

In situ observation of the exchange reaction of formate with molecular formic acid on Ni(110)

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Abstract

The exchange reaction of adsorbed formate on Ni(110) with formic acid in gas phase was studied by the time-resolved infrared reflection absorption spectroscopy (TR-IRAS). It was found that the pre-adsorbed deuterated formate (DCOO(a)) was changed to HCOO(a) in the presence of HCOOD(g) at the temperature region from 240 to 300 K. In such a temperature region, the formate was stable on the surface in vacuum and the decomposition of formate was not observed. It was suggested that the pre-adsorbed DCOO(a) was desorbed as DCOOD accepting deuterium atom from HCOOD. The activation energy of the exchange reaction was estimated to be 23 ± 2 kJ mol⁻¹. The reaction order with respect to formic acid pressure was 0.3 ± 0.1 , while that as to the coverage of DCOO(a), was unity. Taking into account all the experimental results, the exchange of pre-adsorbed formate with post-exposed formic acid is suggested to proceed via forming a hydrogen-bonded intermediate complex on the formate's site, because all the sites were already occupied by formate. The small activation energy of the exchange reaction is discussed on the basis of 'adsorption-assisted desorption'. We propose that when desorption and adsorption are coupled, the activation energy of the exchange reaction should be described as a sum of the potential energy profiles of a desorbing and an adsorbing molecule. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The single crystal surfaces have been used in the last three decades to investigate both the

reaction kinetics and the reaction mechanisms. One of the most important subjects in surface science is the elucidation of catalytic reactions. The characterizations of the state and dynamic behavior of adsorbates under reaction condition are indispensable for understanding catalysis, because surface reactions in the presence of gas phase molecules are often different from those

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under vacuum conditions [1]. Even the simplest reaction, such as desorption, is affected by the presence of gas phase. For CO on metal surfaces, the rate of desorption is enhanced by the presence of gaseous CO [2–12] and NO [13], and the activation energy for the desorption of CO(a) in the presence of gaseous CO has been reported to be much smaller than that in vacuum [2–12]. These phenomena have been well known in terms of ‘adsorption-assisted desorption’ (AAD). It is obvious that the AAD is caused by the interaction between the pre-adsorbed species and incident molecules from gas phase.

The presence of gas phase molecules sometimes affects not only on the reversible processes such as adsorption and desorption but also on the irreversible processes such as the decomposition of formate. The enhancement of the rate of the decomposition of formate and the decrease of the activation energy in the presence of gas phase formic acid have been reported for Ni/SiO₂ [14] and Cu/SiO₂ [15] catalysts, and TiO₂(110) [16]. The formate intermediate in the methanol decomposition on Cr₂O₃ is another example; formate decomposes on Cr₂O₃ at 533 K in the presence of methanol in the ambient gas, whereas the formate stays stable under vacuum at the same temperature [17]. The marked difference between the presence and absence of gas molecules may be attributed to the interaction between the chemisorbed species and precursors which are in equilibrium with gas phase. The precursors which exist only in the presence of gas phase are considered to play a key role in the catalytic reactions, although it has not yet well understood.

Recently, we have studied the state and the behavior of formate on Ni(110) in the presence of gas phase formic acid using time-resolved infrared reflection absorption spectroscopy (TR-IRAS). The exchange reaction of formate with gaseous formic acid, which was originally found on Ni/SiO₂ in 1960s by one of the authors [18], was directly observed [19]. In this paper, we have studied the kinetics and the mechanism of the exchange reaction. The origin

of the small activation energy of the exchange reaction has also been discussed on the basis of the ‘adsorption-assisted desorption’.

2. Experimental

All the experiments were carried out in an ultrahigh vacuum chamber equipped with quadrupole mass analyzer (Q-MS) and LEED-AES optics with base pressures below 2×10^{-10} Torr (1 Torr = 133 Pa) as described previously [20,21]. For IRAS measurements, a narrow band mercury cadmium telluride detector was used with Mattson RS 2 spectrometer. The p-polarized IR beam irradiated the surface with the incident angle of 83° passing through NaCl windows.

