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DYNAMIC BEHAVIOR OF REACTION INTERMEDIATES ON CATALYST SURFACES IN THE WORKING STATE: BEHAVIOR OF FORMATE ION DURING THE DECOMPOSITION OF FORMIC ACID ON Ni/SiO_2 CATALYST

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The reactivity of the formate ions on Ni/SiO_2 catalyst was examined during the course of the formic acid decomposition. It is of great interest to note that the reactivity was markedly increased by the presence of formic acid in the ambient gas compared to that at the same coverage under vacuum. It is accordingly suggested that the formate ion behaves as reaction intermediate through the interaction between the formic acid molecules in the ambient gas.

1. Introduction

The mechanism of catalytic decomposition of formic acid on metals has been extensively studied by many people [1]. It is generally accepted that the decomposition of formic acid takes place through the decomposition of formate ion as a reaction intermediate which is observed on the surface of metal catalysts by means of infrared spectroscopy. The catalytic activity of various metals for this reaction is, accordingly, explained on the basis of the stability of these surface formates: If the formate is either too stable or too unstable, the activity should be low, exhibiting the highest activity somewhere between at an optimum stability to give a volcano shaped curve when the catalytic activity of various metals is plotted against the heat of formation of their formate salts.

If the rate determining step is the decomposition of formate ion, the rate of decomposition of four isotope species, HCOOH, HCOOD, DCOOH and DCOOD, should be classified into two groups, the former two, and the latter two species. However, the rate of decomposition of the four species on a silver catalyst actually gave four different rates in the following order [2]:

$\mathrm{HCOOH} > \mathrm{HCOOD} > \mathrm{DCOOH} > \mathrm{DCOOD}$

The concept of "adsorption assisted decomposition" or "bimolecular associated effect" which was recently proposed [3,4] and the possibility of having such assisted decomposition of surface formate ion was examined in the case of Ni/SiO_2.

2. Experimental

6.1% Ni/SiO_2 catalyst was prepared by impregnating nickel nitrate aqueous solution into Aerosil 200 (Nippon Aerosil Co. Ltd.). 40 mg of the catalyst was pressed into a disk and placed in a infrared cell which was connected to a closed gas circulation system. Prior to each experiment the catalyst was treated with hydrogen at 400 ° C for two hours, and was evacuated for one hour at 400 ° C. The surface concentrations as well as the kinetic behavior of each of the adsorbed species were examined during the reaction by infrared spectroscopy (JASCO IR-810 Grating Spectrometer).

The deuterated formic acids, HCOOD, DCOOH and DCOOD, were obtained from MSD isotopes, and the decomposition rate of each of the isotope species was studied.

3. Results and discussion

When formic acid vapor was introduced on Ni/SiO_2 catalyst in the temperature range from 100 to 120 ° C, the decomposition products were hydrogen and carbon dioxide. Figure 1 gives the changes in the partial pressures of hydrogen and formic acid, and the amounts of chemi- as well as physi-sorbed formic acid with reaction time. During the decomposition the volume of the hydrogen formed was equal to that of carbon dioxide. The dependence of the decomposition rate of the formate ion upon its coverage was studied by estimating the rate of hydrogen formation at various amounts of surface formate ion. As shown in fig. 2, the rate of the decomposition demonstrated a good correlation with the coverage, but it is of great interest that the reactivity of the surface formate ion is markedly increased by the presence of formic acid vapor. The activation energies of the reaction were approximately the same in the presence and absence of formic acid in the vapor phase, which were 19.2 and 19.8 kcal/mol, respectively. Figure 3 shows the dependence of the rate of formic acid decomposition upon the formic acid pressure, which is a first order reaction with respect to formic acid.

When ^{13}C-formic acid vapor was introduced into the catalyst, the infrared spectra of the adsorbed species showed a shift in antisymmetric vibration compared to that of ^{12}C-formic acid. When ^{12}C-formic acid vapor was introduced on top of such adsorbed layer, the adsorbed formate ion was readily replaced by the non-labelled species even at room temperature at a rate much faster than the decomposition rate.

