Studies of the Urushibara Catalysts. I. Some Structural Features Revealed by X-Ray Diffraction

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Since the discovery of the Urushibara nickel catalyst[1], some modifications in the preparation of the catalyst have been successively performed; thereby several varieties of the catalyst, such as U–Ni–B[2-5], U–Ni–BA[6,7], U–Ni–NH$_3$[8], U–Ni–CB[4], U–Ni–A[3-5,9,10], U–Ni–AA[11] U–Ni–CA[4] and U–Ni–A(HCl)[5], have been developed. The Urushibara cobalt, copper and iron catalysts, namely, U–Co–B[4,8,12-14], U–Co–CB[4], U–Co–A[4,13], U–Co–A(HCl)[14], U–Cu[4], U–Cu–C[4,5], U–Fe(II)[14] and U–Fe(III)[14], have also been reported on. With these catalysts, various kinds of organic compounds have successfully been reduced, as with the corresponding Raney catalysts.

In the present paper, a brief study of the crystal structures of the Urushibara nickel and iron catalysts by means of X-ray diffraction is presented.

Experimental

Samples.—Newly prepared catalysts or those recovered after use and then stored were used.

X-Ray Diffraction.—The crystal structures of the catalysts were examined by the X-ray powder diffrac-

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1) Y. Urushibara, This Bulletin, **25**, 280 (1952).

2) Y. Urushibara and S. Nishimura, ibid., **27**, 480 (1954).

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12) S. Saito, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **76**, 351 (1956).

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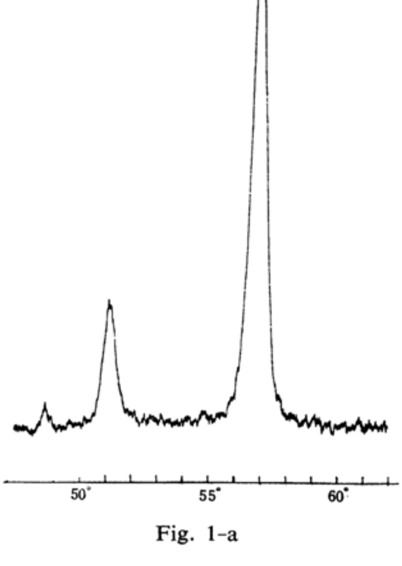