The Ni(110) surface was cleaned by Ar⁺ ion-sputtering and annealed at 1023 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 on the back of the crystal. The formic acid (HCOOH, DCOOH and H¹³COOH from Isotec; 95% in water solution) 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 Ni(110) surface was made by TR-IRAS in the following manner. The Ni(110) surface was adequately exposed by DCOOH until it was fully covered with DCOO(a) at 300 K at the pressure of 5×10^{-7} Torr. After the evacuation of the chamber below 1×10^{-9} Torr (it took about 10 min), the data acquisition was started at $t = 0$ s. The TR-IRA spectra with a resolution of 4 cm⁻¹ were obtained at every 9.04 s and averaged over 100 scans for a spectrum. The base pressure of the chamber was kept below 1×10^{-9} Torr for the first 100 s. At $t = 100$ s, HCOOH gas was introduced to the chamber at a constant pressure through electrically operated valves. These measurements were

made at several surface temperatures in the range of 240–300 K, and several pressures in the range of 1×10^{-5} – 5×10^{-8} Torr.

3. Results and discussion

3.1. TR-IRAS observations during the replacement of surface formate with gas phase formic acid

The behavior of formate in the presence of gas phase formic acid was studied by TR-IRAS. Fig. 1 shows the TR-IRA spectra of the reaction of formate with the isotopically labeled formic acid on Ni(110) at 300K. Fig. 1A shows the change in IRA spectra of pre-adsorbed DCOO(a) on Ni(110) by the introduction of HCOOD gas at the pressure of 5×10^{-7} Torr. The main

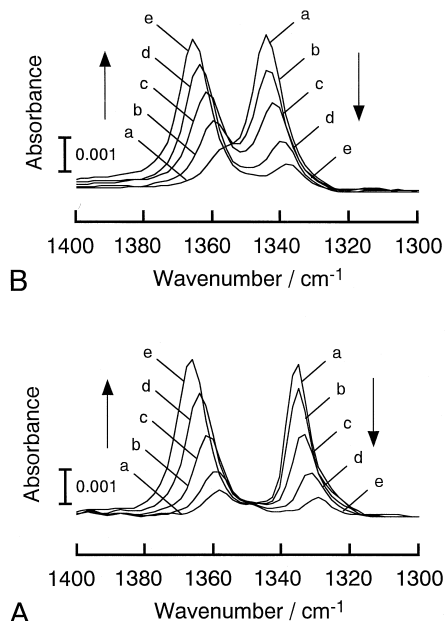
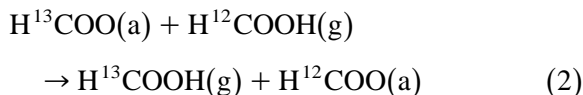
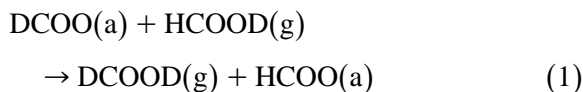


Fig. 1. Change of IRA spectra of DCOO(a) by the introduction of HCOOD(g) (A), and that of $H^{13}COO(a)$ by the introduction of $H^{12}COOH(g)$ (B) at 300 K. Traces (a) were recorded in vacuum and (b), (c), (d), and (e) at 25, 100, 300, 1000 s, respectively, were measured after the admission of isotopic labeled formic acid at the constant pressure of 5×10^{-7} Torr.

peak appearing at 1334 cm^{-1} is assigned to the band of $\nu_s(\text{OCO})$ of DCOO(a), while the weak peak at around 1360 cm^{-1} is assigned to the band of $\nu_s(\text{OCO})$ of HCOO(a) which is an isotope impurity [20]. When HCOOD was introduced onto DCOO(a)-covered surface, the peak intensity of $\nu_s(\text{OCO})$ band of pre-adsorbed DCOO(a) began decreasing, and that of HCOO(a) commenced increasing until the band of DCOO(a) disappeared completely. It should be noted that the peak position of the $\nu_s(\text{OCO})$ bands of DCOO(a) and HCOO(a) shifted about 10 cm^{-1} as the reaction proceeded, however, it is due to the dipole–dipole coupling among the same isotope species as we reported previously [20]. By the quantitative analysis of Fig. 1A, it was confirmed that the decrement of the coverage of DCOO(a) corresponded to the increment of HCOO(a), i.e., the DCOO(a) was exchanged by HCOO(a) due to the introduction of HCOOD (g). The more direct evidence for the exchange of formate by the exposure of formic acid was obtained by the isotope labeling of the carbon of pre-adsorbed formate. Fig. 1B shows the change of the TR-IRA spectra by the exposure of $H^{12}COOH$ gas on $H^{13}COO(a)$ -covered Ni(110). The main peak at 1345 cm^{-1} is assigned to the $\nu_s(\text{OCO})$ band of $H^{13}COO(a)$, and a small peak at 1360 cm^{-1} to that of $H^{12}COO(a)$. The similar decrement of the band of pre-adsorbed $H^{13}COO(a)$ and increment of that of $H^{12}COO(a)$ due to the introduction of $H^{12}COOH(g)$ was observed, indicating that $H^{13}COO(a)$ was replaced by $H^{12}COO(a)$.