The rates of decomposition of four isotope species, HCOOH, HCOOD, DCOOH and DCOOD, were measured on the nickel catalyst, which gave four different rates in the following order; HCOOH > HCOOD > DCOOH > DCOOD, as given in table 1, which strongly demonstrates that the decomposition of the surface formate ion is not the only rate-determining step of the overall

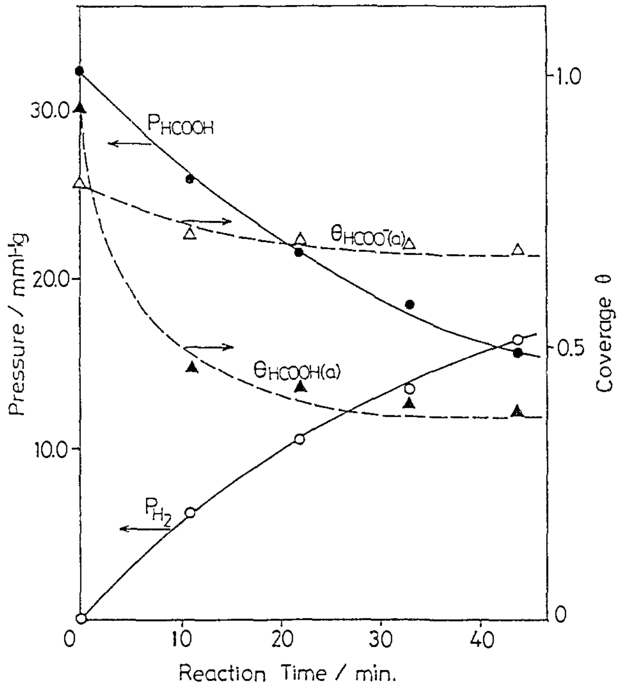

Fig. 1. Pressure and coverage changes with reaction time. Pressure of formic acid, (●); pressure of hydrogen, (○); Coverage of physisorbed formic acid, (▲); and the coverage of formate ion, (△).

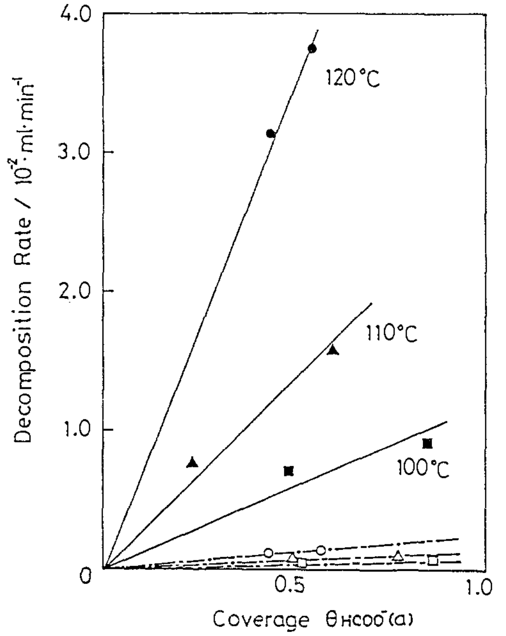

Fig. 2. The decomposition rate as a function of coverage and temperature over Ni/SiO_2 catalyst. Under 11 torr formic acid, ———; under vacuum, - — - — -: $T = 120$ °C, (●, ○), $T = 110$ °C, (▲, △), $T = 100$ °C, (■, □).

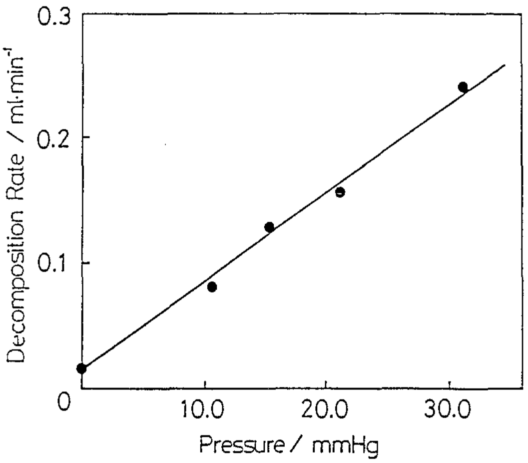

Fig. 3. Dependence of the decomposition rate on the pressure of formic acid over Ni/SiO_2 catalyst. $T = 120$ ° C, formate ion coverage; 0.8.

Table 1

Relative rates of decomposition of the isotopic species of formic acid over Ni and Ag catalysts.

HCOOH	HCOOD	DCOOH	DCOOD
1	0.55	0.26	0.12 over Ni at 120 ° C
1	0.74	0.59	0.20 over Ag at 190 ° C [2]

reaction, but some other processes, such as the interaction between the molecules in vapor phase and the surface formate ion, would be involved in the rate determining step. Such behavior also suggests the overall reaction taking place through the interaction between formic acid molecules in the ambient gas and the surface formate.

References

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