Fig. 1-a

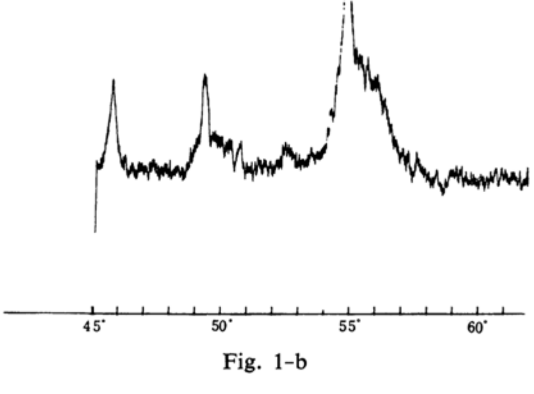

Fig. 1-b

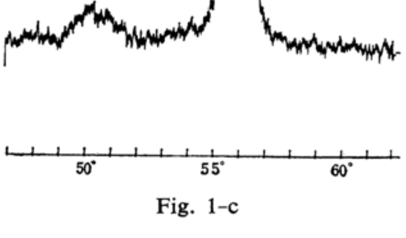

Fig. 1-c

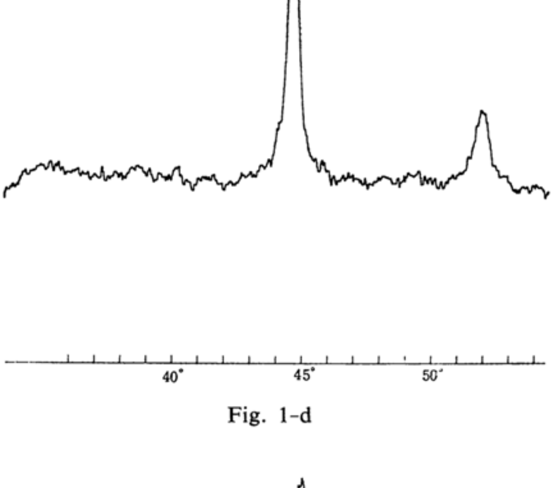

Fig. 1-d

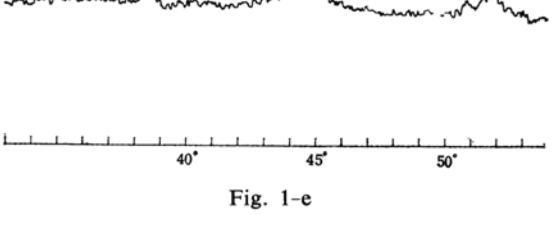

Fig. 1-e

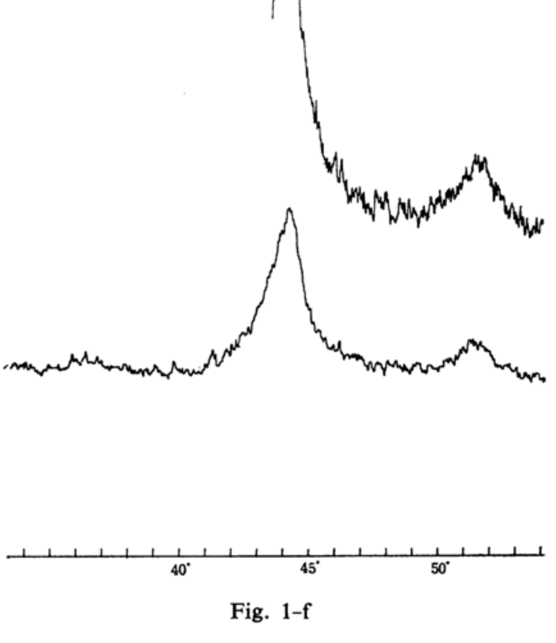

Fig. 1-f

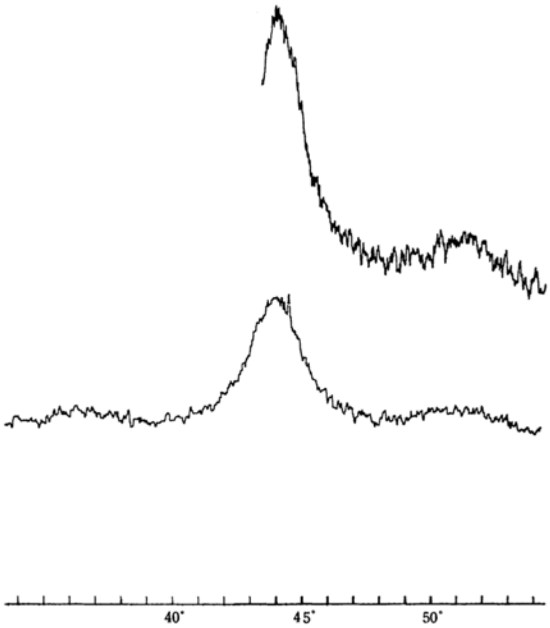

Fig. 1-g

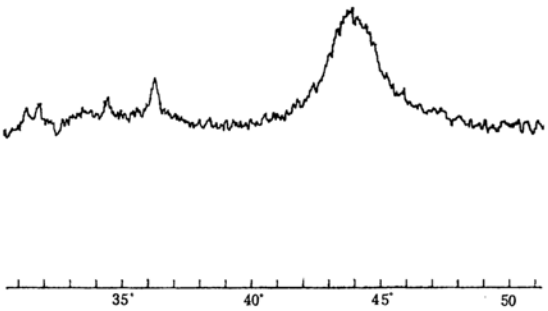

Fig. 1-h

Fig. 1. X-Ray diffraction diagrams of Urushibara nickels and Urushibara irons.
a. U-Fe(III)-BA b. U-Fe(II) c. U-Fe(III)
d. U-Ni-BA e. U-Ni-AA f. U-Ni-A
g. U-Ni-A h. U-Ni-A prepared from nickel acetate.

tion method. Cu-K_α radiation was used for the Urushibara nickel catalysts, and Fe-$K_{\alpha,\beta}$ radiation, for the Urushibara iron catalysts. The diffraction diagrams were obtained by means of a recording X-ray diffractometer.

