Infrared Studies of Formic Acid, Chemisorbed on Copper, Nickel and Zinc

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The catalytic decomposition of formic acid into hydrogen and carbon dioxide, $HCOOH \rightarrow H_2 + CO_2$, has been studied kinetically by many researchers, and the mechanisms of the decomposition were often suggested in recent years[1]. However, it may be admitted that these mechanisms are established on the kinetic data without any exact knowledge of the adsorbed state of formic acid. Considering such situations, the present authors attempted to solve the problem by the infrared absorption technique which had been explored by Eischens et al.[2], i. e., the infrared spectra of formic acid adsorbed on metal surface were measured, and were compared with those of gaseous formic acid and solid formates.

Experimental

The catalysts studied were copper, nickel and zinc, each being dispersed in the extra fine powder of silica. Each metal catalyst was prepared by the thermal decomposition of the corresponding formate, followed by its reduction

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[1] a) G. M. Schwab and E. Schwab-Agallidis, *J. Am. Chem. Soc.*, **71**, 1806 (1949). b) D. A. Dowden et al., *Trans. Faraday Soc.*, **42**, 680 (1948). c) G. Rienäcker and N. Hansen, *Z. Elektrochem.*, **60**, 887 (1956).

[2] R. P. Eischens, S. A. Francis and W. A. Pliskin, *J. Phys. Chem.*, **60**, 194 (1956).

with hydrogen at 200°C. The spectrum was measured at room temperature with Hilger H-800 spectrometer. The cell, which was constructed so as to be heated from the outside to reduce the catalyst enclosed, was laid horizontally before the slit of the spectrometer. The cell was made of pyrex glass and was similar to that described by Eischens. The windows of the cell and the thin plate supporting the catalysts were made of sodium chloride. It was ascertained previously that all the metal-silica-catalysts had no absorption bands in the spectral region concerned, and also that there was no absorption band caused by the interaction of formic acid with the windows and plates of sodium chloride in the same region.

Results

The absorption spectra of chemisorbed formic acid could be obtained from the bands which remained when the excess of free formic acid was desorbed by evacuating the cell until the strongest absorption band of free formic acid at 1740 cm^{-1} disappeared. These bands of chemisorbed formic acid, as shown in Table I, do not coincide with those of gaseous formic acid (1740 cm^{-1} and 1380 cm^{-1}). Typical spectra of formic acid chemisorbed on copper and zinc are shown in Fig. 1 and Fig. 2, where the pressure of gaseous formic acid is reduced successively in the order a, b and c. It is found generally that the absorption intensity of these bands increases in comparison with those of gaseous formic acid, according as its pressure decreases.

TABLE I

INFRARED ABSORPTION BANDS OF FORMIC ACID CHEMISORBED ON COPPER, NICKEL AND ZINC, OF THE CORRESPONDING SOLID METAL FORMATES AND OF FORMATE ION (cm^{-1})

Modes of vibration	Formic acid chemisorbed on			Metal formates of			Formate ion[3]
	Cu	Ni	Zn	Cu	Ni	Zn	
ν_4	1560	1600	1590	1580	1570	1580	1585
ν_5	1400	1380	1360(?)	1400	1400	1400	1385
ν_2	1360	(?)		……[a]	……[a]	……[a]	1351

a) As Nujol oil was used, these bands were masked.

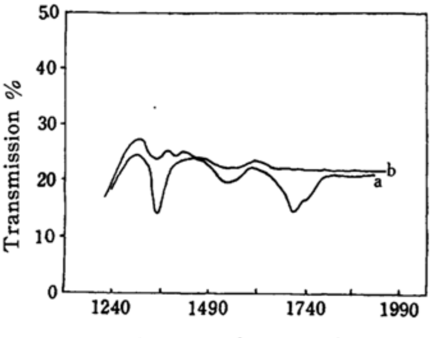

Fig. 1. Absorption spectrum of formic acid chemisorbed on copper catalyst.

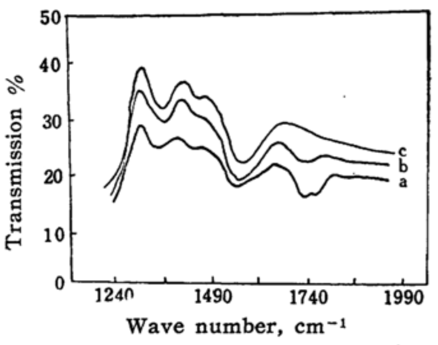

Fig. 2. Absorption spectrum of formic acid chemisorbed on zinc catalyst.

In the table, the bands of metal formates $(HCOO)_2Cu \cdot 2H_2O$, $(HCOO)_2Ni \cdot 2H_2O$ and $(HCOO_2)Zn \cdot xH_2O$ obtained are shown for the sake of reference. The spectra of these formates coincide fairly well with those of several formates in the literature[4]. Since the accuracy in measuring wave number of the maximum absorption was low, predominantly owing to weakness of the absorption, the last figures in the table were round figures.

Discussion

In each catalyst, two or three bands were observed. In Table I they are given the notations of the ν_4, ν_5 and ν_2 vibrations, because they seem to correspond to the antisymmetric ν_4 and ν_5 vibrations and to the symmetric ν_2 vibration of formate ion*, respectively. However, the other two symmetric vibrations, designated as ν_1 and ν_3, which will appear near 2825 cm^{-1} (ν_1) and 775 cm^{-1} (ν_3), were not observed. The ν_1 vibration would be masked by the strong and broad absorption bands of silica, while the ν_3 vibration would be hard to detect because of the small transmission of the sample in this region, even if there is. Moreover, it is noteworthy

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[3] Landolt-Börnstein, "Zahlenwerte und Funkionen", 1, 2 Teil, p. 237 (1951).