Spectra in Fig. 1 demonstrate the exchange reaction of the pre-adsorbed DCOO(a) to HCOO(a) and $H^{13}COO(a)$ to $H^{12}COO(a)$ by the exposure of HCOOD and $H^{12}COOH$, respectively. These results confirm that the pre-adsorbed formate was exchanged by the post-exposed formic acid. In the course of the exchange reaction, any products from the decomposition of formic acid such as H_2 , CO_2 , CO and H_2O were not observed by Q-MS. Thus, in conclusion, the pre-adsorbed formate was desorbed as formic acid by the transfer of hydrogen

(deuterium) atom from formic acid as given in Eqs. (1) and (2).



This phenomenon should be regarded as one of the ‘adsorption-assisted desorption’ which has been well studied in the case of CO [2–13]. However, in the present case, the mechanism of the exchange is more complex than the case of CO(a), because the replacement proceeds through a chemical reaction; the hydrogen atom is transferred from incident formic acid to the pre-adsorbed formate. Furthermore, it must be noted that the formation of formate from formic acid on Ni(110) has been considered to be irreversible in vacuum as expressed by Eq. (3) [22].



On Ni(110) surface, we have reported that the hydrogen atoms produced on the formation of formate from formic acid readily desorbed as H₂ above 240 K [20]. Moreover, formate does not desorb as formic acid by the exposure of H₂ at 300 K as reported previously [20]. The desorption of formic acid from formate, accompanied by the transfer of hydrogen atom, was observed in the present study to occur only when gaseous formic acid is exposed. Thus, the presence of gaseous formic acid is essential for the exchange reaction.

3.2. Kinetic analysis of the exchange reaction

In order to reveal the exchange reaction in more detail, kinetic analysis was performed. The rate of the exchange reaction (r) is defined as,

$$r = -k\theta_{\text{DCOO}}^m P_{\text{HCOOD}}^n \quad (4)$$

where, k , θ_{DCOO} , and P_{HCOOD} are the rate constant, the amount of DCOO(a) on the surface fully covered by formate, and the pressure of HCOOD, respectively. The superscripts m and n are the orders of reaction with respect to the coverage of formate and the pressure of HCOOD, respectively.

First, the reaction order m was determined. A good linear relationship between $\ln\{\theta_{\text{DCOO}}(t)\}$ and t was obtained as shown in Fig. 2, which confirms that the rate of reaction has the first order dependence on θ_{DCOO} at full coverage of formate. It suggests that the reaction occurs uniformly on the surface.

Next, the order of reaction for the formic acid pressure, n , was determined. The dependence of the rate of the exchange reaction on the pressure of formic acid (n) was estimated to be 0.3 ± 0.1 at 300 K in the pressure range of HCOOD from 1×10^{-6} to 5×10^{-8} Torr as shown in Fig. 3. If the rate-determining step (RDS) is the adsorption of HCOOD molecules to the vicinity of formate, the value of n should be unity. The small value of 0.3 (< 1) indicates that the active sites are more or less covered with the reactive formic acid, and the RDS is suggested to be the reaction between the DCOO(a) and HCOOD(a). The reaction probability of an impinged formic

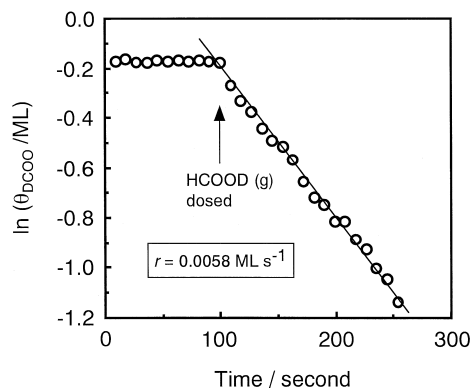


Fig. 2. Dependence of the rate of exchange reaction on the coverage of DCOO(a) at 300 K. HCOOD gas was continuously introduced at the constant pressure of 5×10^{-7} Torr after $t = 100$ s. The slope of the plots ($t > 100$ s) represents the rate of the exchange reaction.