Results and Discussion

The preparation of the Urushibara catalyst can be divided into two steps, the preparation of precipitated metal and the digestion of it with acid or alkali. Supposing that the relation of the precipitated metal to the Urushibara catalyst is similar to that of the Raney alloy to the Raney catalyst, the method of preparation of the Urushibara catalyst has some resemblance to that of the Raney catalyst. However, the precipitated metal is essentially different from the Raney alloy. For example, the precipitated nickel is obtained by the reduction of the nickel ion with zinc dust, and it is a mixture of zinc grains covered with precipitated nickel metal and some zinc compounds. The treatment of the precipitated nickel with acid removes the zinc compounds and the major part of the zinc grains to give the Urushibara nickel A. The Urushibara method is one way to prepare fine particles of a metal, and the obtained metal particles may be different from the Raney catalyst in nature. It is possible that the particles could be merely fine particles of the metal and have no catalytic activity. In fact, however, these particles of metals obtained by the Urushibara method have been proved to be as active as the Raney catalysts. Accordingly, the particles must have special crystal structures.

In the catalytic hydrogenation of 2-butyne-1,4-diol to 2-butene-1,4-diol with an Urushibara iron catalyst$^{14)}$, the author has observed that the U-Fe(II) or U-Fe(III) which is prepared from ferrous or ferric chloride and zinc dust has catalytic activity, while the U-Fe(III)-BA, prepared from ferric chloride and aluminum grains in nearly the same manner as that used to prepare the U-Ni-BA, has not.

The reason why the U-Fe(II) and U-Fe(III) have catalytic activities and the U-Fe(III)-BA has not, may be supposed to be due to the difference in their crystal structures. Their X-ray diffraction diagrams are shown in Fig. 1-a, b and c. The diffraction diagram of the U-Fe(III)-BA (Fig. 1-a) shows a good agreement with that of a sample considered to be pure α-iron and the position of the peak shifts only slightly (0.3°) in diffraction angle (2θ: 51.1° and 56.8°, the former is Fe-K_β reflection) from that corresponding to the reflection from the (110) plane in the regular configuration of α-iron (cf. Table I; All peaks in Fig. 1-b and c also show the same shift). In contrast with the diagram of the U-Fe(III)-BA, the U-Fe(II), which is recovered after the hydrogenation of 2-butyne-1,4-diol$^{14)}$ and which contains much zinc, gives the sharp peaks of zinc in the diffraction diagram (2θ: 45.8°, 49.4° and 54.9°) in addition to the diffused peaks of iron (2θ: about 50° and 55.3°) (Fig. 1-b, cf. Table I). The U-Fe(III), which is also recovered after use, gives the same diffused peaks of iron, but the peaks of zinc can not be observed, probably indicating that the sample contains, if any, but a trace of zinc (Fig. 1-c). Why does the inactive U–Fe(III)–BA give a regular diffraction diagram of α-iron while the active U–Fe(II) and U–Fe(III) do not ? Further investigation of this problem will give a clue to clarify the substantial feature of the activity of the Urushibara catalysts.

Urushibara et al.[15] have studied the Urushibara nickel catalysts in detail. As the X-ray diffraction of the Urushibara nickels gave only a diffused peak reflected from the plane regarded as (111) of nickel, which has a face-centered cubic structure, they concluded that the development of the crystal lattices in the Urushibara nickels is insufficient and thus that the nickel exists not in a state of crystals, but in a state of crystallites (Table II). The fact was also revealed by electron diffraction[16].

TABLE I. X-RAY DATA FOR NICKEL (FACE-CENTERED CUBIC STRUCTURE), α-IRON (BODY-CENTERED CUBIC STRUCTURE) AND ZINC (HEXAGONAL CLOSEST PACKED STRUCTURE)

	$(h\,k\,l)$	Interplanar spacing d Å	Diffraction angle* 2θ (°)	Intensity
Ni	(111)	2.03	44.58(Cu)	1.00
	(200)	1.76	51.9 (Cu)	0.50
	(220)	1.244	76.50(Cu)	0.32
	(311)	1.061	88.05(Cu)	0.32
α-Fe	(110)	2.0268	57.10(Fe)	1.00
	(200)	1.4332	85.0 (Fe)	0.19
	(211)	1.1702	111.7 (Fe)	0.30
Zn	(101)	2.094	43.3 (Cu) 55.2 (Fe)	1.00
	(002)	2.473	36.3 (Cu) 46.1 (Fe)	0.53
	(100)	2.308	39.1 (Cu) 49.7 (Fe)	0.40

* The figures are the values of 2θ derived from the interplanar spacing of each plane by using the value of Cu-K_α or Fe-K_α.

