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Catalytic Activities of Ni Alloys Expressed by Surface and Bulk Compositions

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The surface compositions of three kinds of powdered alloys with different structures, Cu–Ni (fcc–fcc), Fe–Ni (bcc–fcc), and Co–Ni (hcp–fcc), were determined by the penetration of β-rays of ^{63}Ni mixed previously in the alloy, then the effect of the respective alloy structure both of the surface and of the bulk on the catalytic hydrogenation of ethylene was studied. The surfaces of these alloys were found to be Ni-poor for the wide range of alloy composition. The catalytic activity expressed by each surface composition was difficult to explain by the physicochemical properties of the surface. The activity expressed by the bulk composition of Cu–Ni of fcc structure was high in the region of unfilled *d*-band, and so were that of Fe–Ni and that of Co–Ni in the region of fcc structure. The activity of Fe–Ni for the dimerization of ^{14}C-ethylene was studied, of whose activity the similar tendency was observed as found in the hydrogenation reaction. These could be interpreted as the results of the positive contribution of the dissolved hydrogen in bulk to the catalytic reactions.

INTRODUCTION

Various binary alloys have been used in catalytic reactions changing the proportion of each metal to clarify the cooperative role of each metal (*1–8*). Since the disagreement of alloy composition of the surface with that of the bulk had been proved (*9–13*), the attention has been especially paid to the relation between the reactivity and the surface composition of the alloy employed, the effect of the bulk being neglected.

The development of new instruments as Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) for the analysis of surface composition has helped to extend the fundamental concepts of the surface structure of alloys (*14–18*). However, the specimens used in these studies are limited in massive state, which can only be prepared by the fusion of two pure metals. Powdered alloys are usually prepared from metal carbonates or nitrates. They have very large surface area and roughness, which are advantageous for the tests of catalytic activity, and which makes the applications of AES and XPS to these alloys under ultrahigh vacuum (UHV) condition of great difficulty.

Recently, the measurement of the surface composition of powdered Ni alloys by the penetration of β-rays emitted from ^{63}Ni was developed in our laboratory (*19, 20*). Since β-rays of ^{63}Ni (of whose average energy is 18 keV (*21*), coming from inner layers of metal particle are weakened by self-absorption, it is possible to determine the amount of radioactive Ni on the surface layers of the powdered alloys without using the UHV techniques.

The purpose of this study is to elucidate the effects of both surface and bulk structure on the catalytic activities in hydrogenation reaction of ethylene on three Ni alloy catalysts: Cu–Ni (fcc–fcc), Fe–Ni (bcc–fcc), and Co–Ni (hcp–fcc).

The formation of dimer of ethylene, which is responsible for the contamination

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TABLE 1

The Details of the Reaction on Each Alloy

Catalyst	Reactants	Ratio	Initial pressure (Pa)	Temp. (°C)
(1) Cu–Ni	Ethylene and H_2	1 : 1	2.7×10^3	0
(2) Fe–Ni	Ethylene and H_2	1 : 1	2.7×10^3	0
(3) Co–Ni	Ethylene and H_2	1 : 1	3.3×10^3	30

of the active sites in the hydrogenation reaction, was ascertained using Fe–Ni alloys and ^{14}C-ethylene as a tracer.

EXPERIMENTAL

Each powdered alloy catalyst was prepared as usual from the mixed solution of nitrates, in which ^{63}Ni was previously mixed so that specific activity of 0.3 mCi/mol might be gained. The temperature of calcination was 500°C.

In each test of catalytic reaction, 0.1 g of unreduced powder was placed at the reaction vessel. The temperature of reduction with hydrogen was 350°C for Cu–Ni, 385°C for Fe–Ni, and 300°C for Co–Ni. The conditions of hydrogenation reaction of ethylene are shown in Table 1. In these reactions, Nos. 1 and 2 were carried out by statistical method, and No. 3 was by the flow method, where the flow rate in the reaction tube was set at 900 cm^3/min. The rates of reaction of ethylene were determined by the decrease in pressure.

The radioactivity of ^{63}Ni included in the surface layers of each alloy was measured by 2π gas-flow counter as reported elsewhere (*20*). The number of atomic layers given by the penetration of β-rays was calculated by the equation

$$A = A_0 \int_0^x \exp(-\mu x)dx \qquad (1)$$

where A is the counting rate of the sample, A_0 the counting rate of first layer (calculated), μ the absorption coefficient for metal, and x the number of the layer of metal.

In the procedure of the assay of dimer, ^{14}C-ethylene was preadsorbed on Fe–Ni alloy under the pressure of 13.3 Pa at 0°C, then 10^3 Pa of the mixture (1 : 1) of ordinary ethylene and hydrogen was added. The amount of ^{14}C-butane produced together with ethane was measured by radio-gas-chromatography. The specific activity of ^{14}C-ethylene used was 0.25 Ci/mol.

RESULTS

The absorption coefficient of β-rays of ^{63}Ni is given as 2.0 cm^2/mg for Ni film in the thickness below 0.15 mg/cm^2 (*20*). This value is applicable to Cu, Fe, and Co, because the difference in the specific gravity of these metals is small (<10%). The number of penetration calculated using this absorption coefficient was 175 layers for the powdered Cu–Ni alloy. The composition of outer layers can be determined by placing a thin film made of Mylar or Sealon between Ni alloy and cathode of the 2π-counter to intercept the weakened β-rays. The average value of 15 layers was obtained by Mylar film and that of 50 layers of Sealon film (*20*). The composition of the outer layers was to some extent Cu-rich (10–20%) in comparison with that of 175 layers.

