

Exchange Reaction of Adsorbed Formate with Gaseous Formic Acid on Ni(110) Studied by Time-Resolved Fourier Transform Infrared Reflection Absorption Spectroscopy

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The dynamic behavior of adsorbed formate on Ni(110) in the presence of gaseous formic acid was studied by time-resolved infrared reflection absorption spectroscopy. The preadsorbed formate (DCOO(a)) was replaced by the postexposed formic acid (HCOOD) to form HCOO(a) on Ni(110) in the temperature region between 230 and 300 K, where the formate was stable under vacuum and no decomposition of formate was observed. It was confirmed that the preadsorbed DCOO(a) desorbed as DCOOD accompanied by formation of HCOO(a) via the deuterium atom transfer from HCOOD.

Introduction

The surface reactions of adsorbed species under gaseous molecules are often different from those under vacuum.¹ For example, the desorption of CO(a) from metal surfaces is known to be affected by the presence of gas-phase CO^{2–5} and NO.⁶ These phenomena have been well-known in terms of “adsorption-assisted desorption (AAD)”.^{1–6} The presence of gas-phase molecules affects the behavior of not only the simple processes such as adsorption and desorption but also some more complex processes such as the decomposition of formate.^{7–10} The enhancement of the rate of decomposition of formate and the decrease of its activation energy by the presence of gas phase molecules have been reported for Ni/SiO₂⁷ and Cu/SiO₂⁸ catalysts. It was also reported that the structure of formate changed when formic acid vapor was introduced on formate-covered Cu(100)⁹ and NiO(111)¹⁰ surfaces.

The characterization of the behavior of adsorbates in the presence of reactant molecules in the gas phase is indispensable for elucidating the mechanism of heterogeneous catalysis. In an earlier study by Tamaru and co-workers in the 1960's, it was proposed that the surface formate on Ni/SiO₂ desorbs as formic acid in the presence of formic acid in the ambient gas phase.¹¹ Although the formation of formate from formic acid has been considered to be irreversible on most metal surfaces,¹² the formate does desorb as formic acid in the presence of formic acid in the gas phase. For understanding the reaction mechanism, the use of well-defined single-crystal surfaces and in situ observation of the adsorbates are useful. In the present study, we observed that adsorbed formate on Ni(110) readily desorbed as formic acid by the exposure to formic acid at 230–300 K by means of time-resolved infrared reflection absorption spectroscopy (TR-IRAS), well below the temperature where decomposition of formate proceeds (above 340 K).

Experimental Section

All experiments were carried out in an ultrahigh vacuum chamber equipped with a quadrupole mass analyzer (Q-MS) and LEED–AES optics with base pressures below 2×10^{-10} Torr as described previously.^{13,14} The Ni(110) surface was cleaned by Ar ion sputtering and annealed at 1023 K. The formic acid (HCOOD, DCOOD, and H¹³COOH from Isotec Inc.; 95% in water solution) was dried completely by anhydrous copper sulfate and purified by vacuum distillation and freeze–pump–thaw cycles.

For IRAS measurement, a narrow-band mercury cadmium telluride detector was used with Mattson RS 2 spectrometer. Real-time observation of the exchange process between adsorbed formate and gas-phase formic acid on a Ni(110) surface was made by TR-IRAS. The TR-IRA spectra were obtained every 9.04 s with a resolution of 4 cm^{–1} and averaged over 100 scans for a spectrum.

Results and Discussion

We first examined the structure of formate formed by exposure to DCOOD on Ni(110) by means of IRAS under vacuum as shown in Figure 1a. The peaks around 2188, 1334, and 770 cm^{–1} are assigned to the $\nu(\text{C–D})$, $\nu_s(\text{OCO})$, and $\delta_s(\text{OCO})$ bands of DCOO(a), respectively.^{13,14} It is noted that the peaks of in-plane and out-of-plane C–D deformation modes and $\nu_{as}(\text{OCO})$ of DCOO(a), which are expected at around 1000–1800 cm^{–1}, were not observed. On the basis of the surface selection rules of IRAS, the absence of these deformation modes on the spectrum shows that the C–D bond is perpendicular to the surface.^{13,14} A small amount of the contamination of CO(a) and HCOO(a) was also observed on the Ni(110) surface fully covered by DCOO(a). A weak peak around 1360 cm^{–1}

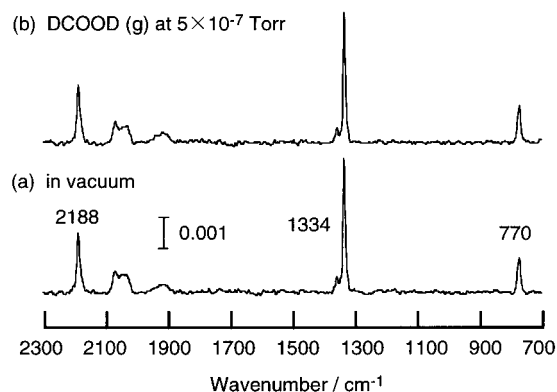


Figure 1. IR spectra of DCOO(a) formed on Ni(110) at 300 K after sufficient evacuation (a) and in the presence of DCOOD gas at a pressure of 5×10^{-7} Torr (b).