The size of the crystallites can be calculated by means of a modified Scherrer's formula :

$$D_{hkl}=\frac{0.9\,\lambda}{\beta_{1/2}\cos\theta}$$

where D_{hkl} is the mean thickness of the crystallites in the perpendicular direction to the $(h\,k\,l)$ plane (Å) (This value is usually called the size of the crystallites.), λ, the wave length of the applied X-ray (Å), and $\beta_{1/2}$, the half value breadth (rad.). The calculation of the size of the crystallites in the Urushibara nickels prepared under various conditions led the cited authors to the following conclusions[15]: (1) The more vigorously the reaction of nickel chloride solution with zinc dust takes place, the smaller the size of the crystallites becomes. That is, crystallites increase in size in the following order ; conc. $NiCl_{2\,aq.sol.}$+Zn dust, 100°C< conc. $NiCl_{2\,aq.sol.}$+Zn dust, room temp.<dil. $NiCl_{2\,aq.sol.}$+Zn dust, 100°C<dil. $NiCl_{2\,aq.sol.}$+Zn dust, room temp. (2) The activity of the nickel catalyst declines as the size of the crystallites increases. Supposing that the crystallites are cubic and that the activity of

TABLE II. X-RAY DIFFRACTION DATA OF U-Ni CATALYSTS (QUOTED FROM THE REPORT BY URUSHIBARA ET AL.[15])

Sample	Solvent	Concentration of nickel chloride	Temperature of the exchange reaction with zinc dust °C	Reagent for digestion	Temperature of digestion °C	Size of D_{111} Å	Position of peak for (111) plane 2θ (°)
U-Ni-B	H_2O	2 g./10 ml.	100	20% $NaOH_{aq}$	80	41	43.9
U-Ni-B	H_2O	2 g./10 ml.	Room temp.	20% $NaOH_{aq}$	80	48	44.1
U-Ni-B	H_2O	2 g./100 ml.	100	20% $NaOH_{aq}$	80	52	44.0
U-Ni-B	H_2O	2 g./100 ml.	Room temp.	20% $NaOH_{aq}$	80	59	44.1
U-Ni-B	H_2O	2 g./100 ml.	100	20% $NaOH_{aq}$	Room temp.	41	44.0
U-Ni-A	H_2O	2 g./10 ml.	100	10% $AcOH_{aq}$	Room temp.	37	43.8
U-Ni-A	H_2O	2 g./10 ml.	100	10% $AcOH_{aq}$ then 30% $AcOH_{aq}$	Room temp.	44	43.9
U-Ni-A	H_2O	2 g./10 ml.	100	20% $AcOH_{aq}$	55	49.5	44.0
U-Ni-B	C_2H_5OH	2 g./10 ml.	80	20% $NaOH_{aq}$	80	38	43.85
U-Ni-B	C_2H_5OH	2 g./100 ml.	80	20% $NaOH_{aq}$	80	46	44.0
U-Ni-B	C_2H_5OH	2 g./100 ml.	Room temp.	20% $NaOH_{aq}$	80	61	44.3
U-Ni-A	Ethylene glycol	2 g./10 ml.	160	12.5% $AcOH_{aq}$	Room temp.	41	44.0
U-Ni-B	Ethylene glycol	2 g./10 ml.	120	20% $NaOH_{aq}$	80	43	43.9
U-Ni-B	Ethylene glycol	2 g./10 ml.	Room temp.	20% $NaOH_{aq}$	80	42	43.9

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15) Y. Urushibara, M. Kobayashi, S. Nishimura and H. Uehara, *Shokubai*, **12**, 107, 160 (1956).

16) Y. Urushibara, S. Yamaguchi and M. Kobayashi, This Bulletin, **29**, 815 (1956).

