Synthesis and decomposition of formate on a Cu(111) surface — kinetic analysis

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Abstract

The kinetics of formate synthesis and formate decomposition on a Cu(111) surface has been studied using an XPS apparatus combined with a high-pressure flow reactor. The activation energy of the formate synthesis by hydrogenation of CO_2 at 1 atm and a mole ratio of $CO_2/H_2 = 1$ is determined to be 64.1 ± 2.2 kJ mol^{-1}. A kinetic analysis concludes that the formation rate cannot be explained by a simple Langmuir–Hinshelwood mechanism. A new Eley–Rideal mechanism is proposed. The rate constant of the formate decomposition is very different depending on the preparation method of formate, that is, synthesis by hydrogenation of CO_2 at 1 atm and adsorption of HCOOH on an oxygen-covered Cu(111) surface in UHV. However, the activation energies of the decomposition for both cases are close to each other, meaning that the frequency factor of the rate constant is different for the two cases. This can be explained by the different surface structures of formate previously observed by STM. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Methanol synthesis by hydrogenation of CO or CO_2 using Cu/ZnO-based catalysts is a very important industrial process. Over twenty years, extensive studies have been performed concerning the mechanism, the role of ZnO, and the active species [1–9]. However, no consensus has been obtained regarding these problems. This may be due to the complication of reaction conditions and catalyst materials. First, one should classify the studies of methanol synthesis

into the hydrogenation of CO or CO_2, because both CO and CO_2 can be hydrogenated to methanol, depending on the catalyst materials and the reaction conditions [1,3,4,6,9]. It has been reported that on Cu/ZnO-based catalysts CO_2 is more readily converted to methanol compared to CO [3,10].

As for methanol synthesis from CO_2 and H_2 over Cu/ZnO-based catalysts, the debate on the role of ZnO is focused on the ''Cu morphology effect'' [11–13] and ''active site creation model'' [14–24]. The former has been independently proposed by Yoshihara and Campbell [11], Ovesen et al. [12], and Hadden et al. [13], who have reported that the morphology of the

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Cu particles on ZnO influences the methanol synthesis activity of industrial Cu/ZnO catalysts, and the active surface of the Cu particles mainly consists of the Cu(110) plane. On the other hand, we have found that the role of ZnO in Cu/ZnO catalysts is to create active sites on the surface of the Cu particles in our project on the mechanistic study of methanol synthesis using both surface-science techniques and classical methods for powder catalysts. We initially proposed that ZnO_x species partly cover the Cu surface leading to the formation of Cu^+ species in the vicinity of the ZnO_x, and that both Cu^0 and Cu^+ cooperate to catalyze methanol synthesis, based on the results using Cu/ZnO catalysts [14] as well as $Cu/SiO_2 + ZnO/SiO_2$ physical mixtures [15]. To prove this model, we have carried out the surface-science study to measure the methanol synthesis activity of a Zn-deposited Cu(111) model catalyst at a high pressure of 18 atm. It has been clarified that the deposition of Zn promotes the methanol synthesis activity of Cu(111). However, the Zn species was found to be metallic during methanol synthesis; therefore, we modified the previous model of the Cu^+ active site and present the model of a $Cu^0–Zn^0$ active site [16,17].

If a catalyst model can be once established on a single-crystal surface, one can further look into the microscopic mechanism, the nature of the active site, and the kinetic feature at an atomic level using a variety of modern surface-science techniques, such as XPS, AES, IRAS, STM, LEED, and so on. Furthermore, the usage of a high-pressure reactor in the surface-science study is of great advantage to examine catalytic reactions. We have thus studied the active site and the intermediates of the methanol synthesis on the Zn/Cu(111) model catalyst by STM [18], IRAS [19], and XPS [16,20] using the high-pressure reactor. We then attempted to quantitatively describe the methanol synthesis on Zn/Cu(111) by kinetics. This is the first paper in our project concerning the kinetics of the reactions constituting the methanol synthesis.

The formate species is an important intermediate of the methanol synthesis by the hydrogenation of CO_2. It has been found that the addition of Zn to Cu(111) does not promote the synthesis of formate by the hydrogenation of CO_2 [20,25], indicating that the formate is synthesized on metallic copper atoms as reported on Cu(100) [26]. The promotional effect of Zn on the methanol synthesis is thus responsible for the latter processes such as the hydrogenation of formate or dioxymethylene [20,25]. Here, we studied the kinetics of the formate synthesis on a clean Cu(111) surface.