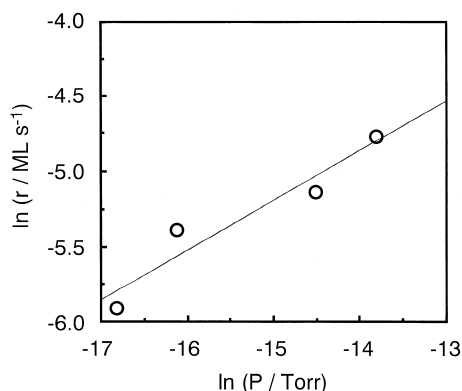


Fig. 3. Dependence of the rate of the exchange reaction on the pressure of HCOOD gas at 300 K.

acid for the exchange reaction was roughly estimated to be the order of 0.01 at 300 K because the rate of the exchange reaction was $0.0058 \pm 0.0005 \text{ ML s}^{-1}$ at the pressure of HCOOD of $5 \times 10^{-7} \text{ Torr}$ (the value corresponding to the rate of flux of 0.5 ML s^{-1}) as shown in Fig. 2. This result also supports that the RDS is the reaction between the DCOO(a) and HCOOD(a).

The activation energy of the exchange reaction was determined by measuring the rate of the reaction at the fixed pressure of HCOOD at $5 \times 10^{-7} \text{ Torr}$ while varying the temperatures between 240 and 300 K. The Arrhenius plot is shown in Fig. 4 and the activation energy was estimated as $23 \pm 2 \text{ kJ mol}^{-1}$.

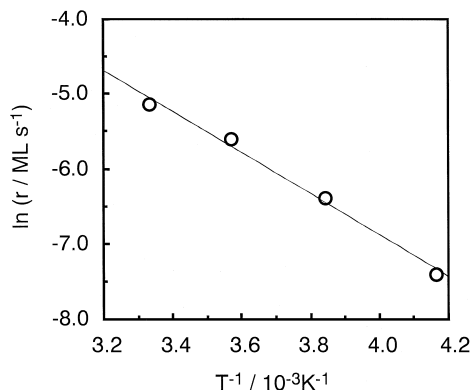


Fig. 4. Arrhenius plot for the exchange reaction of DCOO(a) on Ni(110) with HCOOD gas at the pressure of $5 \times 10^{-7} \text{ Torr}$.

3.3. IRA spectra of adsorbed formic acid on full-covered Ni(110) by formate

The analysis of the order of reaction on the pressure of HCOOD for the exchange reaction suggested that the RDS is the reaction step after adsorption of HCOOD which then reacts with the formate. Therefore, we studied the adsorption of formic acid on formate-covered Ni(110) by IRAS. Above 200 K, there appeared no difference between the IRA spectra recorded in the presence and the absence of formic acid in gas phase; such an increase of the coverage of formate in the presence of gas phase was not observed. However, on cooling the surface below 200 K, a new species was detected. Fig. 5 shows the IRA spectra of DCOO(a) on Ni(110) surface recorded in vacuum at 180 K (bottom spectrum), and the differential IRA spectra between that measured in vacuum and those

