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Behavior of Adsorbed Formate in the Presence of Gaseous Formic Acid on Cu(110)

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Abstract Pre-adsorbed DCOO(a) on Cu(110) was exchanged with HCOO(a) in the presence of HCOOD gas at 300 K. The DCOO(a) desorbed as DCOOD after accepting a deuterium atom from the introduced HCOOD. The exchange reaction rate on Cu(110) was over 5 times faster than that on Ni(110) reported previously. This was a result of differences in the interactions between the metal surfaces and the formate.

Keywords Cu(110) · Exchange reaction · Formate · Gaseous formic acid

1 Introduction

Well-defined single crystal surfaces have been used to clarify surface reaction mechanisms. One of the most important research subjects in surface science is the elucidation of catalytic reaction mechanisms. Observation of the state and dynamic behavior of adsorbates under reaction conditions is indispensable in developing an understanding of catalysis, because the behavior of adsorbates in the presence of gas phase molecules is often different from the behavior in vacuum [1]. Even the desorption of adsorbed CO from a metal surface is affected by the presence of gaseous CO [2] and NO [3]. The activation energy for the desorption of adsorbed CO in the presence of gaseous CO has been reported to be much lower than in vacuum [2]. These phenomena are well known as adsorption-assisted desorption [1–5].

The presence of gas phase molecules sometimes affects not only reversible processes such as adsorption and desorption, but also irreversible processes such as the decomposition of an adsorbate. An increased reaction rate and a decreased activation energy of formate decomposition have been reported for Ni/SiO_2 [6] and Cu/SiO_2 [7] catalysts in the presence of gas phase formic acid. Although formate is generated as an intermediate in methanol decomposition on Cr_2O_3, this formate decomposes on Cr_2O_3 at 533 K if methanol is present in the ambient gas, whereas the formate remains stable under vacuum at the same temperature [8].

The marked difference between the presence and absence of gas phase molecules may be attributed to interactions between the pre-adsorbed species and incident molecules from the gas phase. We studied the state and behavior of formate on Cu(110) in the presence of gas phase formic acid using time-resolved infrared reflection absorption spectroscopy (TR-IRAS). Pre-adsorbed formate was exchanged with gas phase formic acid via hydrogen atom transfer. The exchange reaction of formate with gaseous formic acid was originally observed on Ni/SiO_2 in the 1960s [9], and was directly observed on a well-defined Ni(110) surface [10, 11]. A similar exchange reaction was observed on Cu(110), but its reaction rate was faster than on Ni(110). We also carried out the kinetic analysis of the exchange reaction.

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2 Experimental

All of the experiments were carried out in an ultrahigh vacuum chamber equipped with a quadrupole mass analyzer and LEED-AES optics at base pressures below 2×10^{-10} Torr (1 Torr = 133.32 Pa), as described previously [10, 11]. For IRAS measurements, a narrow-band mercury cadmium telluride (MCT) detector was used with a Mattson RS-2 spectrometer. A *p*-polarized infrared beam was used to irradiate 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 780 K. The sample temperature was controlled to within ±0.1 K using a programmable temperature controller, and was measured by a chromel–alumel thermocouple spot-welded to the back of the crystal. The formic acid (HCOOD, DCOOD) was dried completely by anhydrous copper sulfate and purified by vacuum distillation and freeze–pump–thaw cycles.

Real-time observation of the exchange process between adsorbed formate and gas phase formic acid on a Cu(110) surface was made by TR-IRAS 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. After evacuation of the chamber to below 1×10^{-9} Torr, data acquisition commenced. TR-IRA spectra with a resolution of 4 cm^{-1} were obtained approximately every 9.04 s, and these were averaged over 100 scans to generate a spectrum. HCOOD gas was introduced to the chamber at a constant pressure through electrically operated valves after data acquisition had began. These measurements were made at several surface temperatures in the range of 300–330 K, and at several pressures in the range of 1×10^{-8}–5×10^{-7} Torr. These values were set in the range of measurable reaction rate. In the normal IRA spectra (Fig. 1), the resolution was 4 cm^{-1} and 1,024 scans were averaged to obtain a spectrum. In the temperature programmed desorption (TPD) measurements, five different mass numbers were simultaneously monitored.