2. Experimental

The experiments were carried out in an ultra-high-vacuum (UHV) apparatus with a high-pressure flow reactor (up to 30 atm) [16,27,28]. This apparatus was composed of two chambers, a UHV surface analysis chamber (below 2×10^{-10} Torr) for XPS measurements and a preparation chamber (below 3×10^{-8} Torr) equipped with the high-pressure flow reactor.

A Cu(111) single-crystal disc (10-mm diameter, 1-mm thickness, 99.999%) used in this study was polished only on one plane. The accuracy of the plane was within $1°$. The sample was cleaned by Ar^+ sputtering at room temperature and 623 K for 10 min and then annealed at 800 K for 20 min. The cleanliness of the sample was checked by XPS. The sample temperature was measured by a chromel–alumel thermocouple attached to the rear side of a sample holder.

The formate synthesis by the hydrogenation of CO_2 was performed in the flow reactor using a gas mixture of $CO_2/H_2 = 380$ Torr/380 Torr at a total feed rate of 80 cm^3 min^{-1} and reaction temperatures of 323–353 K. The H_2 (99.99999%) and CO_2 (99.999%) used in this reaction were further purified by molecular sieves cooled in liquid nitrogen and cold acetone (233 to 243 K), respectively. After the reaction, the reaction gas was instantly pumped away, and the sample was then transferred from

the reactor to the analysis chamber, where the coverage of formate species was measured by XPS. The coverage of the formate species (Θ_{HCOO}) was determined from the area of O1s and C1s peaks at 531.5 eV and 288.2 eV, respectively [16]. The coverage $\Theta = 1$ corresponded to the number of the Cu surface atoms.

Formate species were also prepared by exposure of an oxygen-preadsorbed Cu(111) ($\Theta_O = 0.04$) surface to 5 L (L = langmuir = 10^{-6} Torr s) of formic acid at 300 K in UHV. Formic acid was purified by freeze–pump–thaw cycles. The isothermal decomposition of the formate species prepared by the hydrogenation of CO_2 or the adsorption of formic acid was performed in the analysis chamber. The sample covered with formate species was rapidly heated to a desired temperature and then kept at the constant temperature. The XPS measurements were then repeatedly performed to trace the decomposition of formate.

3. Results

3.1. Kinetics of formate synthesis

The synthesis of formate by hydrogenation of CO_2 on the clean Cu(111) surface was carried out at atmospheric pressure ($P_{CO_2} = P_{H_2} = 380$ Torr) and 323–353 K in the high-pressure reactor. The kinetics was examined by repeatedly measuring the formate coverage with XPS after each reaction run at a reaction temperature. Only formate species was formed on the post-reaction Cu(111) surface, showing an O/C atomic ratio of two estimated by the XPS peak areas as well as the characteristic C1s and O1s binding energies of formate at 288.2 and 531.5 eV, respectively. The saturation formate coverage was estimated to be 0.24. We have partly reported the formate synthesis or the up-take curve of the formate species elsewhere [20,25]. Here, we analyze the kinetic feature of the formate synthesis on Cu(111).

The initial rate (r_{HCOO}^0) of the formate synthesis and the reaction order in formate coverage were estimated by the uptake curve of the formate species. If the reaction rate is first-order in $(1 - \Theta_{HCOO}/\Theta_{HCOO}^{sat})$, the following equation can be established:

$$r_{HCOO} = \frac{d\Theta_{HCOO}}{dt} = r_{HCOO}^0 \left(1 - \frac{\Theta_{HCOO}}{\Theta_{HCOO}^{sat}}\right)$$

$$= r_{HCOO}^0 \left(1 - \frac{\Theta_{HCOO}}{0.25}\right), \tag{1}$$

$$\ln\left(1 - \frac{\Theta_{HCOO}}{0.25}\right) = -\frac{r_{HCOO}^0}{0.25}t, \tag{2}$$

where the saturation coverage of formate (Θ_{HCOO}^{sat}) is assumed to be 0.25, considering the present results and the $c(2 \times 4)$ structure previously observed by STM [25,29].