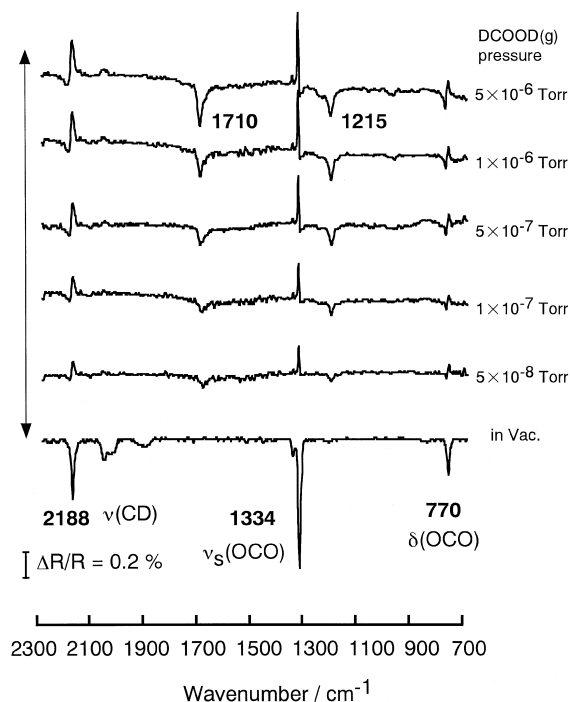


Fig. 5. IRA spectrum of DCOO(a) on Ni(110) at 180 K recorded in vacuum (bottom) and the difference spectra between that measured in vacuum and those recorded in the presence of DCOOD gas at the indicated pressures.

recorded in the presence of DCOOD gas at 180 K at the pressures from 1×10^{-6} to 5×10^{-8} Torr. By exposing the DCOO(a)-covered Ni(110) to DCOOD(g), new peaks were observed at 1710 and 1215 cm^{-1} and increased in parallel with the increase of the pressure of DCOOD. On the other hand, the peak intensities of $\nu(\text{C-D})$ and $\nu_s(\text{OCO})$ of pre-adsorbed DCOO(a) at 2188 and 1334 cm^{-1} , respectively, were decreased concurrently. The change of IRA spectra with the change of the pressure of DCOOD(g) was reversible, and the IRA spectrum recorded in vacuum was restored by evacuation. These results confirm that the decrease of peak intensities of formate on IRA spectra is caused by the adsorption of the new species (1710 and 1215 cm^{-1}) which is in adsorption equilibrium with gas phase.

In order to assign the new peaks at 1710 and 1215 cm^{-1} , the IRA spectrum was measured by changing the formic acid in gas phase from DCOOD to HCOOH at the fixed pressure of 1×10^{-6} Torr (Fig. 6). The new peaks observed at 1710 and 1215 cm^{-1} in DCOOD(g) shifted to 1734 and 1174 cm^{-1} under HCOOH(g), respectively. Because these frequencies are close to the bands of $\nu(\text{C=O})$ and $\nu(\text{C-O})$ of gaseous formic acid [$\nu(\text{C=O}) = 1744 \text{ cm}^{-1}$ and $\nu(\text{C-O}) = 1174 \text{ cm}^{-1}$ for

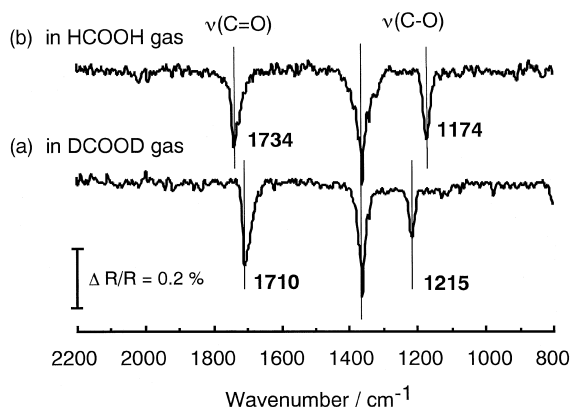


Fig. 6. IRA spectra of HCOO(a) on Ni(110) at 180 K recorded in the presence of DCOOD(g) and HCOOH(g) at the pressure of 1×10^{-6} Torr.

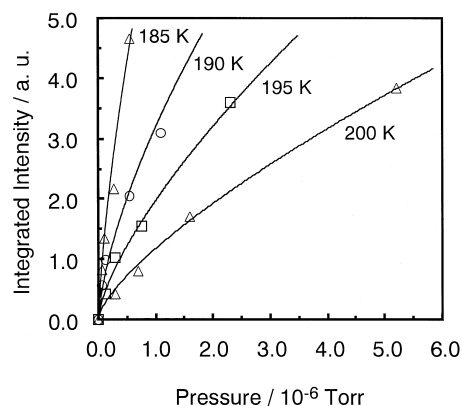


Fig. 7. Adsorption isotherms of DCOOD on DCOO(a)-covered Ni(110). The amount of adsorbed DCOOD was evaluated from the integrated peak intensity of $\nu(\text{C=O})$ band of DCOOD in IRA spectra shown in Fig. 5.

HCOOH, and $\nu(\text{C=O}) = 1704 \text{ cm}^{-1}$ and $\nu(\text{C-O}) = 1244 \text{ cm}^{-1}$ for DCOOD [23]), the new peaks are assigned to the $\nu(\text{C=O})$ and $\nu(\text{C-O})$ bands of adsorbed formic acid, respectively.