3 Results and Discussion

3.1 Exchange Reaction

Figure 1a shows an IRA spectrum of adsorbed formate on Cu(110) under vacuum. The peaks around 2173, 1329, and 762 cm^{-1} are assigned to the ν(C-D), ν_s(OCO), and δ(OCO) bands of DCOO(a), respectively [10, 12]. The peak at 1,293 cm^{-1} is also assigned to ν_s(OCO), which is a chemically distinct species from that associated with the peak at 1,329 cm^{-1} [13]. Peaks of the in-plane and out-of-plane C-D deformation modes and ν_{as}(OCO) of DCOO(a), which were expected at 1,000–1,800 cm^{-1}, were not observed. On the basis of the surface selection rules of IRAS, the absence of these deformation modes and the asymmetric stretching mode from the spectrum indicates that the C-D bond is perpendicular to the surface [12]. Figure 2 shows the relationship between the peak area of ν(C-D), ν_s(OCO) and exposure amount of DCOOD gas on a clean Cu(110) surface. By using about 10 L (Langmuir) of formic acid, a fully covered surface of formate was obtained. Additional formic acid exposure did not change the peak area.

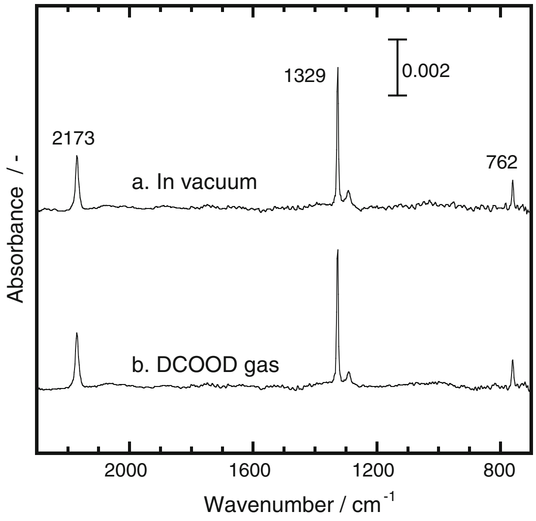

Fig. 1 IRA spectra of DCOO(a) formed on Cu(110) at 300 K after sufficient evacuation (*a*) and in the presence of DCOOD gas at a pressure of 5×10^{-8} Torr (*b*)

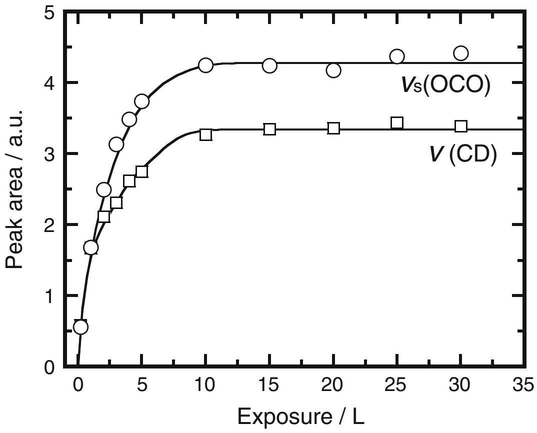

Fig. 2 Relationship between the peak area and exposure amount of DCOOD gas at 300 K

The changes in the IRA spectrum of DCOO(a) in the presence of formic acid vapor were studied. When DCOO(a)-covered Cu(110) was exposed to DCOOD gas at a pressure of 5×10^{-8} Torr at 300 K (Fig. 1b), no changes in the IRA spectrum, such as an increased intensity of those

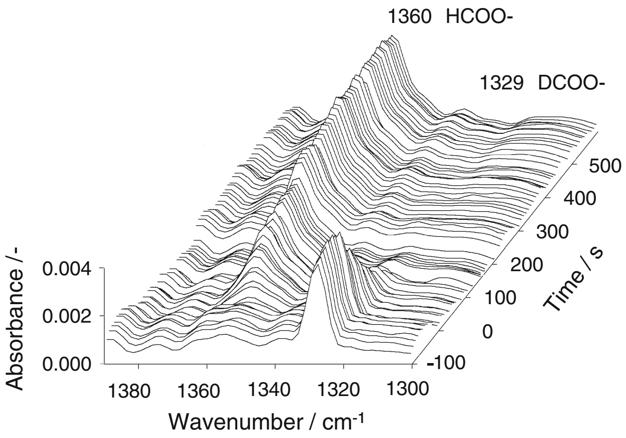

Fig. 3 TR-IRAS during the exchange reaction of DCOO(a) with gas-phase HCOOD on Cu(110) at 300 K, at a pressure of 5 × 10^{-8} Torr