Fig. 1 shows $\ln(1 - \Theta_{HCOO}/0.25)$ vs. t for the reaction temperatures of 323, 333, 343 and 353 K. Better linearity was obtained for the first-order plot in $(1 - \Theta_{HCOO}/0.25)$ compared with the half or the second-order plot. The reaction order was thus determined to be unity, and the initial rate could be estimated by the slope of the linear plots in Fig. 1. The rate at
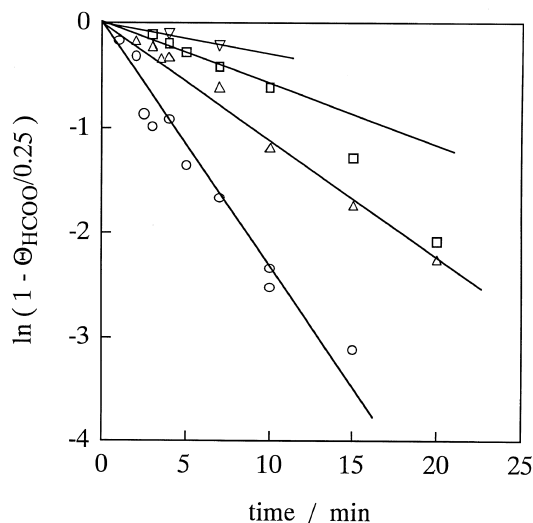

Fig. 1. Ln $(1 - \Theta_{HCOO}/0.25)$ vs. reaction time in the synthesis of formate from 380 Torr CO_2 and 380 Torr H_2 on a clean Cu(111) surface at 353 (○), 343 (△), 333 (□) and 323 (▽) K.
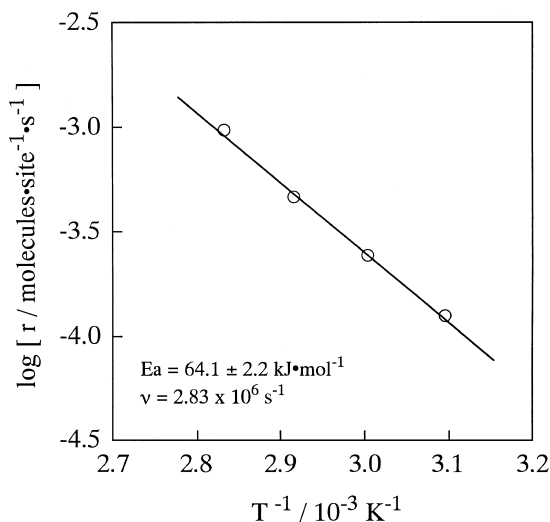
Fig. 2. Arrhenius plot of the initial rates of formate synthesis derived from the slopes of the linear plots in Fig. 1.

323 K, for example, was determined to be 1.25×10^{-4} molecules site^{-1} s^{-1}. From the Arrhenius plot of the initial rates shown in Fig. 2, the activation energy was determined to be 64.1 ± 2.2 kJ mol^{-1}. This value was not so different from that on Cu(100) (55.6 ± 8.0 kJ mol^{-1}) [26]. The pre-exponential factor was determined to be 2.83×10^6 molecules site^{-1} s^{-1}.

3.2. Kinetics of formate decomposition

3.2.1. Formate species synthesized by hydrogenation of CO_2

The decomposition kinetics of the formate species synthesized by the hydrogenation of CO_2 was evaluated by continuously measuring the time course of C1s and O1s peak areas due to formate species in UHV at reaction temperatures of 360, 363, 369 and 375 K. No other species except for formate was detected by XPS, indicating that the decomposition of formate proceeds by the well-known pathway producing CO_2 and H_2 as follows [26,30–33]:

$$HCOO_a \rightarrow CO_2 + \frac{1}{2}H_2 + 2*. \qquad (3)$$
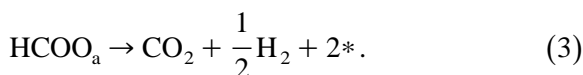
Assuming the first-order in the formate coverage, the following equation can be written for the rate of the formate decomposition:

