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Decomposition of Formic Acid on Silver Catalyst —Adsorption Measurement during Surface Catalysis—

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The mechanism of the decomposition of formic acid over reduced silver catalyst has been studied by means of the adsorption measurement during surface catalysis. It was found that the decomposition of formic acid on the silver catalyst at 100°C was first order at lower pressures of formic acid, while at medium pressures it was zero order, the reaction rate being independent of the pressures of ambient formic acid; in the first region the amount of adsorbed formic acid was proportional to the pressure of formic acid, and in the second region it was constant, independent of the pressure of formic acid in the ambient gas. The second region corresponds to "saturation" in an ordinary sense. At pressures of formic acid higher than that in the "saturation" region the amount of adsorbed formic acid increases again linearly with the pressure of formic acid. The linear relation between the reaction rate and the amount of formic acid adsorbed during the reaction was observed over the whole range of the pressure of formic acid studied. It is accordingly concluded that a surface unimolecular reaction in terms of the adsorbed formic acid is the rate-determining step. The exchange reaction of surface formic acid with those in the ambient gas was studied and it was demonstrated all the formic acid in the adsorbed layer accordingly participated in the exchange reaction. The numbers of surface silver atoms occupied by one molecule of adsorbed formic acid at the saturation points at various temperatures are estimated from the number of surface silver atoms and the amount of formic acid adsorbed at the zero-order kinetics. The number of surface silver atoms occupied by one molecule of adsorbed formic acid increases linearly with temperature.

The rate of chemical reaction is generally determined by the reactivities of the reacting species of the rate-determining step. In the case of heterogeneous catalysis, the concentration of some of the reaction intermediates, as well as those of reacting species in the ambient gas, may be determined by the techniques to measure adsorption during the course of the reaction.[1] The dependence of the reaction rate upon the concentration of each of the species on the catalyst surface and those in the ambient gas would reveal the reactants of the rate-determining step or the mechanism of the overall reaction. By means of this approach, the decomposition of formic acid has been previously studied by the authors over such metal oxides as alumina and zinc oxide which are typical dehydration and dehydrogenation catalysts respectively.[2]

The decomposition of formic acid over metal catalysts has been studied extensively by many investigators. Fahrenfort, van Reijen and Sachtler[3] studied the kinetic behaviour of the formate ion on a nickel surface and concluded that the decomposition of formic acid over a nickel catalyst proceeded *via* formate ion as a key intermediate. They correlated accordingly the activities of various metals for the decomposition of formic acid with the heat of formation of their formates which gave a "volcano-shaped" curve.

On the other hand, the examination of the kinetic behaviour of surface formate layers in more detail during the decomposition of formic acid over nickel catalyst has revealed that the reaction proceeds through two different mechanisms: a part of the overall reaction proceeds between formic acid molecule and the surface not covered by the formate ion, and that *via* the surface formate ion.[4] Consequently, it is of great interest to elucidate the reaction mechanism of the dehydrogenation reaction of formic acid over a silver catalyst which is a typical metal on the left-hand side of the "volcano-shaped" curve.

The mechanism of the decomposition of formic acid over reduced silver catalyst has been previously studied by means of the adsorption measurement

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[1] K. Tamaru, *Advances in Catalysis*, **15**, 65 (1964).

[2] Y. Noto, K. Fukuda, T. Onishi and K. Tamaru, *Trans. Faraday Soc.*, **63**, 2300, 3072, 3081 (1967).

[3] T. Fahrenfort, L. L. van Reijen and W. M. H. Sachtler, "The Mechanism of Heterogeneous Catalysis," ed. by J. H. de Boer, Elsevier, Amsterdam (1963), p. 23.

[4] K. Fukuda, Y. Noto, T. Onishi and K. Tamaru, *Trans. Faraday Soc.*, **64**, 522 (1968).

during surface catalysis.[5] It has been accordingly suggested to be most probable that the decomposition rate of formic acid over the silver catalyst is proportional to the amount of formic acid adsorbed. In this study, the kinetic behavior of the adsorbed species on a silver catalyst was examined in more detail by using a silver catalyst having greater specific surface area, and the dependence of the rate of the overall reaction upon the concentration of chemisorbed species was determined.