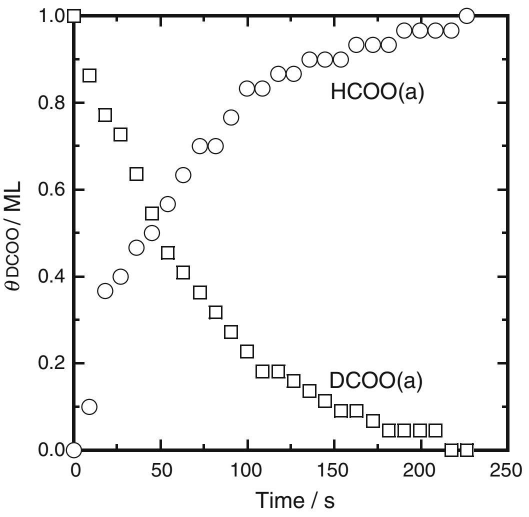

Fig. 4 Changes in DCOO(a) and HCOO(a) coverages during the exchange reaction

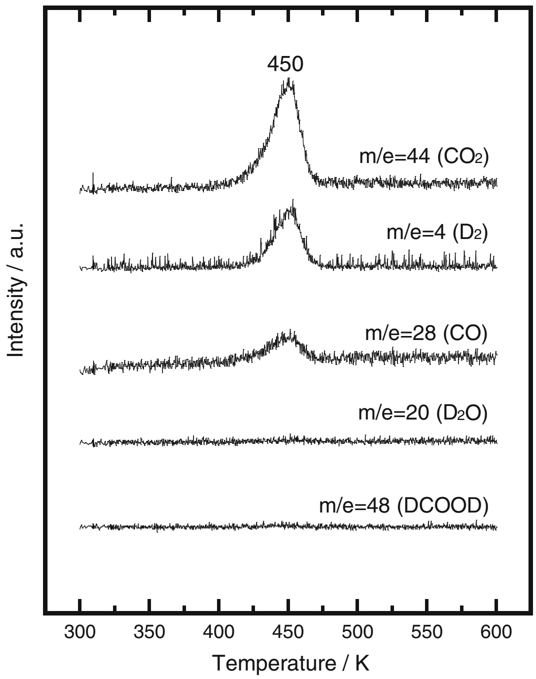

Fig. 5 TPD curves of DCOO(a) adsorbed on Cu(110)

IRAS peaks (ν(C-D), ν_s(OCO), and δ(OCO) bands), were observed compared with a spectrum obtained in vacuum (Fig. 1a). However, when isotopically labeled formic acid HCOOD was introduced to the DCOO(a)-covered surface, the IRA spectra changed significantly. Figure 3 shows TR-IRA spectra of the surface exposed to gaseous HCOOD at 300 K. The IRA spectra from −100 to 0 s (during the first 100 s) contained a ν_s(OCO) band associated with DCOO(a) at 1,329 cm^{-1}. When HCOOD vapor at 5 × 10^{-8} Torr was introduced onto the surface at 0 s (100 s later), the peak intensity of the ν_s(OCO) band due to the pre-adsorbed DCOO(a) began to decrease, whereas that of the ν_s(OCO) band due to HCOO(a) at 1,360 cm^{-1} began to increase. The coverages of DCOO(a) and HCOO(a) were estimated from the peak areas, and the changes in these coverages are shown in Fig. 4 as a function of time. In previous reports [14], the formate could form 0.5 monolayer (ML) c(2 × 2) structures, and a high coverage (0.67 ML) (3 × 1) structure when formic acid reacted with more than 0.25 ML coverage of O atoms. In this study, the total coverage at 0 s was normalized to 1 ML. The simultaneous decrease in DCOO(a) and increase in HCOO(a) due to the introduction of HCOOD indicate that DCOO(a) is exchanged with HCOO(a). Note that during the exchange reaction, the total coverage of formate (DCOO(a) + HCOO(a)) remained unchanged.