$$r_d = -\frac{d\Theta_{HCOO}}{dt} = k_d \Theta_{HCOO}, \qquad (4)$$

$$\log \Theta_{HCOO} = \log \Theta^0_{HCOO} - \frac{k_d t}{2.303}. \qquad (5)$$

The linear relationship between $\log \Theta_{HCOO}$ and t shown in Fig. 3 indicates that the rate of the decomposition is first-order in the formate coverage, in agreement with the results obtained for Cu(110) by analysis of TPD [31]. The rate constants, k_d, estimated by the slopes in Fig. 3 were 1.7×10^{-5}, 2.7×10^{-5}, 3.9×10^{-5}, and 8.8×10^{-5} s^{-1} at 360, 363, 369, and 375 K, respectively. The activation energy of the formate decomposition and the pre-exponential factor were then determined to be 112.8 ± 12.4 kJ mol^{-1} and 4.0×10^{11} s^{-1}, respectively, by the Arrhenius plot of k_d shown in Fig. 4. These values are both smaller than those for Cu(100), 155 kJ mol^{-1} and 5.4×10^{17} s^{-1} [26], indicating that the formate decomposition on Cu surfaces is a structure-sensitive reaction. However,

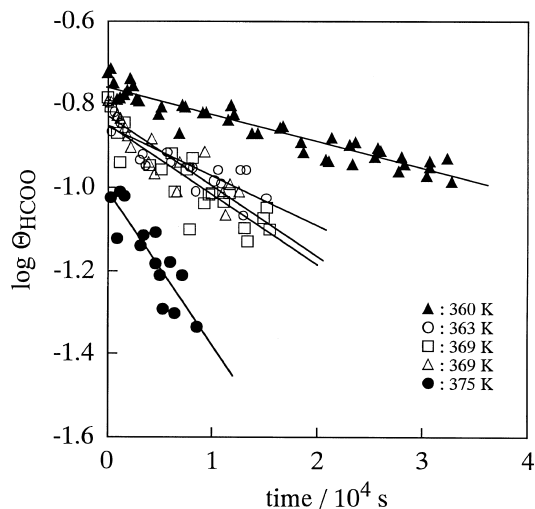Fig. 3. Log Θ_{HCOO} vs. reaction time in the isothermal decomposition of formate synthesized by hydrogenation of CO_2 on a Cu(111) surface.
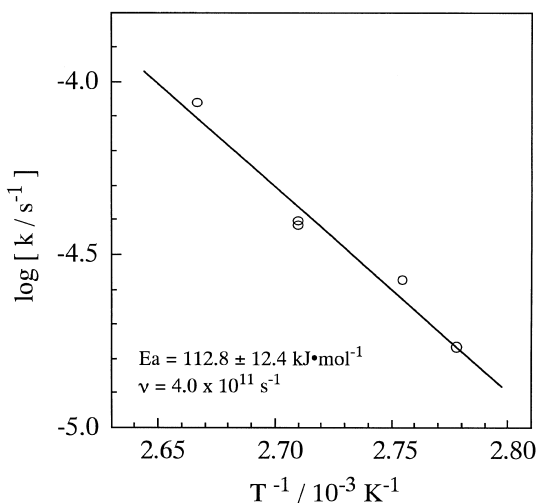
Fig. 4. Arrhenius plot of the rate constants derived from the data of Fig. 3.

Fig. 5. Log Θ_{HCOO} vs. reaction time in the isothermal decomposition of formate prepared by adsorption of formic acid on oxygen-preadsorbed Cu(111) surface ($\Theta_O = 0.04$).

the rate constants of 1.7×10^{-5} s^{-1} (360 K) and 1.4×10^{-4} s^{-1} (375 K) on Cu(100) estimated by us using the cited data are close to the values on Cu(111).

3.2.2. Formate species prepared by HCOOH adsorption

It is well known that formate is easily formed by the adsorption of formic acid on oxygen-pre-covered Cu surfaces in UHV by the following reactions [34]:

$$HCOO + O_a + 2* \rightarrow HCOO_a + OH_a,$$

$$HCOOH + OH_a + * \rightarrow HCOO_a + H_2O,$$

$$2OH_a \rightarrow H_2O + O_a + *,$$
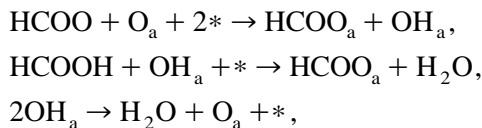
where the pre-adsorbed oxygen or OH_a abstracts proton from formic acid leading to the formation of the formate species. We thus prepared the formate species by the exposure of an oxygen-preadsorbed Cu(111) ($\Theta_O = 0.04$) to 5 L of formic acid.