Experimental

The apparatus employed was an ordinary closed circulating system similar to that previously described.[2] The amount of adsorbed species on the catalyst surface can be calculated from the amount of the reactant introduced into the system and the pressure and composition of the circulating gas. The adsorption of formic acid by apparatus was measured spearately and was taken into consideration in estimating the adsorption on the catalyst surface during the reaction. The circulating gas was analyzed by gas chromatography, where dioctyl sebacate and molecular sieve 13X were used in the separation columns: the former for formic acid, water and carbon dioxide, and the latter for carbon monoxide and hydrogen. The silver catalyst was prepared from silver nitrate according to the method adopted by Benton and Drake.[6] The catalyst was reduced for about 160 hr at 100—120°C with circulating hydrogen gas.

The surface area of the catalyst was 7×10^5 cm^2 (61 g), which was determined by the BET method by means of nitrogen adsorption at liquid nitrogen temperature.

Results

A typical result at 100°C is given in Fig. 1, where the amount of carbon dioxide evolved, the amount of adsorbed formic acid on the silver catalyst and the partial pressure of formic acid in the gas phase are plotted against the reaction time. The composition of the adsorbed species was the same as that of formic acid as is given in Fig. 2. (It does not always follow, however, that the adsorbed species is in the form of formic acid.) The decomposition of formic acid on the silver catalyst at 100°C was first order at lower pressures of formic acid, while at medium pressures it was zero order, the reaction rate being independent of the pressures of ambient formic acid; in the first region the amount of adsorbed formic acid was proportional to the pressure of formic acid and in the second region it was constant, independent of the pressure of formic acid in the ambient gas. The second region corresponds to "saturation" in an ordinary sense.

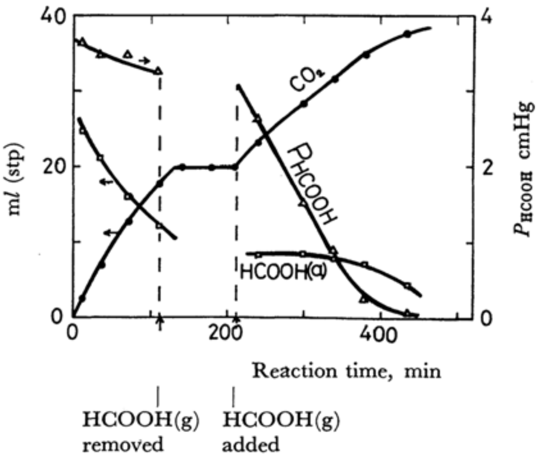

Fig. 1. Decomposition of formic acid on Ag at 100°C.

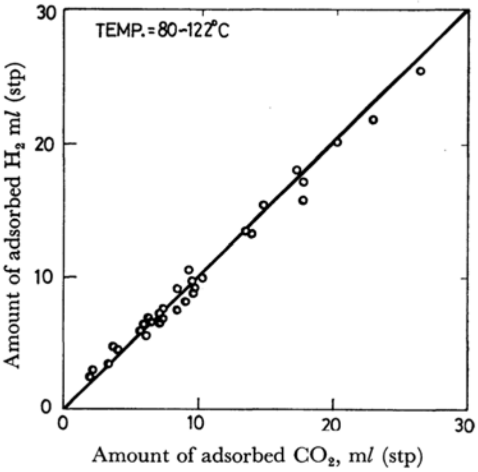

Fig. 2. Composition of adsorbed species on Ag.

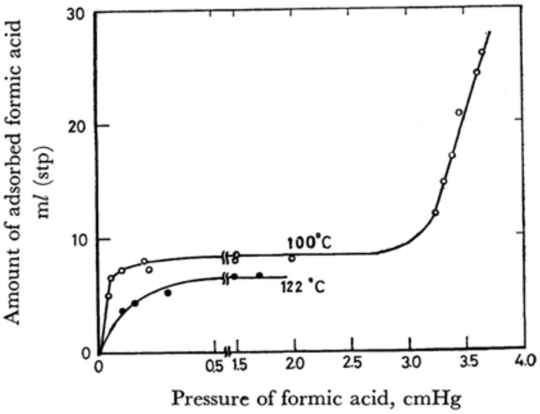

Fig. 3. Adsorption of formic acid during the decomposition on Ag.

