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The Decomposition of Formic Acid on the Intermetallic Compounds of 3d-Transition Metals

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The catalytic behavior of the intermetallic compounds of Cr-Co, Fe-Cr, Fe-Mo, Ni-V and Fe-V systems on the decomposition reaction of formic acid was studied by the usual static method and compared with that of some alloys and manganese. A zeroth-order decomposition reaction was observed throughout the catalysts employed and the adsorption of formic acid on the catalysts during the decomposition reaction approched to the saturation value under the experimental condition, i. e., under the pressure range of 10—20 mmHg, and at the temperature of 200—300°C. The activation energy of the reaction varied from 13.5 to 20.7 kcal./mol. for various catalysts. It has been also found that the activation energy of the reaction catalyzed by the intermetallic compounds increased with the ratio of the electrons in d- and s-bands to atom of the catalyst.

The low catalytic activity of an intermetallic compounds as compared with the corresponding alloy is generally attributed to the presence of some linkage of covalent nature in the compound.

The catalytic behavior of alloys of silver, gold, and copper with other metals has been studied by Schwab,[1] and it has been revealed that the activation energy of the catalytic decomposition of formic acid on copper-tin alloy catalyst became higher with increasing content of tin in the alloy from about 24 kcal./mol., making a very distinct maximum (33 kcal./mol.) at the phase (20 atomic % of tin) which has a deformed body-centered cubic lattice. Then, the energy falls again with the increasing content of tin in the alloy.

On the other hand, the binary alloys of the 3d-transition metals, chromium-cobalt, iron-chromium, iron-molybdenum, nickel-vanadium and iron-vanadium, have sigma phases, and the sigma phase of the crystals of these alloys are intermetallic compounds having the deformed body-centered cubic lattice. The 3d-transition metals have partially filled *d* electron levels, and the ratio of electron to atom in these compounds is around seven.

The present work deals with the catalytic behavior of some intermetallic compounds of 3d-transition metals on the decomposition reaction of formic acid, was compared with some alloys and with metallic manganese having seven electrons in the d- and s-bands of the atom.

Experimental

Apparatus.—The experiment was carried out by a usual static method. The volume of the system corresponded to 702.3 ml. at 30°C, with the reaction vessel held at 250°C.

Material.—A certified reagent grade formic acid (98—100%) obtained from Merck was dried over anhydrous cupric sulfate, and distilled under a reduced pressure at room temperature. The purified acid was stored in a cold and dark place.

Catalysts.—The metallic manganese used was prepared from manganese oxide. The oxide was reduced at 250°C for 300 hr. by circulating hydrogen. The alloy catalysts, chromium-cobalt, iron-chromium, iron-molybdenum, nickel-vanadium and iron-vanadium were prepared by the fusion of the components having the suitable composition for the formation of the sigma phases, as is shown in Table I, followed by a heat-treatment at about 1000°C for a week in a reaction vessel in an atmosphere of argon. All the catalysts were used as 100 mesh powder. The phase composition and the lattice constant in the sigma phase of each alloy are summarized in Table I, together with the temperatures of the heat-treatment used in the preparation of the intermetallic compound. The specimens of the catalysts prepared were subjected to the X-ray diffraction measurements to confirm the formation of intermetallic compounds, and the lattice constants of these catalysts were found to be in agreement with the reported values for the corresponding intermetallic compounds. The surface areas of these catalysts

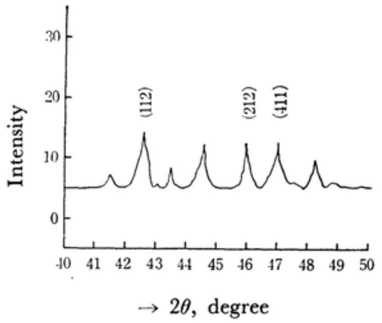

Fig. 1. X-Ray diagram of Fe-Cr powder with Cu*Kα* radiation and Ni filter.

