However, a fully covered surface could be obtained by exposing a clean Ni(110) surface to less than 5 L of formic acid,[5] suggesting that the sticking probability of formic acid on Ni(110) was higher than on Cu(110). The formic acid on Ni(110) may also be more tightly bound than on Cu(110). Therefore, under certain conditions, the formate might desorb more easily on Cu(110) because of this weaker interaction but not desorb on Ni(110).

In conclusion, when a DCOO(a)-covered Cu(110) surface was exposed to $H_2$ gas, the preadsorbed DCOO(a) desorbed as DCOOH, revealing the transfer of a hydrogen atom from $H_2$. The exchange reaction from DCOO(a) to HCOO(a) observed for Ni(110), reported previously, did not occur on Cu(110). We considered that this was a result of difference in the interaction between the metal surface and the formate. The desorption order with respect to the hydrogen pressure was 0.87, and the desorption order with respect to the formate coverage was unity, suggesting that the rate-determining step was the reaction between the preadsorbed formate and hydrogen adsorbed on the surface and that the reaction occurred uniformly on the surface.

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