Adsorption isotherms at several surface temperatures between 200 and 185 K were measured to estimate the heat of adsorption of the molecularly adsorbed formic acid as shown in Fig. 7. The amount of the adsorbed formic acid, θ , was estimated by integrating the peak intensity of the band ($\nu(\text{C=O})$) at 1710 cm^{-1} . From a series of the adsorption isotherms, the isosteric heat of adsorption (ΔH) was obtained by Clausius–Clapeyron equation,

$$\frac{d \ln P}{d(1/T)_{\theta = \text{const}}} = - \frac{\Delta H}{R},$$

where, P , T , and R are the pressure of gas phase DCOOD, temperature at surface, and gas constant. The plots of $\ln P$ vs. $1/T$ at several coverages of adsorbed formic acid are shown in Fig. 8, and the isosteric heat of adsorption (ΔH) thus obtained are plotted against coverage in Fig. 9. The extrapolation of heat of adsorption in Fig. 9 gives the value of $64 \pm 5 \text{ kJ mol}^{-1}$ at $\theta = 0$. The heat of adsorption of the physisorbed formic acid on Ni(110) was estimated to be 11.4 kJ mol^{-1} taking into account the activation energy for the desorption which

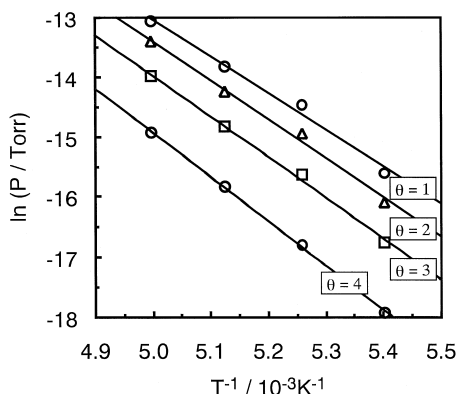


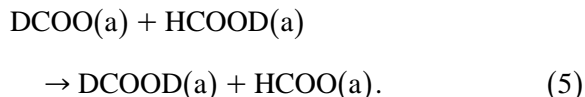
Fig. 8. The plots of $\ln P$ vs. $1/T$ at several coverages of adsorbed formic acid. These plots were derived from the results shown by the spectra in Fig. 7 and the coverage θ of DCOO(a) is represented in arbitrary unit.

was obtained by Wach and Madix using molecular beam relaxation spectrometry [24,25]. The heat of adsorption of formic acid (64 kJ mol^{-1}) obtained in these experiments is considerably higher than that of physisorption of formic acid (11.4 kJ mol^{-1}). This fact confirms that the adsorbed formic acid observed in Fig. 5 is tightly bonded to the surface rather than the physisorbed species; there is a strong attractive interaction between the formic acid and the surface, although the surface is fully covered by formate. If one simply employs the surface selection rule of IRAS, the decrement of peak intensities of the $\nu(\text{C-D})$ and $\nu_s(\text{OCO})$ bands of DCOO(a) in Fig. 5 may be induced by the tilting of DCOO(a) due to the lateral interaction with adsorbed formic acid. The transformation of the structure of formate by the adsorption of formic acid has been reported on Cu(100) surface [26,27]. However, the change of the absorption coefficient of the bands of formate by the coadsorbed formic acid is another possibility for the decrease of the integrated intensities.

3.4. The mechanism of the exchange reaction of formate with molecular formic acid on Ni(110)

In the course of the exchange reaction, three steps are involved: (1) the adsorption of HCOOD(g) on DCOO(a)-covered surface, (2)

the reaction of DCOO(a) with HCOOD(a) accompanied by the transfer of deuterium atom from HCOOD(a) to DCOO(a), and (3) the desorption of DCOOD(a). As discussed in Section 3.2, the RDS of the exchange reaction is the second of the three steps as,



The reaction sites on which the exchange reaction occurs may be the sites where the formate is pre-adsorbed, because the possible sites where formic acid chemisorbs and dissociates into formate and hydrogen atom are already occupied by formate. The observed reaction order as to the coverage of formate ($m = 1$) supports this mechanism, i.e., the reaction proceeds homogeneously on the surface fully covered by formate. Since the hydrogen atom adsorbed on the formate-covered Ni(110) is known to readily desorb as H_2 above 240 K [20], the transfer of hydrogen atom should proceed directly from formic acid to formate. These facts confirm that the formation of DCOOD(a) from pre-adsorbed DCOO(a) and HCOOD(a) to form HCOO(a) proceed via the formation of a hydrogen-bonded intermediate complex on a common site as shown in Scheme 1.