Table III. X-Ray diffraction data of U-Ni-A

No.[a]	Sample	Concentration of nickel ion[b]	Temperature of the exchange reaction with zinc dust °C	Reagent for digestion	$\beta_{1/2}$(°)	Position of peak 2θ(°)	Size of the crystallites Å[c]
31[d]	U-Ni-A	1 g./14 ml.	100	13% AcOH$_{aq}$	1.5	44.4	57.4
32[d]	U-Ni-A	1 g./14 ml.	100	13% AcOH$_{aq}$	1.6	44.4	53.9
33[d]	U-Ni-A(HCl)	1 g./14 ml.	100	0.75 N HCl	2.0	44.0	43.1
34-a	U-Ni-A	1 g./14 ml.	100	13% AcOH$_{aq}$	2.4	43.8	35.5
34-b	U-Ni-A	1 g./14 ml.	100	13% AcOH$_{aq}$	2.2	43.8	38.7
34-c	U-Ni-A(HCl)	1 g./14 ml.	100	0.75 N HCl	2.4	43.6	35.5
35-a	U-Ni-A	1 g./14 ml.	100	13% AcOH$_{aq}$	2.1	43.9	40.8
35-b	U-Ni-A	1 g./14 ml.	100	13% AcOH$_{aq}$	2.1	43.9	40.8
35-c	U-Ni-A(HCl)	1 g./14 ml.	100	1.5 N HCl	1.7	43.9	50.4
36	U-Ni-A	1 g./14 ml.	100	13% AcOH$_{aq}$	2.0	43.9	42.8
37-a	U-Ni-A	1 g./14 ml.	100	13% AcOH$_{aq}$	2.1	43.7	40.7
37-b	U-Ni-A	1 g./14 ml.	100	20% AcOH$_{aq}$	2.2	43.7	38.9
38	U-Ni-A	1 g./14 ml.	100	20% AcOH$_{aq}$	2.1	43.6	40.6
39	U-Ni-A	1 g./14 ml.	100	20% AcOH$_{aq}$	2.1	43.6	40.6
310	U-Ni-A	1 g./14 ml.	100	20% AcOH$_{aq}$	2.3	44.0	37.2

a) The samples 34-a, b and c are the different catalysts prepared from the same precipitated nickel. The 35-a, b, c and 37-a, b are the similar groups respectively.

b) 1 g. of the nickel ion is supplied by 4.04 g. of nickel chloride ($NiCl_2\cdot6H_2O$).

c) The figures were calculated by the modified Scherrer's formula.

d) The sample was prepared about 4 years ago.

Table IV. X-Ray diffraction data of some special U-Ni-A

No.	Sample	Concentration of nickel ion[a]	Temperature of the exchange reaction with zinc dust °C	Reagent for digestion	$\beta_{1/2}$(°)	Position of peak 2θ(°)	Size of the crystallites Å[b]
41	U-Ni-A(s)	1 g./6 ml.	Room temp. about 60	13% AcOH$_{aq}$	2.2	44.0	39.0
42	U-Ni-A(s)(HCl)	1 g./6 ml.	Room temp. about 60	1 N HCl	2.0	43.8	42.6
43	U-Ni-A(s)	1 g./6 ml.	Room temp. about 60	20% AcOH$_{aq}$	2.3	44.1	37.2
44	U-Ni-A(s)	1 g./6 ml.	Room temp. about 60	20% AcOH$_{aq}$	2.1	44.1	40.8
45	U-Ni-A(s)	1 g./6 ml.	Room temp. about 60	20% AcOH$_{aq}$	2.2	44.0	39.0
46	U-Ni-A(s)	1 g./6 ml.	Room temp. about 60	20% AcOH$_{aq}$	2.3	44.0	37.2
47	U-Ni-A[c]	1 g./31 ml.	100	13% AcOH$_{aq}$	2.2	43.9	38.9
48	U-Ni-A[c]	1 g./31 ml.	100	13% AcOH$_{aq}$	1.8	43.3	47.4
49	U-Ni-A[c]	1 g./31 ml.	100	13% AcOH$_{aq}$	2.0	43.4	42.6
410	U-Ni-A[c]	1 g./31 ml.	100	13% AcOH$_{aq}$	2.0	44.0	43.1
411	U-Ni-A[c]	1 g./31 ml.	100	13% AcOH$_{aq}$	2.0	43.9	42.8
412	U-Ni-CA	1 g./14 ml.	Room temp.	10% AcOH$_{aq}$	1.9	43.7	45.0
413	U-Ni-CA	1 g./14 ml.	Room temp.	10% AcOH$_{aq}$	2.1	43.9	40.8
414	U-Ni-CA	1 g./14 ml.	Room temp.	13% AcOH$_{aq}$	2.0	43.8	42.6
415	U-Ni-CA	1 g./14 ml.	Room temp.	13% AcOH$_{aq}$	2.0	44.0	43.1

a) 1 g. of the nickel ion is supplied by 4.04 g. of nickel chloride ($NiCl_2\cdot6H_2O$) or by 4.24 g. of nickel acetate $(CH_3COO)_2Ni\cdot4H_2O$.

b) The figures were calculated by the modified Scherrer's formula.

c) In place of nickel chloride, nickel acetate was used to prepare the precipitated nickel (sample nos. 47-411).