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[5] K. Tamaru, *Trans. Faraday Soc.*, **55**, 824 (1959).

[6] A. F. Benton and L. C. Drake, *J. Am. Chem. Soc.*, **54**, 2186 (1932).

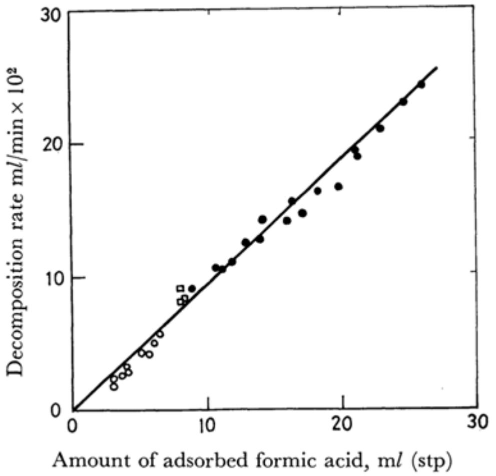

Fig. 4. Dependence of the reaction rate upon the amount of adsorbed formic acid at 100°C.

The dependence of the amount of formic acid adsorbed during the reaction upon the partial pressure of formic acid is given in Fig. 3, which shows that at lower temperatures the adsorption of formic acid reaches a "saturation" value at lower pressures, and increases again at higher pressures.

The dependence of the reaction rate upon the amount of adsorbed formic acid at 100°C is given in Fig. 4, which is obtained from three runs at 100°C. It is shown from Fig. 4 that the reaction rate is proportional to the amount of formic acid adsorbed. It should be noted here that the linear relation between the reaction rate and the amount of formic acid adsorbed during the reaction was observed over the whole range of the pressure of formic acid studied. Thus the reaction rate (r), $d(CO_2)/dt$, is expressed by the following equation;

$$r = kX_{\mathrm{ads.}} \qquad (1)$$

or

$$r = k\theta_{\mathrm{HCOOH}} \qquad (1')$$

where $X_{\mathrm{ads.}}$ is the amount of adsorbed formic acid.

The zero order reaction rate at 80—122°C was divided by the corresponding saturation amounts of adsorbed formic acid to obtain the specific rate for the equal amount of adsorption at full coverages. The dependence of the calculated rates upon the reaction temperature gave an activation energy of 29.8 kcal/mol as shown in Fig. 5. The apparent frequency factor was 3.86×10^{15} min^{-1}. Thus the reaction rate was expressed by the following equation;

$$r = X_{\mathrm{ads.}}(3.86 \times 10^{-15}) \exp(-29.8 \times 10^3/\boldsymbol{R}T) \text{ ml/min}, \qquad (2)$$

where $X_{\mathrm{ads.}}$ is the amounts of adsorbed formic acid at zero-order kinetics at each temperature.

The exchange reaction of formic acid on the surface with that in the ambient gas was studied in the circulation system. In this experiment HCOOH was first introduced in the system and was decomposed at 100°C for a short time, then the gas phase was evacuated rapidly, the reaction vessel being cooled to about 10°C to prevent further decomposition and desorption of the formic acid remaining on the surface. Then DCOOD was introduced in the system and the change in D-content in the ambient formic acid molecule at 60°C was followed with time to study the exchange reaction. The procedure itself involved some ambiguity in its initial stage, but the exchange rate could be followed in such a manner. The ratio of HCOO/DCOO in the formic acid vapour was estimated by the infrared technique from the intensity of CH and CD stretching bands of adsorbed isotopic mixture of formic acid over fresh alumina.[2]

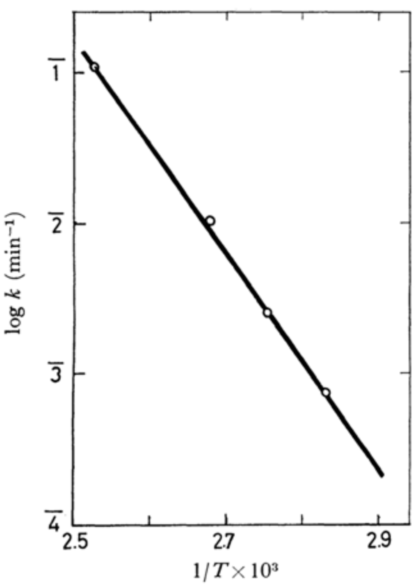

Fig. 5. Temperature dependence of the decomposition rate.