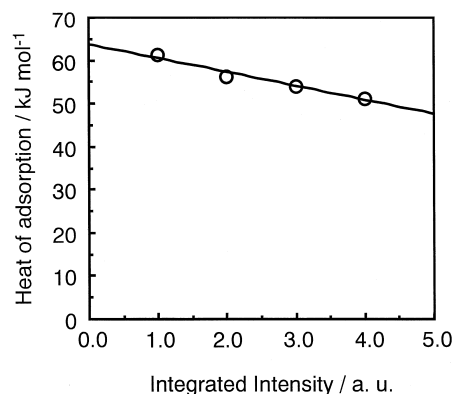
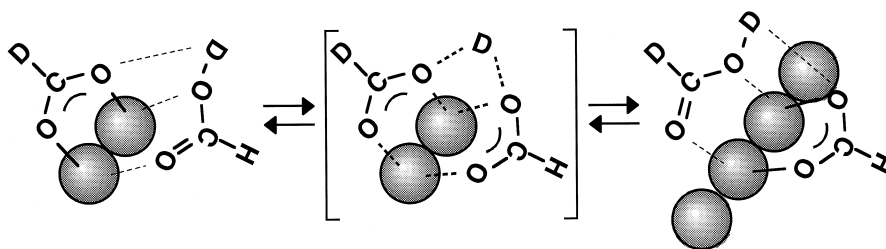


Fig. 9. Isotheric heat of adsorption of DCOOD on DCOO(a)-covered Ni(110) as a function of amount of adsorbates.



Scheme 1. The proposed mechanism of the exchange reaction of formate with molecular formic acid on Ni(110).

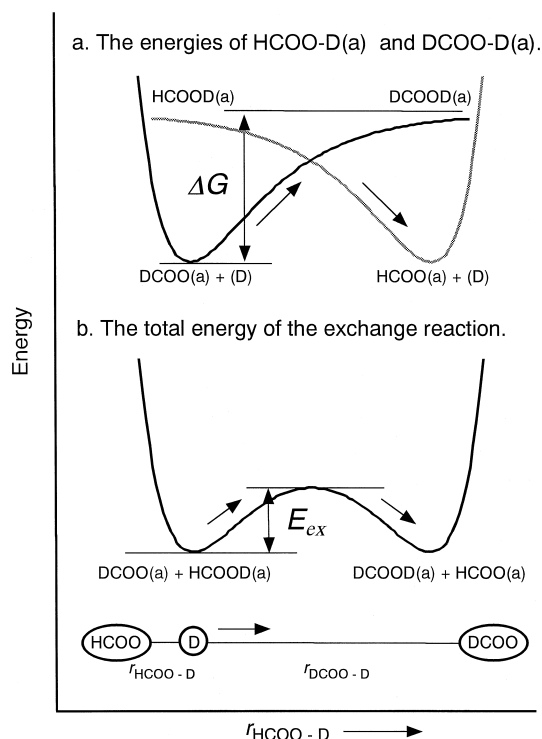
3.5. The decrease of activation energy in 'adsorption-assisted desorption'

The activation energy was estimated to be about 23 kJ mol^{-1} . This value is very small compared with the heat of formation of formate on nickel catalyst which was reported by Sachtler and Fahrenfort as ca. 400 kJ mol^{-1} [28,29]. It is widely reported that the 'adsorption-assisted desorption' occurs at the temperature which are significantly lower than those of thermal desorption, and the activation energy of the AAD is known to be always smaller than that of desorption in vacuum [2–13].

Most of the experiments for the AAD are performed in the presence of the unoccupied site [2–12] where the post-introduced molecules adsorbs. However, in the present study, the post-introduced formate (formic acid) adsorbs on a formate-covered site. Therefore, one site model should be considered; the pre-adsorbed and post-adsorbed species interact and react on one site. In such a case where both desorption and adsorption depend on each other, we should consider the change of total energy of the reaction system which could be described as a sum of the energies of desorbing and adsorbing molecules.