TABLE V. X-RAY DIFFRACTION DATA OF U-Ni-BA AND U-Ni-AA

No.	Sample	Concentration of nickel ion[a]	Temperature of the exchange reaction with aluminum grains °C	Reagent for digestion	$\beta_{1/2}$(°)	Position of peaks, 2θ(°) (111), (200)	Size of D_{111}, Å[b]
51	U-Ni-BA	1 g./15 ml.	50～70	20% $NaOH_{aq}$	0.6	44.6, 51.9	143.6
52	U-Ni-BA	1 g./15 ml.	50～70	20% $NaOH_{aq}$	0.6	44.6, 52.0	143.6
53	U-Ni-BA	1 g./15 ml.	50～70	20% $NaOH_{aq}$	0.8	44.5, 51.8	107.8
54	U-Ni-BA	1 g./15 ml.	50～70	20% $NaOH_{aq}$	0.5	44.6, 51.9	172.3
55	U-Ni-BA	1 g./15 ml.	50～70	20% $NaOH_{aq}$	0.9	44.5, 51.8	95.7
56	U-Ni-BA	1 g./15 ml.	Room temp.	20% $NaOH_{aq}$	0.7	44.59, 51.9	123.1
57	U-Ni-AA	1 g./15 ml.	50～70	40% $AcOH_{aq}$ and $NaCl_{aq}$.	0.7	44.4, 51.7	123.2

a) 1 g. of the nickel ion is supplied by 4.04 g. of nickel chloride ($NiCl_2 \cdot 6H_2O$).

b) The figures were calculated by the modified Scherrer's formula.

the nickel catalyst is proportional to the total surface area of the crystallites, the following relation may be deduced, as the total surface area of the nickel catalyst of a definite weight may be roughly said to be in inverse proportion to the size of the crystallites:

Activity of catalyst × Size of crystallites = const. This relation was certified by their experiments. (3) The size of the crystallites was not affected by the temperature of digestion and by the kind of digesting reagent.

The results of X-ray diffraction of the various Urushibara nickels obtained by the present author are tabulated in Tables III, IV and V. The size of the crystallites of the U-Ni-A(s)* shown in Table. IV, Nos. 41—46, are generally smaller than that of the U-Ni-A shown in Table III. If the activity of a nickel catalyst is mainly decided by the size of the crystallites, as has been pointed out by the cited authors, the U-Ni-A(s) should be more active than the U-Ni-A. In fact, the U-Ni-A(s) was proved to be somewhat inferior in activity to the U-Ni-A[5]. In the case of catalytic reduction under high pressure, the apparent activity of a catalyst may be considerably affected by the following factors: (1) The presence and amount of the texture necessary for metal particles to be active as a catalyst; (2) Weight of a catalyst; (3) Apparent size of the catalyst grains; (4) Dispersability of a catalyst into a solution (This factor may be decided by the size of the grains of a catalyst and the presence of contaminating substances. It must be noted that the Urushibara nickels B are contaminated by a large quantity of zinc and zinc compounds); (5) Reaction temperature; (6) Pressure of hydrogen gas; (7) Kind and volume of solvent; (8) Method and degree of agitation; and (9) Nature and purity of the sample to be reduced. A proper selection of experimental conditions may control factors 5 to 9. With the Urushibara catalysts, factors 1 to 4 vary with the method of preparation. The weight of the U-Ni-A(s), prepared to contain a definite quantity of nickel, is usually somewhat smaller than that of the U-Ni-A. Supposing that factors 3 and 4 are similar in them, the inferiority of the U-Ni-A(s) to the U-Ni-A in activity may mainly be ascribed to factor 1. Certainly factor 1 plays an important rôle in the actual activity of the catalyst.