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[1] G. M. Schwab, *Trans. Faraday Soc.*, **17**, 689 (1946).

Table I. Catalysts

	A	B	B atomic-%	Heat-treat. temp., °C	Lattice const. *a*	Lattice const. *c*
	Mn				3.774	3.533
σ phase	Cr	Co	37	1200	8.750	4.540
	Fe	Cr	50	800	8.790	4.559
	Fe	Mo	50	800	9.188	4.812
	Ni	V	33	1200	8.966	4.641
	Fe	V	50	1100	8.930	4.660
α+σ phase	Fe	Cr	42	—	—	
	Fe	Mo	49	—	—	
	Fe	V	42	—	—	

Table II. The relationship between the activation energies and the ratios of electron to atom of catalysts

Catalyst		Surface area m^2/g.	Electron : atom* ratio	Activation energy, kcal./mol.
Mn		0.76	7.00	26.8
Intermetallic compound	Cr-Co	0.87	7.12	20.7
	Fe-Cr	0.95	7.02	18.0
	Fe-Mo	1.87	7.00	20.0
	Ni-V	1.10	6.65	15.5
	Fe-V	1.51	6.47	13.5
Alloy	Fe-Cr	1.07	7.16	7.2
	Fe-Mo	1.75	7.02	10.0
	Fe-V	1.35	6.74	4.4

* P. A. Beck, "Electronic Structure and Alloy Chemistry of the Transition Elements," John Wiley & Sons, New York and London (1963), p. 106

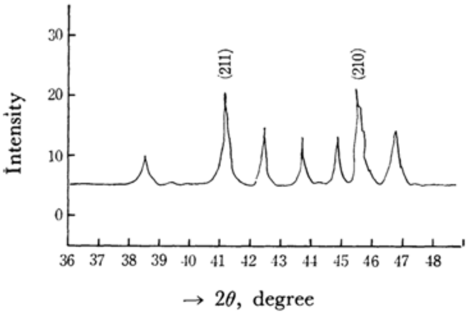

Fig. 2. X-Ray diagram of Ni-V powder with Cu-*K*α radiation and Ni filter.

were determined by the B. E. T. method by using nitrogen gas at the temperature of liquid nitrogen (cf. Table II).

Procedure.—The alloy or the intermetallic compound (approximately 10 g.) placed in the reaction vessel was maintained at 350°C for 20 hr. under a pressure of less than 10^{-6} mmHg, and reduced with hydrogen (1 atm.) at 350°C for 48 hr. Then the reaction vessel was kept at the same temperature under a vacuum overnight. After this treatment, a known amount of the purified formic acid was introduced into the reaction system and the decomposition reaction was followed by measuring the pressure of the reaction system at suitable time intervals. The composition of the reaction products was determined by mass spectrometry. In most cases, the products were found to be carbon dioxide and hydrogen. The decomposition reaction was carried out over the range of temperatures from 200 to 300°C and the range of the pressures from 10 to 20 mmHg.

Results

The catalytic decomposition of formic acid was carried out in the presence of carbon dioxide or hydrogen to find out the influence of the reaction products on the decomposition reaction. No

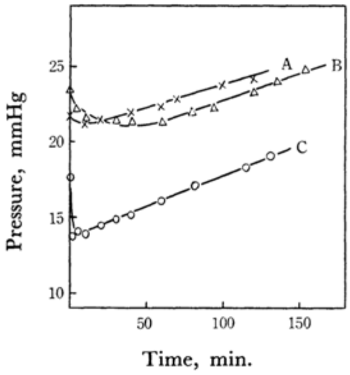

Fig. 3. The decomposition of formic acid on Mn at 225°C in the presence of H_2 and CO_2.
A: with 6.98 mmHg H_2, B: with 7.05 mmHg CO_2, C: pure formic acid

appreciable effect on the reaction rate is observed, as is shown in Fig. 3.