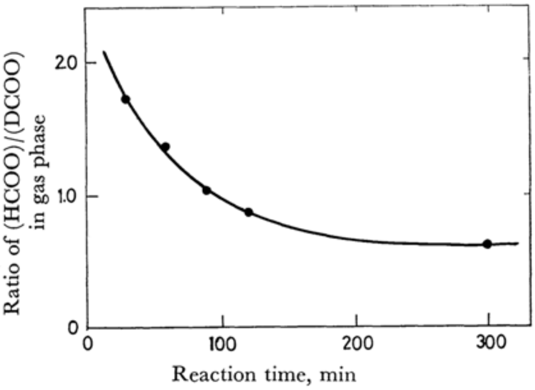

Fig. 6. Exchange reaction of surface formic acid on Ag with DCOOD at 60°C.

The exchange reaction proceeded at a comparatively slow rate as shown in Fig. 6. In this case the total amount of adsorbed formic acid was 14 m*l* (stp) at 60°C and the exchangeable formic acid on the surface was approximately estimated to be 13 m*l* (stp), which substantially corresponded to all the surface formic acid. All the formic acid in the adsorbed layer accordingly participated in the exchange reaction.

Discussion

The mechanism of the decomposition of formic acid over silver catalysts has been studied by many investigators. Otaki studied kinetic isotope effect in the decomposition of formic acid over a reduced silver catalyst.[7] He found the decomposition rate of various deuterium-substituted formic acid to be in the following decreasing order $HCOOH > HCOOD > DCOOH$. Schwab and Watson recently found the isotope effect in the decomposition of formic acid over a silver foil catalyst, where the order of the decomposition rate was $HCOOH > HCOOD > DCOOH > DCOOD$.[8]

Hirota, Kuwata and Asai studied the adsorption of formic acid on various metals by the infrared technique and reported that formate ion was detected on a silver surface.[9] From these observations they presumed that the primary step of the decomposition of formic acid over silver catalyst was the formation of surface formate which is subsequently followed by the processes as follows;

(1) $HCOO^-(ads.) + H^+(ads.) \rightarrow H_2 + CO_2$

(2) $2HCOO^-(ads.) \rightarrow H_2 + 2CO_2 + e$

(3) $HCOO^-(ads.) + HCOOH(ads.)$
$\rightarrow H_2 + CO_2 + HCOO^-(ads.)$

(4) $HCOOH(ads.) \rightarrow H_2 + CO_2$

(5) $2H^+(ads.) + 2e \rightarrow H_2$

where each of these reactions was slow as compared with the formation of surface formate. Hirota and his coworkers suggested a possibility of participation of neutral formic acid molecule adsorbed on the catalyst surface.[10]

It was shown in Fig. 4 that the overall reaction rate is proportional to the total amount of adsorbed formic acid. It is accordingly concluded that a surface unimolecular reaction in terms of the adsorbed formic acid is the rate-determining step.

Block and Kral previously proposed a unimolecular mechanism for the decomposition of formic acid on a silver wire catalyst from their study on the kinetic isotope effects for various deutero-formic acids.[11] They assumed that the C–H and O–H bond in formic acid molecule cleaved at the same time in the rate-determining step, showing that the calculated kinetic isotope effects agreed with the experimental values fairly well. Eley and Leutic also proposed a unimolecular mechanism for the decomposition of formic acid on metal catalysts.[12,13] In those cases, however, any direct experimental basis for a unimolecular mechanism does not seem to be presented.

The results given in Fig. 4 and those of the exchange reaction, demonstrate that the formic acids adsorbed on the catalyst surface during the decomposition reaction behaves uniformly and the coverage of the silver surface by formic acid, which was directly measured during the decomposition, agrees with that of the active region in the surface which was estimated from the reaction kinetics, assuming that the reaction rate is proportional to the coverage of the active region. The characteristic dependences of both coverages upon pressure were quite similar as shown in Figs. 3 and 4, which strongly suggest that the coverage over the active region during the reaction agrees with that of the whole surface.