The U-Ni-BA, prepared from a nickel chloride solution and aluminum grains, gives two sharp peaks in the X-ray diffraction diagram corresponding to the reflection from the (111) and (200) planes of nickel, and the position of the peaks lies at the regular angle position for nickel (Fig. 1-d, cf. Table. I). On the other hand, the Urushibara nickel A, prepared from either nickel chlorid or nickel acetate soultion and zinc dust, gives only a diffused peak, and the position accepted as a peak shifts from the regular position to a lower angle (Fig. 1-f, g and h) (In Fig. 1-h some peaks of zinc and zinc oxide are also observed). Occasionally, another diffused peak is observed (Fig. 1-f).

In Scherrer's formula, the calculated values of D_{hkl} are greatly affected by small differences in the value of $\beta_{1/2}$, but not so seriously by those in the values of θ. Samples Nos. 34-a, b and c (Table. III) are the Urushibara nickel catalysts prepared from the same precipitated nickel by separate treatment with the same or different acids. Samples Nos. 35-a, b, c and Nos. 37-a, b form respective groups of the same kind. In each group small differences in the value of $\beta_{1/2}$ cause a difference of several Å in the value for D_{hkl}. However, the values of $2\ \theta$ are nearly equal in each group. The author has paid attention to the 2θ values.

Many workers have pointed out that in an

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* The notation(s) implies temporarily the catalyst obtained from the precipitated metal prepared by the simplified method[5].

actual crystal small blocks (crystallites) of 10～0.1μ in sizes are disorderly accumulated into a so-called "mozaic structure". The smallness of the crystallites and the disorder of accumulation cause an enlargement in the breadth of the X-ray diffraction peaks. In the crystallites having a regular lattice arrangement, however, an enlargement in the breadth of the diffraction peaks takes place at the positions of definite angles determined by the interplanar spacing of the substance, and a large shift of the diffraction angle does not take place. Thus, it is conceivable that the (111) and (200) planes of nickel are indeed present in the U-Ni-BA, but there is much less probability of them in the Urushibara nickel A and B. Why is such a curious phenomenon observed only in the Urushibara nickel A and B? To clarify this problem, the process of preparing the precipitated nickel must be taken into account. The situation is considered to be similar to that of the formation of an evaporated film. From studies of evaporated films by means of electron diffraction, the phenomenon of oriented overgrowth or epitaxy has been brought to light[17]. A definite relation exists between the orientation of the crystallites of the deposit and that of the substrate crystals. The crystal structure of the crystallites in a evaporated film is generally in accordance with the structure of the crystal in the macro state. However, some exceptions have been found. Schulz[18] observed that the oriented overgrowth of crystallites occured in the evaporated films of those substances, which usually crystallize in the cesium chloride structure when, they were evaporated on lithium fluoride, sodium chloride, potassium bromide or mica, and that in such evaporated films there were many substances not with the original structure of the cesium chloride type but with the structure of the sodium chloride type. In the case of the formation of the precipitated nickel from a nickel salt solution and zinc dust, such a epitaxy may be possible to happen. Nickel, having a face-centered cubic structure (abbreviated as f. c. c. structure) in the normal state, is known to be possible to have a hexagonal closest packed structure (abbreviated as h. c. p. structure), as the difference in the energies of the two packings may not be so large. Thus, nickel can crystallize into a h.c.p. structure on the surface of zinc which normally has a h. c. p. structure. On this basis, it is presumed that such a epitaxy happens in the preparation of the precipitated nickel, and that the nickel precipitated on the surface of zinc may crystallize in a h. c. p. structure because it may grow larger on the embryo crystallites to some extent. The state in which nickel has a complete h. c. p. structure is temporarily named the ideal h. c. p. state. In this ideal h.c.p. state, the X-ray diffraction diagrams of Urushibara nickel A and B should be composed of sharp peaks and the position of peaks should be located in the diffraction angle very close to those of zinc (cf. Table I). Besides, in this state the crystals of nickel should come to contain many lattice defects, such as vacancies and dislocations, because the lattice constant of nickel is forced to be unusual. This hypothesis is quite successfully applied to interpreting the diffraction diagrams of the Urushibara nickel A and B.

In the actual Urushibara nickel A and B, the diffraction peaks are diffuse, and the position of the peak, which is divided into many small peaks, shifts to an angle higher than the ideal position. This may be caused by the small size of the crystallites and by the deformation of the structure of the crystallites from the ideal h. c. p. structure. If the extent of the shift of a peak from the position for the ideal h. c. p. structure is proportional to the degree of the deformation from the ideal h. c. p. structure to the proper f. c. c. structure, the amount of lattice defects will be in inverse proportion to the extent of the shift in the diffraction angle. The lattice defects may offer proper seats and spaces in which a foreign atom or molecule (for example, H or H_2) may be so loosely locked that it can move freely to some extent. As such places may be active centers of a catalyst, the more the lattice defects and present in the crystallites, the more active the crystal will become as a catalyst.