It is useful to employ Scheme 2 to model this idea. Considering the transfer of the deuterium atom from HCOOD(a) (post-adsorbed formic acid) to pre-adsorbed DCOO(a) following the process depicted by Scheme 1, we can define two quantities: $r_{\text{HCOO-D}}$ and $r_{\text{DCOO-D}}$, the length of HCOO-D bond and that of DCOO-D bond as

illustrated by the bottom drawing in Scheme 2. The energies of 'desorbing' DCOO(a) and 'adsorbing' HCOO(a) in the course of the exchange reaction may be represented by a function of $r_{\text{DCOO-D}}$, and $r_{\text{HCOO-D}}$, respectively. When the DCOO-D(a) bond begins to form, the HCOO-D(a) bond should be elongated, i.e., the decrease of $r_{\text{DCOO-D}}$ makes the $r_{\text{HCOO-D}}$ to increase. This relationship between $r_{\text{DCOO-D}}$ and



Scheme 2. The energy profiles of the exchange reaction of formate with molecular formic acid. (a) The solid line is the energy of the DCOO-D(a), while the gray line is that of HCOO-D(a). (b) The sum of two potential curves represented in (a).

$r_{\text{HCOO-D}}$ in the course of the exchange reaction should be also explained by the ‘Bond Energy–Bond Order’ relationship [30–33]. Scheme 2a shows conceptually how the energies of the DCOO-D(a) and HCOO-D(a) change as the reaction proceeds. The energy of a typical HCOO-D(a) as a function of $r_{\text{HCOO-D}}$ will look like the gray line in Scheme 2a, while that of DCOO-D(a) as a function of $r_{\text{HCOO-D}}$ will be represented as indicated by the solid line because the increment of $r_{\text{HCOO-D}}$ results in the decrease of $r_{\text{DCOO-D}}$.

Now we consider what happens during the exchange reaction. At the initial stage of the break up of the HCOO-D bond, the potential energy of the HCOO-D(a) will go down along the gray line toward the valley at HCOO(a) + D(a) in Scheme 2a because HCOO(a) is more stable than HCOOD(a). However, once the DCOO-D bond begins to form, the potential energy of DCOO-D(a) will climb up along the solid line in Scheme 2a. During the exchange reaction, the scission of the HCOO-D bond occurs simultaneously with the formation of the DCOO-D bond. Thus, the total energy should be described as the sum of the two curves in Scheme 2a as shown in Scheme 2b. The free energy for the formation of formate from formic acid and the activation energy for the exchange reaction are represented as ΔG and E_{ex} in Scheme 2, respectively. Scheme 2 clearly shows that the activation energy of the exchange reaction is always smaller than the free energy of the formation of formate.

We can find out similar discussion in the classical mechanism of the acid catalyzed transfer of proton from acid to the reactant proposed by Evans and Polanyi [32–34]. This model, although includes some assumptions and thus is not quantitative, may be serve understanding the potential energy profiles in tri-atomic reactions and has been adopted in understanding the chemical dynamics. For more detailed and quantitative discussion, the potential energy surface should be calculated by quantum chemistry.

4. Summary

The exchange reaction of formate (DCOO(a)) on Ni(110) with gaseous formic acid (HCOOD) was investigated below the decomposition temperature of formate (340 K) by means of TR-IRAS. When HCOOD gas was admitted on the DCOO(a)-covered Ni(110) surface, the pre-adsorbed DCOO(a) was desorbed as DCOOD revealing the transfer of deuterium atom from HCOOD. The activation energy of the exchange reaction was obtained as $23 \pm 2 \text{ kJ mol}^{-1}$. The reaction order with respect to the formic acid pressure was 0.3 and that with respect to the coverage of DCOO(a) was unity, suggesting that the rate-determining step was the reaction of formate with reversibly adsorbed formic acid on formate-covered surface. The reversibly adsorbed formic acid which would be the precursor of the exchange reaction was observed by IRAS, and the isosteric heat of adsorption was estimated to be $64 \pm 5 \text{ kJ mol}^{-1}$.

It was suggested that the exchange reaction, which took place during the desorption of pre-adsorbed formate and the formation of formate from post-exposed formic acid, proceeded on the formate-covered site via the formation of a hydrogen-bonded complex. The origin of the small activation energy in the exchange reaction has been also discussed.

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