The decomposition of the formate species was then examined in UHV by measuring the peak areas of C1s and O1s, while keeping the sample temperature constant at 346-358 K. No adsorbed species except for formate was detected by XPS, indicating that the formate species decomposed to CO_2 and H_2. Fig. 5
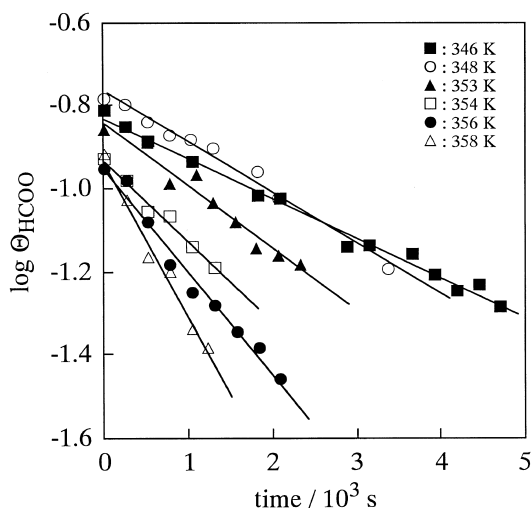
shows log Θ_{HCOO} as a function of time at 346–358 K. Again, the decomposition rate was first-order in the formate coverage as obtained for the decomposition of the formate synthesized from CO_2 and H_2 (Fig. 3). The rate constants determined by the slopes of the lines in Fig. 5 were, for example, 2.2×10^{-4} s^{-1} and 8.7×10^{-4} s^{-1} at 346 K and 358 K, respectively. Fig. 6 shows the Arrhenius plot derived
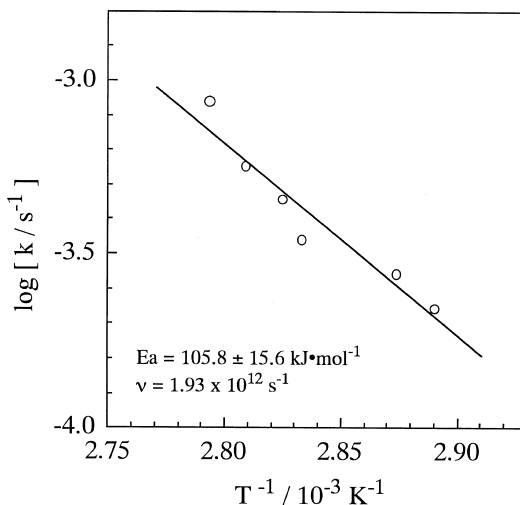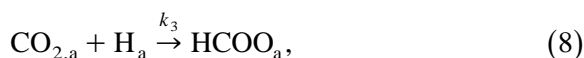

Fig. 6. Arrhenius plot of the rate constants derived from the data of Fig. 5.

from the rate constant data of Fig. 5. The slope gives an activation energy of 105.8 ± 15.6 kJ mol^{-1}, which is very close to the value of 112.8 kJ mol^{-1} measured for the formate synthesized from CO_2 and H_2. It is, however, very interesting that the absolute values of the rate constants at 590–360 K obtained for the formate prepared by HCOOH adsorption were 20–50 times greater than those for the formate synthesized from CO_2 and H_2. This may be explained by the difference in the adsorption structure of formate as discussed later. The pre-exponential factor for the decomposition was estimated to be 1.93×10^{12} s^{-1} by the Arrhenius plot of Fig. 6, which was ~ 5 times greater than that for the formate species synthesized from CO_2 and H_2.

4. Discussion

4.1. Mechanism of formate synthesis

Our current purpose is to describe quantitatively the kinetics of methanol synthesis by the hydrogenation of CO_2 over Cu(111) and Zn/Cu(111) surfaces. As the first step, we studied the kinetics of formate synthesis on a clean Cu(111) surface because formate has been found to form as a stable reaction intermediate on clean Cu surfaces and no promotion of Zn was seen for the formate synthesis on Cu(111) [20,25]. Taylor et al. [26] already reported the kinetics of the formate synthesis on Cu(100), in which the mechanism is assumed to be the following simple Langmuir–Hinshelwood model:

$$\frac{1}{2}H_2 + * \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} H_a, \tag{6}$$

$$CO_2 + * \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} CO_{2,a}, \tag{7}$$

$$CO_{2,a} + H_a \overset{k_3}{\rightarrow} HCOO_a, \tag{8}$$

where $*$ and X_a stand for the vacant site and an adsorbed species of an atom or a molecule X,