The pressure-time curve of the reaction on a manganese catalyst at 250°C gave a characteristic S shape, as is shown in Fig. 4. The rapid decrease of the pressure of the reaction system in the first few minutes can be reasonably attributed to the adsorption of the acid on the catalyst surface. After about 100 min., the slight decreace in activity due to the influence of poisoning of the catalyst caused by a negligible amount of water which was produced by a side decomposition reaction became appreciable. However, the S curve has a good linear part at reaction times between 20 and 100 min.

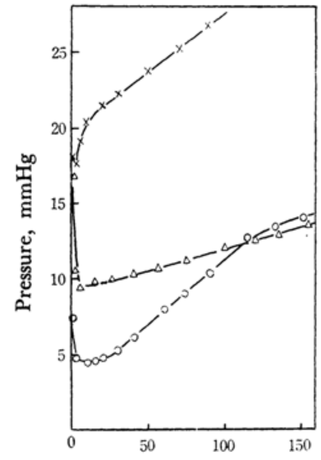

Fig. 4. The pressure-time curves for the decomposition of formic acid, on Mn.
—×— at 250°C, P_0 18.13 mmHg
—○— at 250°C, P_0 7.44 mmHg
—△— at 225°C, P_0 17.32 mmHg

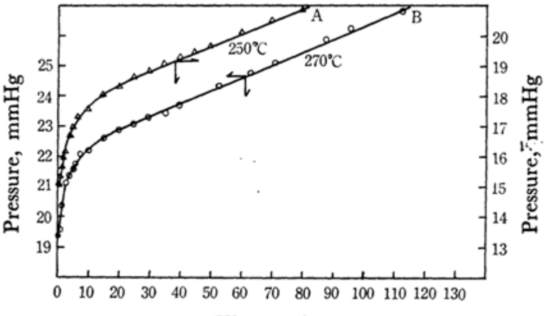

Fig. 5. The pressure-time curves for the decomposition of formic acid.
A. Fe-V intermetallic compound, B. Fe-Mo alloy

The change in pressure in the decomposition of formic acid on the iron-vanadium intermetallic compound and the iron-molybdenum alloy are indicated in Fig. 5. In both experiments, the time-pressure curve clearly indicates the presence of an inflection point, the first part with a steeper slope, ending at the reaction time of about 5 min., and the second part with a flatter slope. This fact suggests that the reaction first occurs at the most active points of the surface of the catalyst, after which the activity remained almost constant.

The rate constants of the zeroth-order decomposition reactions at different temperatures were obtained, their logarithms are plotted against $1/T$, i. e., the reciprocal of the absolute temperature (Fig. 6). The curve in Fig. 7 indicates how the values of the activation energies on the intermetallic compounds are correlated with the ratios of the electrons in the d- and s-bands to the atom of the catalysts.

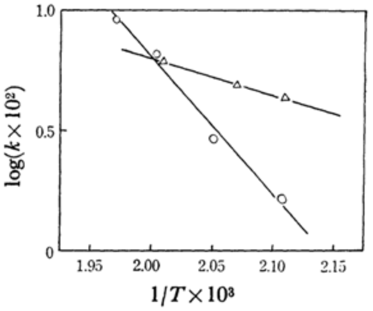

Fig. 6. Arrhenius plots for the decomposition of formic acid.
○ Mn 26.8 kcal./mol.
△ Cr-Co 20.7 kcal./mol.

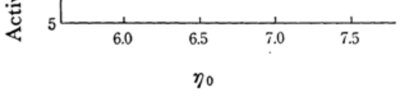

Fig. 7. The drop of the activation energy of the decomposition of formic acid by intermetallic compound is plotted against the ratio of electron in s- and d-bands to atom of catalyst.

Discussion

In the present work every effort has been made to prepare intermetallic compound catalysts which are homogeneous both in bulk and on surface. The homogeneity of the catalysts was confirmed by the X-ray diffraction measurements.