The author draws the following conclusions from the above considerations:

(1) In the Urushibara nickel A and B, nickel may have a h. c. p. structure which has been somewhat deformed to the f. c. c. structure. On the contrary, in the Urushibara nickel BA, nickel has a normal f. c. c. structure as a whole, for it is prepared from nickel chloride solution and aluminum, which has the f. c. c. structure. Thus, the Urushibara nickel BA is regarded as a catalyst of quite a different type from the Urushibara nickel A and B. Accordingly, it is naturally accepted that the shape of the diffraction diagram and the activity of the Urushibara nickel BA are quite different from those of the Urushibara nickel A and B.

(2) If a nickel catalyst, prepared by any method, gives a diffraction diagram similar to those of the Urushibara nickels, it will possess a similar catalytic activity when other factors are disregarded.

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17) D. W. Pashley, *Advances in Physics*, 5, 173 (1956).

18) L. G. Schulz, *Acta Cryst.*, 4, 487 (1951).

(3) In the Urushibara nickel A and B, the higher the catalyst in activity, the smaller the extent of the shift of a peak in the diffraction angle from the ideal position of the peak for the h. c. p. structure of nickel. Thus, the reason why the U–Ni–A(s) is somewhat inferior in activity to the usual U–Ni–A may naturally be understood by comparing the 2θ values of the former with those of the latter. The same relation can be observed between the U–Ni–A(s) and the U–Ni–CA or the U–Ni–A prepared from nickel acetate solution and zinc dust.

(4) If each catalyst has the same crystal structure, the activity of a catalyst will be affected by the size of the crystallites.

The above considerations may also be successfully applied to solving the problems which lie in the Urushibara iron catalysts. Iron exists in the following two allotropic crystal modifications: at the lower temperature, iron crystallizes as α-Fe in a body-centered cubic structure (abbreviated as b. c. c. structure).

$$\underset{\text{(b.c.c.)}}{\alpha\text{–Fe}} \overset{910°\text{C}}{\rightleftarrows} \underset{\text{(f.c.c.)}}{\gamma\text{–Fe}} \overset{1400°\text{C}}{\rightleftarrows} \underset{\text{(b.c.c.)}}{\delta(\alpha)\text{–Fe}}$$

As aluminum has a f. c. c. structure and as there is an intimate relation between the lattice planes in the b. c. c. and the f. c. c. structure*, iron in the U–Fe(III)–BA must crystallize into a b. c. c. structure. This is the reason why the diffraction diagram of the U–Fe(III)–BA coincides with that of the α–Fe.

Iron in the ideal h.c.p. state must be greatly strained as the stable b. c. c. structure at low temperature is forced into the h. c. p. structure. Then it will get catalytic activity. In the actual U–Fe(II) and U–Fe(III), the crystal lattices of iron may be in the relation of coherency to those of zinc, and then there may be many lattice defects in them. Therefore, the reason why the U–Fe(II) and U–Fe(III) have catalytic activity and the U–Fe(III)–BA has not may be ascribed to the difference in their crystal structures.

Naturally the crystal structure of the metal in a Urushibara catalyst is affected to some extent by the temperature and the concentration of the solution to be applied in the preparation of a precipitated metal. The author esteems the effect of concentration as more important than that of temperature. That is, the decreased concentration of a metal ion in a solution may exert the favorable effect upon the crystal structure necessary for the metal to have catalytic activity, in consideration of the values in the Tables II, III and IV. However, further study is required in this area. As it has been widely recognized that special sections in the crystal of a metal are preferentially attacked by an acid, a digesting reagent for the precipitated metals may exert some secondary action on the Urushibara catalyst. The solution of the subject also belongs to the studies of the future.

Summary

Some structural features in the Urushibara catalysts were revealed by means of X-ray diffraction, and a hypothesis regarding the activity of the Urushibara catalysts was proposed.

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* $\{110\}_{\text{b.c.c.}} \longleftrightarrow \{100\}_{\text{f.c.c.}}$ A similar relation has been observed in the epitaxial growth of the CsCl type (b. c. c.) into the NaCl type(f: c. c.)[18].