respectively; k is the rate constant. In this set of reactions (6), (7) and (8), the adsorptions of H_2 and CO_2 are assumed to be in equilibrium, and reaction (8) is rate-limiting. The reverse reaction of Eq. (8) or the decomposition of formate is neglected in the formate synthesis experiment if the temperature is below ~ 350 K. Thus, the rate equations of reactions (6)–(8) can be described as follows:

$$k_1 P_{H_2}^{\frac{1}{2}} \Theta_* = k_{-1} \Theta_H, \tag{9}$$

$$k_2 P_{CO_2} \Theta_* = k_{-2} \Theta_{CO_2}, \tag{10}$$

$$r_{HCOO} = r_3 = k_3 \Theta_{CO_2} \Theta_H. \tag{11}$$

Here, Θ^* is the coverage of the vacant site, which is approximately expressed by the following equation, assuming no CO_2 coverage because of a very small adsorption energy of CO_2 on Cu surfaces [26,35]:

$$\Theta^* = 1 - \Theta_H - \frac{\Theta_{HCOO}}{\Theta_{HCOO}^{sat}}. \tag{12}$$

From Eqs. (9), (10) and (12), the coverages of H_a and $CO_{2,a}$ are expressed by the following:

$$\Theta_H = \frac{\dfrac{k_1}{k_{-1}} P_{H_2}^{\frac{1}{2}}}{1 + \dfrac{k_1}{k_{-1}} P_{H_2}^{\frac{1}{2}}} \left(1 - \frac{\Theta_{HCOO}}{\Theta_{HCOO}^{sat}}\right), \tag{13}$$
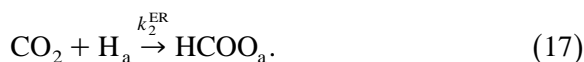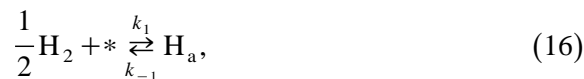
$$\Theta_{CO_2} = \frac{\dfrac{k_2}{k_{-2}} P_{CO_2}}{1 + \dfrac{k_1}{k_{-1}} P_{H_2}^{\frac{1}{2}}} \left(1 - \frac{\Theta_{HCOO}}{\Theta_{HCOO}^{sat}}\right). \tag{14}$$

Accordingly, the formation rate of formate can be described as follows:

$$r_{HCOO} = \frac{k_3 k_1 k_2}{k_{-1} k_{-2}} P_{CO_2} P_{H_2}^{\frac{1}{2}} \frac{\left(1 - \dfrac{\Theta_{HCOO}}{\Theta_{HCOO}^{sat}}\right)^2}{\left(1 + \dfrac{k_1}{k_{-1}} P_{H_2}^{\frac{1}{2}}\right)^2}. \tag{15}$$

This equation means that the formation rate is second-order in $(1 - \Theta_{HCOO}/\Theta_{HCOO}^{sat})$, which is in disagreement with the experimental data of the first-order plot as shown in Fig. 1. That is, the kinetics of formate synthesis cannot be described by the simple Langmuir–Hinshelwood model.

Currently, we are preparing to establish a new mechanism consistent with the kinetic data obtained by both XPS and IRAS measurements, which will be reported in detail elsewhere [36]. The new model is an Eley–Rideal mechanism in which a CO_2 directly inserts into a metal-H bond. This is the well-known mechanism of formate synthesis in organometallic chemistry [37,38], where the insertion is thought to proceed as shown in Scheme 1 based on the ab initio calculation [39].If this is the case on the Cu surface, a set of reactions can be described as follows:

$$\frac{1}{2}H_2 + * \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} H_a, \tag{16}$$

$$CO_2 + H_a \overset{k_2^{ER}}{\rightarrow} HCOO_a. \tag{17}$$

The formation rate of formate is given by the following equation:

$$
\begin{aligned}
r_{HCOO} &= k_2^{ER} P_{CO_2} \Theta_H \\
&= \frac{k_1 k_2^{ER}}{k_{-1}} \frac{P_{CO_2} P_{H_2}^{\frac{1}{2}}}{1 + \frac{k_1}{k_{-1}} P_{H_2}^{\frac{1}{2}}} \left(1 - \frac{\Theta_{HCOO}}{\Theta_{HCOO}^{sat}}\right),
\end{aligned}
\tag{18}
$$