Although the decomposition of formic acid has been much studied,[2-4] it has often proved difficult to elucidate its mechanism. Recently, it has been confirmed that the formic acid is adsorbed on the surface of metal as formate ions which are observed by means of infrared spectra.[5,6]

In the case of the present work, the following scheme was presented as the mechanism of the decomposition of formic acid on a 3d-transition metal catalyst.

$$\mathrm{M + HCOOH \rightleftarrows M/H^+ + HCOO^-} \qquad (1)$$

$$\mathrm{M + HCOO^- \rightleftarrows M/HCOO^-} \qquad (2)$$

$$\mathrm{M/HCOO^- \rightarrow M^-/H + CO_2} \qquad (3)$$

$$\mathrm{M/H^+ \rightleftarrows M^+/H \rightleftarrows M^+ + H} \qquad (4)$$

$$\mathrm{M^-/H + M^+ + H \rightarrow 2M + H_2} \qquad (5)$$

In the initial step, the formic acid molecule is dissociated by chemisorption, yielding formate ions, $\mathrm{HCOO^-}$, and adsorbed hydrogen, $\mathrm{M/H^+}$; the measurement of the heat of the adsorption of formic acid on a catalyst made it clear that the catalyst was covered completely by the formic acid at a pressure of about 10 mmHg at 150°C. It can, therefore, be assumed that the decomposition of adsorbed ions is the rate-determining step; in this stage the adsorbed formate ions donate electrons to the catalyst, resulting in the decomposition of the formate ions into carbon dioxide and chemisorbed hydrogen. According to the above-stated mechanism, the reaction should be of the zeroth-order. In fact, the present results indicate that the reaction is of the zeroth-order in all the cases under the experimental conditions (see Figs. 3 and 4).

The activation energy was found to increase with the ratio of electrons in the d- and s-bands to the atom of the intermetallic compounds excepting the case of the iron-molybdenum catalyst. The relatively high activation energy in the case of iron-molybdenum catalyst might be due to a larger d character of molybdenum, though it was expected to be the same or lower than that of the case of iron-chromium from the ratio of the electrons in d- and s-bands to the atom.

The decrease of the heat of adsorption of hydrogen on metals or intermetallic compounds with the increase in the ratio of electrons in d- and s-bands to the atom of the catalyst was reported by one of the present authors (I. M.)* (see Fig. 8).

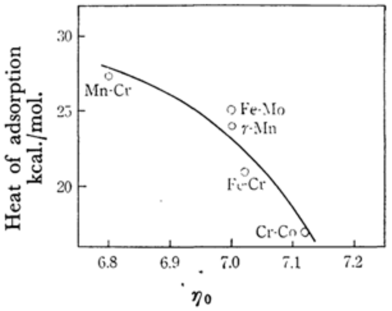

Fig. 8. The drop of the heat of adsorption of hydrogen with the degree of coverage of 0.3 is plotted against the ratio of electron in s- and d-bands to atom of catalyst.

Accordingly, an intermetallic compound having low electron concentration should be effective as the catalyst in an electron-donating reaction as in the case of the decomposition of formic acid via formate ion, on the other hand, an intermetallic compound having high electron concentration should be a good catalyst in an electron-accepting reaction as in the case of the above-mentiond adsorption of hydrogen.

It is also evident from Table II that the catalytic activity of an intermetallic compound is poorer than that of an alloy, though they have the same reaction order in the decomposition of formic acid. The detailed discussion about this point will be published in a following paper.

The authers are grateful to Professor Kiyoshi Kamei for his helpful advice.

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[3] G. Renecker and J. Volter, *Z. Anorg. Chem.*, 300 (1959).

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

[5] W. M. H. Sachtler and J. Fahrenfort, " Proc. Inter. Cong. on Catalysis, 2nd Paris, 1960," **1**, 831.

[6] K. Hirota, K. Kuwata, T. Otaki and S. Assai, ibid., 809.

* Ikuya Matsuura, Presented before the 16th Anuual Meeting of the Chemical Society of Japan, April, 1962, Tokyo.