* Theoretical assignment of the vibrations of formate ion was given by T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zassi*), **77**, 381 (1956).

[4] Ll. Puval, H. Gerding et J. Lecomte, *Rec.Trav. Chim.*, **69**, 391 (1950).

that the ν_4, ν_5 and ν_2 vibrations are similar to those of the corresponding metal formates as shown in the table and also to those observed in the liquid solution[4]. Therefore the new bands caused by the adsorbed formic acid may be ascribed to the formate ion present on the surface of the catalysts.

According to the X-ray analysis of these crystals[5] and the spectrochemical studies of their microcrystals[6], a carbon atom combines with a metal atom via an oxygen atom in those crystals which are composed of formate groups (HCOO), metal atoms and water molecules. If the above structure can be extended to such surface complexes, it will be reasonable to assume that the formic acid is not physically adsorbed, but is chemisorbed, dissociating into the hydrogen atom and the formate group. Considering the structure of the metal formates[5], it is possible that the formate ion forms a bridged bond with two metal atoms on the surface. However, the ionic degree of the bond between the oxygen atom and the catalyst cannot be estimated in the present state of experimental accuracy.

It must be pointed out that the ν_5 vibration of formic acid chemisorbed on zinc is a little different from that of formate ion (1385 cm^{-1}), the difference being 75 cm^{-1}. It was supposed that it might owe to the imperfect reduction of the catalyst. However, as the difference decreased to 55 cm^{-1} when an amount of oxygen was chemisorbed, the deviation may be ascribed to some causes other than the chemisorption of oxygen, e. g., the mutual interaction between the chemisorbed chemical species, as pointed out by Eischens[2] and Yang[7]. Concerning this point, further research is required.

The above conclusion supports the "dissociation mechanism" of the Rienäcker[1c], i. e.,

$$HCOOH+H^{+}+2e \rightarrow H_2+HCOO^{-} \qquad (1a)$$

$$HCOO^{-}+[Met] \rightarrow CO_2+[Met]^{-}+H \qquad (1b)$$

but rejects the "monomolecular-mechanism", the essential feature of which is depicted in Fig. 3: i. e.,

$$HCOOH \rightarrow H_2+CO_2 \qquad (2)$$

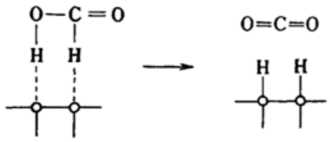

Fig. 3. Eley's Mechanism.

This latter mechanism, which was first proposed for the oxide catalysts by Schwab et al.[1a], was also proposed by Eley et al.[8] in the case of gold-palladium catalysts. Besides the above-mentioned reason, there is another one against Eley's mechanism from the standpoint of the structure of formic acid molecule[3,9], because the chemisorbed formic acid molecule would require higher potential energy to keep such a distorted structure.

It is interesting to mention that the kinetic studies[10] on the decomposition of formic acid on silver catalyst performed by one of the present authors (K. H.) also support the dissociation mechanism; i. e. in the intermediate state of the decomposition at the pressure of 2~3 cm Hg, more hydrogen was always found to exist than carbon dioxide at the temperature between 80~130°C, the maximum deviation of the ratio H_2/CO_2 being ca. 30%. If the decomposition had proceeded monomolecularly in one step as shown in Eq. 2, such a result would surely not have been found, because the decomposition was carried out on the condition that the adsorption of carbon dioxide was negligibly small and the addition of carbon dioxide in the original gas had no effect on the progress of the decomposition.

Therefore, for the several reasons cited above it seems that the dissociation mechanism is better than that of Eley, at least in the case of the metal catalysts. However, Schwab's mechanism may be justified in the case of the oxide catalysts which can act partly as dehydrogenation catalysts and partly as dehydration catalysts. Of course, it can not be asserted from the present experimental data that the free formate ion, $HCOO^{-}$, as described in Rienäcker's paper, exists on the metal surface.

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[5] R. Kiriyama, H. Ibamoto and K. Matsuo, *Acta Cryst.*, **2**, 482 (1954).

[6] S. Yamada, H. Nakamura and R. Tsuchida, This Bulletin, **30**, 953 (1957).

[7] A. C. Yang and C. W. Garland, *J. Phys. Chem.*, **61**, 1504 (1957).

[8] D. D. Eley and P. Lucky, *Trans. Faraday Soc.*, **51**, 1483 (1957).

[9] S. H. Bauer and R. M. Badger, *J. Chem. Phys.*, **5**, 852 (1937).

[10] K. Hirota and T. Otaki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), to be published

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Conclusion

By the use of the infrared absorption technique, it can be concluded that formic acid, chemisorbed on copper, nickel and zinc, dissociates into two groups as HCOO and H at room temperature. Such a conclusion conforms with Rienäcker's mechanism on the dehydrogenation of formic acid. However, it can not be determined at the present state of the study whether or not these groups are linked to the metal atoms by ionic or covalent bonds.

The detailed discussion will be published in near future in addition to the data of kinetic research.

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