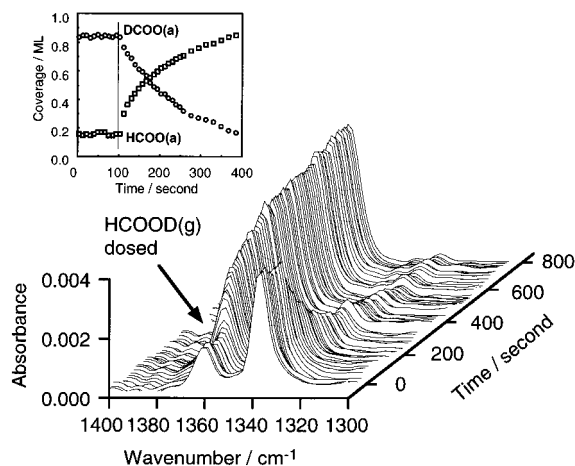


Figure 2. TR-IRA spectra of the $\nu_s(\text{OCO})$ bands of formate during the exchange reaction of DCOO(a) with gas-phase HCOOD on Ni(110) at 300 K. HCOOD was at a pressure of 5×10^{-7} Torr at $t = 100$ s. The spectra were obtained every 9.04 s with a resolution of 4 cm^{-1} and 100 scans per spectrum. The inset in Figure 2 demonstrates the time course of the change of the amounts of DCOO(a) (○) and HCOO(a) (□) by exposing DCOO(a)-covered Ni(110) to HCOOD at 300 K. These plots were estimated from the integration of the TR-IRA spectra shown in Figure 2. The total coverage at $t = 0$ was normalized to 1 monolayer (ML).

is assigned to the band of $\nu_s(\text{OCO})$ of HCOO(a), which was introduced by an isotope impurity contained in the DCOOD gas. The small peaks at 1920, 2035, and 2075 cm^{-1} are assigned to the $\nu(\text{CO})$ band of the coadsorbed CO. The amount of the coadsorbed CO was less than 5% of the surface Ni atoms, and it did not change on further exposure to formic acid at 300 K.^{13,14}

Next, the change of the IR spectrum of DCOO(a) in the presence of formic acid vapor was studied. When DCOO(a)-covered Ni(110) was exposed to DCOOD gas at a pressure of 5×10^{-7} Torr at 300 K (Figure 1b), no changes in the IR spectrum, such as an increment of those peak intensities, were observed compared with that obtained in vacuum (Figure 1a). However, when the isotopically labeled formic acid (HCOOD¹⁵) was introduced to a DCOO(a)-covered surface, the IR spectra significantly changed. Figure 2 shows TR-IRA spectra of formate (DCOO(a)) with the isotopically labeled gaseous HCOOD at 300 K. The IR spectra during the first 100 s ($0 < t < 100$ s) showed the band of DCOO(a) at 1334 cm^{-1} and a small one at 1360 cm^{-1} due to HCOO(a) as mentioned above. When HCOOD vapor of 5×10^{-7} Torr was introduced onto the surface at $t = 100$ s, the peak intensity of the $\nu_s(\text{OCO})$ band of preadsorbed DCOO(a) started to decrease, whereas the band

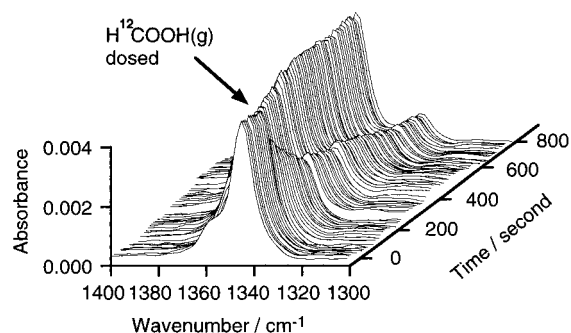
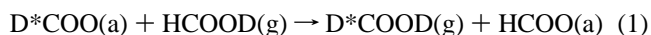