where the formation rate is first-order in $(1 - \Theta_{HCOO}/\Theta_{HCOO}^{sat})$ in good agreement with experimental data. Furthermore, pressure dependencies on the formate formation measured by IRAS
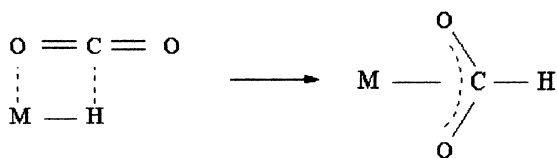
were in fairly good agreement with those calculated by Eq. (18), which will be reported elsewhere [36]. During the hydrogenation of CO_2 on Cu, the major species on the Cu surface is atomic hydrogen except for formate, so that CO_2 has sufficient chances to attack the hydrogen atom.

4.2. Decomposition kinetics

The decomposition rate of formate on Cu(111) was different depending on the preparation method of formate, that is, the synthesis by hydrogenation of CO_2 and the adsorption of formic acid. The XPS measurements showed that the chemical composition of the formate-covered Cu(111) surface was identical for both methods. Also, the hydrogen atom should be absent on Cu(111) at 346–375 K because the associative desorption of H_2 proceeds rapidly around room temperature. In TDS of H_2 on Cu(111), the peak maximum is seen at 300–360 K at a heating rate of 3 K s^{-1} [40]. The difference in the decomposition rate is thus ascribed to a structural effect such as the ordered structures of the formate. We reported the STM studies of the formate species synthesized from CO_2 and H_2 on Cu(111) [20,25]. It has been found that formate species adsorb in a linear row and that the distance between the chains is reduced with increasing formate coverage. The facts indicate that the formate–formate interaction is attractive in the chain, whereas a repulsive interaction operates between the formate chains. The anisotropic interaction between formate species is probably due to the plane structure of the formate species adsorbed in a bidentate structure [25,29]. On the other hand, no chain structure was observed for the formate species prepared by the adsorption of formic acid. The difference in the formate structure may be responsible for that in the decomposition rate. It should be noted here that although the decomposition rates are very different between the two preparation methods, the

Scheme 1.

activation energies of the formate decomposition are very close to each other as shown in Figs. 4 and 6. That is, the frequency factor of the rate constant for the decomposition is different between the synthesis by hydrogenation of CO_2 and the adsorption of HCOOH. If the formate passes through the transition state toward the decomposition by the vibration of the OCO plane toward the Cu surface, the neighboring formate species in a chain may interfere with this vibration by the lateral interaction between formate species. This may be the cause for the small frequency factor of the rate constant for the formate species synthesized from CO_2 and H_2.

5. Conclusions

(1) The formation rate of formate on Cu(111) by the hydrogenation of CO_2 at 323–353 K and 1 atm $(CO_2/H_2 = 1)$ was measured by XPS. The initial rate at 323 K, for example, was measured to be 1.25×10^{-4} molecules site^{-1} s^{-1}. The apparent activation energy and the pre-exponential factor were determined to be 64.1 ± 2.2 kJ mol^{-1} and 2.83×10^6 molecules site^{-1} s^{-1}, respectively. The formation rate was first-order in $(1 - \Theta_{HCOO}/\Theta_{HCOO}^{sat})$, indicating that the kinetics assuming a simple Langmuir–Hinshelwood mechanism is not applicable for the synthesis of formate on Cu(111). An Eley–Rideal mechanism is proposed, in which a CO_2 molecule directly inserts into a Cu–H bond.

(2) The kinetics of formate decomposition on Cu(111) was measured by XPS for the formate species both synthesized by the hydrogenation of CO_2 and prepared by the adsorption of HCOOH on an oxygen-precovered Cu(111) surface. The rate constant, for example, was 1.7×10^{-5} s^{-1} at 360 K for the formate synthesized from CO_2 and H_2, which was much lower than that for the formate prepared by the adsorption of HCOOH, that is, 8.7×10^{-4} s^{-1} at 358 K. In spite of the difference in the values of the rate constant, the activation energies of the formate

decomposition were close to each other, that is, 112.8 ± 12.4 kJ mol^{-1} and 105.8 ± 15.6 kJ mol^{-1} for the formate synthesized by hydrogenation of CO_2 and the formate prepared by the adsorption of HCOOH, respectively. The experimental results indicate that the frequency factor of the rate constant is different for the two preparation methods, which can be explained by the different surface structure of the formate as previously observed by STM.

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