This conclusion is in marked contrast to that in the case of reduced copper catalyst obtained previously by one of the authors,[14] where the reaction rates were independent of the masured adsorption during the reaction, suggesting the heterogeneity of the adsorbed formic acid. Accordingly the adsorption measurements during surface catalysis may demonstrate the heterogeneity and/or homogeneity of the catalyst surface.

It is generally admitted that the following equation can be applied for the zero order reaction,[15]

$$\text{rate} = c_a(\boldsymbol{k}T/\boldsymbol{h}) \exp(-E/\boldsymbol{R}T), \tag{3}$$

where c_a is the number of adsorbed molecules on a unit surface area. Using this equation and the activation energy (E) of 29.8 kcal/mol which was obtained in this study, c_a becomes 1.8×10^{15} molecules per square centimetre at 100°C, while

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[7] T. Otaki, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **80**, 255 (1959).

[8] G. H. Schwab and A. M. Watson, *Trans. Faraday Soc.*, **60**, 1833 (1964).

[9] K. Hirota, K. Kuwata and A. Asai, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **80**, 701 (1959); *Z. Physik. Chem. N. F.*, **21**, 438 (1959).

[10] K. Hirota, K. Kuwata, T. Otaki and A. Asai, Proc. 2nd. Internl. Congr. Catalysis, **1961**, 809 (Technip, Paris).

[11] T. Block and H. Kral, *Z. Electrochem.*, **63**, 182 (1959).

[12] D. D. Eley, *ibid.*, **60**, 797 (1956).

[13] D. D. Eley and P. Leutic, *Trans. Faraday Soc.*, **53**, 1483 (1958).

[14] K. Tamaru, *ibid.*, **55**, 1191 (1959).

[15] S. Glasstone, K. J. Laidler and H. Eyring, "Theory of Rate Processes," McGraw-Hill Book, Co., Inc., N. Y. (1941), p. 376.

the saturation value of the adsorbed formic acid at 100°C is 3.1×10^{14} molecules per square centimetre. It suggests consequently that all of the adsorbed formic acid participates in the decomposition reaction, which is well compatiable with the results obtained from the kinetic studies.

It is of great interest that at pressures of formic acid higher than that in the "saturation" region the amount of adsorbed formic acid increases again linearly with the pressure of formic acid as shown in Fig. 3. In this region of adsorption the reaction rate was proportional to the total amount of adsorbed formic acid. This result also indicates that the adsorbed formic acids uniformly participate in the reaction over the whole range of the pressure of formic acid.

TABLE 1

Temperature °C	Number of surface silver atoms occupied by one molecule of adsorbed formic acid
80	1.7
90	2.1
100	4.4
122	5.2
134	7.2
142	8.7
160	10.8

The numbers of surface silver atoms occupied by one molecule of adsorbed formic acid at the saturation points at various temperatures are estimated from the number of surface silver atoms [1.30×10^{15} for (110) and (111) planes in average], and the amount of formic acid adsorbed at the zero-order kinetics, and are given in Table 1, where the values at 134, 142 and 160°C were obtained previously by one of the authors.[5)]

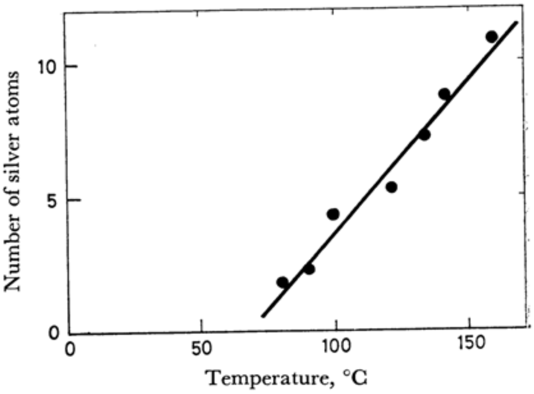

Fig. 7. Dependence of the number of silver atoms occupied by one molecule of absorbed formic acid upon temperature.

It is very interesting to note that the results in these experiments agrees reasonably well with those in the previous paper and the number of surface silver atoms occupied by one molecule of adsorbed formic acid increases linearly with temperature as shown in Fig. 7.

The area occupied by a surface formic acid at full coverage is seemingly determined by the range the surface molecule moves around at saturation, which expands with temperature.