Figure 3. TR-IRA spectra of the $\nu_s(\text{OCO})$ bands of formate during the exchange reaction of $\text{H}^{13}\text{COO(a)}$ with gas-phase H^{12}COOH on Ni(110) at 300 K. H^{12}COOH was at a pressure of 5×10^{-7} Torr at $t = 100$ s. The spectra were obtained every 9.04 s with a resolution of 4 cm^{-1} and 100 scans per spectrum.

assigned to $\nu_s(\text{OCO})$ of HCOO(a) started to increase. The coverages of DCOO(a) and HCOO(a) estimated from the peak intensities in Figure 2 are plotted in the inset of Figure 2 as a function of time. Figure 2 clearly shows that the formate is stable at 300 K in vacuum because the coverage of DCOO(a) and HCOO(a) stayed unchanged for the first 100 s; neither desorption nor decomposition of formate takes place in vacuum at 300 K. The simultaneous decrement of DCOO(a) and increment of HCOO(a) due to the introduction of HCOOD indicates that DCOO(a) was exchanged by HCOO(a). It is noted that during the exchange reaction, the total coverage of formate (DCOO(a) + HCOO(a)) was unchanged.

The more direct evidence for the exchange of formate by the exposure to formic acid was obtained by the isotope labeling of the carbon of preadsorbed formate. Figure 3 shows the change in the TR-IRA spectra by the exposure of $\text{H}^{13}\text{COO(a)}$ -covered Ni(110) to H^{12}COOH vapor. The experimental conditions are the same as those of the above experiments. The main peak at 1345 cm^{-1} is assigned to the $\nu_s(\text{OCO})$ band of $\text{H}^{13}\text{COO(a)}$, and a small peak at 1360 cm^{-1} is assigned to the $\nu_s(\text{OCO})$ band of $\text{H}^{12}\text{COO(a)}$, which is contained in H^{13}COOH gas as an isotope impurity. When H^{12}COOH was introduced onto the $\text{H}^{13}\text{COO(a)}$ -covered surface at $t = 100$ s, the peak intensity of the $\nu_s(\text{OCO})$ band of preadsorbed $\text{H}^{13}\text{COO(a)}$ began to decrease, whereas that of $\nu_s(\text{OCO})$ of $\text{H}^{12}\text{COO(a)}$ started to increase as in the case of DCOO(a) shown in Figure 2.

Figures 2 and 3 demonstrate the exchange reaction of the preadsorbed DCOO(a) to HCOO(a) and $\text{H}^{13}\text{COO(a)}$ to $\text{H}^{12}\text{COO(a)}$ by the exposure to HCOOD and H^{12}COOH , respectively. These results confirm that the preadsorbed formate was exchanged to the formate supplied by the postexposed formic acid. The exchange reaction was observed even at temperatures as low as 230 K. Thus, it is concluded that the preadsorbed formate desorbed as formic acid by the transfer of a hydrogen atom from the postexposed formic acid as shown in eq 1:

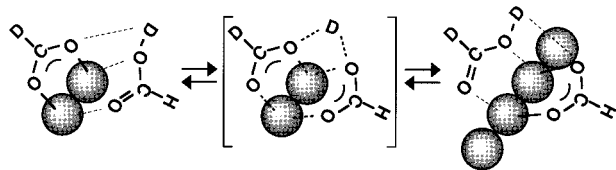


The formation of formate from formic acid on Ni(110) has been considered to be irreversible in vacuum according to eq 2,¹² and as we previously reported, the formate did not desorb as formic acid by the exposure of the formate-covered Ni(110) surface to hydrogen.¹³



The exchange reaction should be driven by the adsorption of postexposed formic acid on the surface. The reaction sites on

SCHEME 1: Proposed Mechanism of Exchange Reaction of Formate with Molecular Formic Acid on Ni(110)



which the exchange reaction occurs may be the site where the formate is preadsorbed because the vacant site where formic acid possibly adsorbs is already occupied by the formate. Since the hydrogen atoms on formate-covered Ni(110) readily desorb as H_2 above 240 K,¹³ the transfer of the hydrogen atom should proceed directly from formic acid to formate. The exchange reaction seems to proceed via formation of a hydrogen-bonded intermediate complex between postexposed formic acid and preadsorbed formate on the same site as shown in Scheme 1. The more detailed kinetics and mechanism of this exchange reaction is now under investigation.

In summary, in situ observation of formate on Ni(110) under gas-phase formic acid confirmed the rapid replacement of formate with gas-phase formic acid by means of TR-IRAS. It was indicated that the preadsorbed formate was desorbed as

formic acid by the direct transfer of a hydrogen atom from postexposed formic acid below the decomposition temperature.

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- (15) In this experiment, we used HCOOD instead of HCOOH in order to avoid the C-H/C-D isotope exchange reaction of preadsorbed DCOO- (a) with H(a) as demonstrated in our previous work (ref 13).