Figure 5 shows TPD curves of D_2 ($m/e = 4$), D_2O ($m/e = 20$), CO ($m/e = 28$), CO_2 ($m/e = 44$), and DCOOD ($m/e = 48$) from a fully covered surface of formate DCOO(a) on Cu(110) at 300 K. The adsorbed formate DCOO(a) decomposed into CO_2 and D_2 around 450 K. The CO peak at 450 K was assigned to the cracking of CO_2.

This exchange reaction was observed at a temperature (300 K) well below the decomposition temperature of the adsorbed formate. The pre-adsorbed formate desorbed as formic acid after the transfer of a hydrogen (deuterium) atom from the formic acid, as given in Eq. (1).

$$\mathrm{DCOO(a)} + \mathrm{HCOOD(g)} \rightarrow \mathrm{DCOOD(g)} + \mathrm{HCOO(a)} \tag{1}$$

This phenomenon should be regarded as adsorption-assisted desorption, which has been well studied in the case of CO [2]. However, in the present case, the mechanism of the exchange reaction is more complex than for CO(a), because the replacement proceeds through a chemical

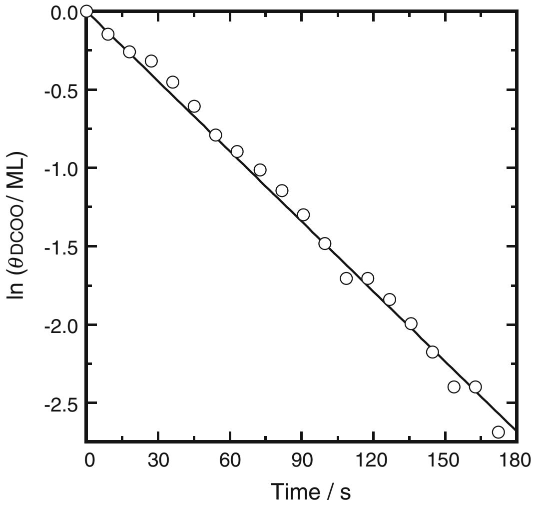

Fig. 6 Relationship between the coverage and time

reaction; the hydrogen atom is transferred from the incident formic acid to the pre-adsorbed formate. Although the formate remained stable under vacuum, it was easily exchanged under gas phase formic acid.

3.2 Kinetic Analysis

To investigate the exchange reaction in more detail, a kinetic analysis was performed. The rate of the exchange reaction (r) can be defined as

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

where k, θ_{DCOO}, and P_{HCOOD} are the rate constant, the coverage of DCOO(a), and the pressure of HCOOD, respectively. The superscripts m and n represent the reaction orders with respect to DCOO(a) coverage and HCOOD pressure, respectively.

The reaction order m was determined. A good linear relationship between ln θ_{DCOO} and time was obtained, as shown in Fig. 6, confirming that the rate of the reaction was first order with respect to formate coverage. This suggests that the reaction occurs uniformly at total sites on the surface.

Next, the reaction order with respect to formic acid pressure n was determined. The value of n was estimated to be 0.3 at 300 K for HCOOD pressures ranging from 1×10^{-8} to 5×10^{-7} Torr, as shown in Fig. 7. If the rate-determining step is the adsorption of HCOOD molecules on the DCOO(a)-adsorbed surface, the value of n should be unity. The much smaller value of 0.3 (<1) indicates that the rate-determining step is the reaction between pre-adsorbed DCOO(a) and adsorbed HCOOD on the fully covered surface of DCOO(a).

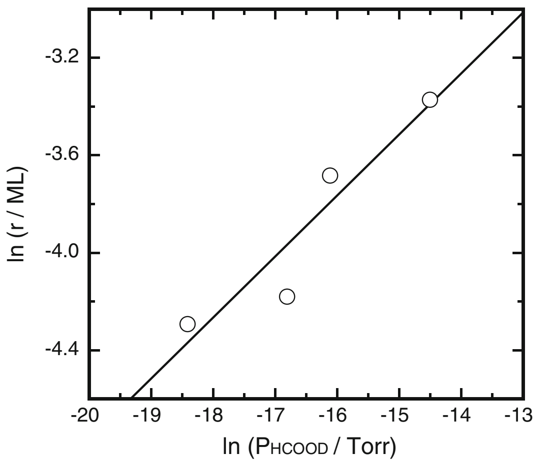

Fig. 7 Dependence of the exchange reaction rate on HCOOD gas pressure at 300 K

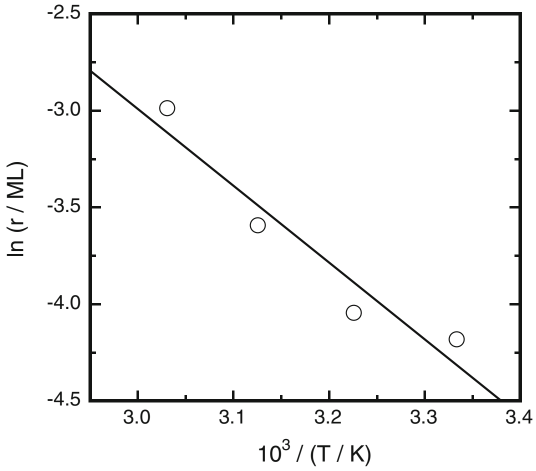

Fig. 8 Arrhenius plot of the exchange reaction of DCOO(a) on Cu(110) with HCOOD gas at a pressure of 5×10^{-8} Torr

The activation energy of the exchange reaction was determined by measuring the rate of the reaction at a fixed pressure of HCOOD of 5×10^{-8} Torr while varying the temperature between 300 and 330 K. The Arrhenius plot is shown in Fig. 8, and the activation energy was estimated to be 33 kJ mol^{-1}.

As shown in Fig. 7, the rate of the exchange reaction was 0.034 ML s^{-1} at 5×10^{-7} Torr. In a previous study, the reaction rate was determined to be 0.0058 ML s^{-1} on Ni(110) at the same pressure and temperature [11]. The reaction rate on Cu(110) was over 5 times that on Ni(110), so the exposure of formic acid required for the formate exchange of all sites on Cu(110) was less than that on Ni(110).

On the other hand, around 10 L of formic acid was required to prepare a fully formate-covered surface on a clean Cu(110) surface, as shown in Fig. 2. However, a fully formate-coveted surface could be obtained by exposing a clean Ni(110) surface to less than 5 L of formic acid [15]. This indicates that formic acid is more strongly attracted to Ni(110) than to Cu(110). In the exchange reaction, three steps are involved: (i) the adsorption of HCOOD(g) on the DCOO(a)-covered surface, (ii) the reaction of DCOO(a) with HCOOD(a) accompanied by the transfer of a deuterium atom (By introducing HCOOD gas on the DCOO(a)-covered surface at 165 K, adsorbed molecular formic acid (HCOOD) was observed. The molecular formic acid does not form multilayers in this temperature. We considered that this adsorbed formic acid was reacted with pre-adsorbed formate), and (iii) the desorption of DCOOD(a). If the adsorbed formate (i) is too tightly bound to Ni(110), reaction (ii) and desorption (iii) would be less likely to occur, and the exposure amount of formic acid required to exchange the formate at all sites on Cu(110) may be less than on Ni(110).

4 Conclusions

The exchange reaction of formate DCOO(a) on Cu(110) with gaseous formic acid HCOOD was investigated at 300 K, well below the decomposition temperature of the adsorbed formate, using TR-IRAS. When HCOOD gas was introduced onto the DCOO(a)-covered Cu(110) surface, the pre-adsorbed DCOO(a) desorbed as DCOOD, revealing the transfer of a hydrogen (deuterium) atom from HCOOD. The activation energy of the exchange reaction was determined to be 33 kJ mol^{-1}. The reaction order with respect to formic acid pressure was 0.3, and the reaction order with respect to DCOO(a) coverage was unity, suggesting that the rate-determining step was the reaction of pre-adsorbed formate with formic acid adsorbed on the surface, and that the reaction occurred uniformly on the surface. The reaction rate on Cu(110) was over 5 times the previously reported rate on Ni(110). This may have been due to differences in the formate-surface interactions. In the near future, we will observe the reaction behavior of HCOOD molecule adsorbed on the DCOO(a)-covered surface at lower temperature, and clarify the reaction mechanism.

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