Figure 1 shows the correlation between the radioactivity of 175 layers of each alloy and the average composition which refers to the atomic ratio of two metals in the mixed solution of the nitrates. If the composition of each alloy is completely homogeneous to the deep interior, the observed radioactivity should be straight as expressed by the dotted lines. However, the results indicate that the radioactivity of each alloy observed in the present study stands far below the dotted lines, which means that the surface of each alloy is extremely Ni-poor.

X-Ray diffraction analysis for crystal structure of each alloy gives the result shown in Fig. 2, which is practically the same as found in the literature (*22*).

Figure 3 shows the specific activities expressed by surface composition and aver-

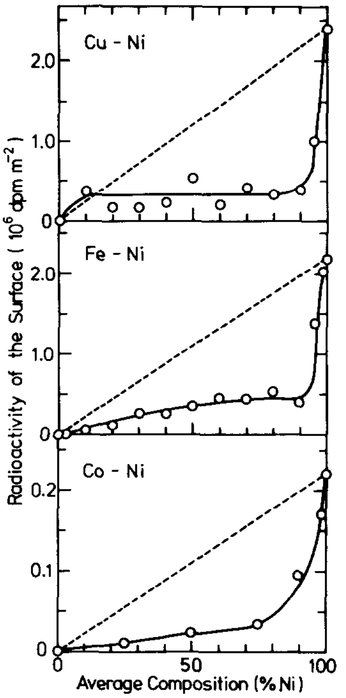

FIG. 1. The specific radioactivity of ^{63}Ni given by the surface layer of each alloy.

age composition of Cu–Ni for the hydrogenation of ethylene. Large activity was recognized in the range from 40 to 90% Ni, when the abscissa expresses the average composition; however, when the abscissa expresses the surface composition, the maximum activity was shifted to near 10% Ni.

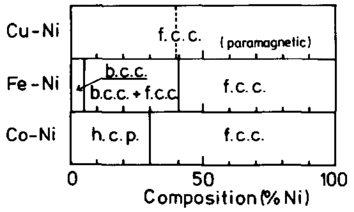

FIG. 2. Crystal structure of alloys used.

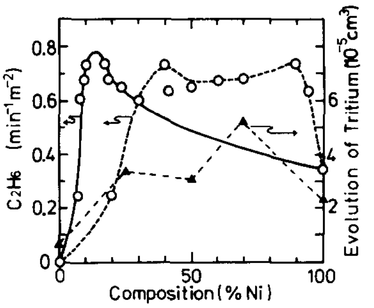

FIG. 3. Catalytic activities for hydrogenation reaction of ethylene on Cu–Ni expressed by surface composition and average compositions. (—O—) Activity expressed by surface composition. (---O---) Activity expressed by average composition. (---▲---) Tritium evolution from Cu–Ni (*30*).

Figure 4 shows the specific activities on Fe–Ni. The activity plotted by the average composition increased stepwise at 10 and 40% Ni, where the respective crystal structure of the bulk is composed of the mixture of fcc and bcc, and of complete fcc. The maximum activity was observed in the narrow range of ca. 20% Ni when the abscissa expresses the surface composition.

Figure 5 shows the results on Co–Ni. A considerably high activity was given by both pure Co and Ni. The activity expressed by the average composition increased stepwise at 30 and 90% Ni, where the bulk structure is fcc, and dropped drastically at Ni-rich region. The range of high activity becomes wider, when the abscissa expresses the surface composition.

Tracer study of the formation of butane by means of ^{14}C-ethylene on Fe–Ni is shown in Fig. 6. The dimerization of ethyl-

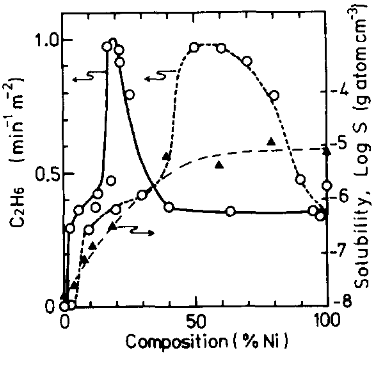

FIG. 4. Catalytic activities for hydrogenation reaction of ethylene on Fe–Ni. The same symbols designated in Fig. 3 are used. The triangle shows the solubility of hydrogen (*43*).

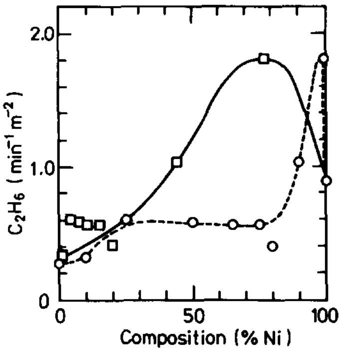

FIG. 5. Catalytic activities for hydrogenation reaction of ethylene on Co–Ni. The same symbols designated in Fig. 3 are used.

ene was found to occur markedly on the alloy of more than 40% Ni whose structure is complete fcc, when the abscissa expresses the average composition. The amount of butane produced was about 2×10^{-8} mol, and that of ethane was 1.2×10^{-4} mol.

DISCUSSION

The surface concentration of Ni was always less than the average composition of all Ni alloys used. This suggests that the nonuniformity of these alloys cannot be explained in terms of thermodynamic properties of the components, i.e., melting point, the free energy of alloy formation, the frequency factor (*12, 13, 23–25*) and the activation energy of self-diffusion and volume diffusion of metal atoms (*26*). The nonuniformity of powdered alloys should be attributed to the difference in the rates of calcination of two nitrates and the rates of reduction of metal oxides produced as pointed out elsewhere (*27*).

The values of the surface composition of Cu–Ni alloy measured using Sealon or Mylar were practically the same as the value measured without using any filter. That is, the composition of the surface is practically the same to the extent of ca. 100 layers which is estimated to be about 20% of the radius of alloy particle. It is noticeable that this average value for the 100 layers of the surface agrees with that given by AES (*14, 15*) for several layers.

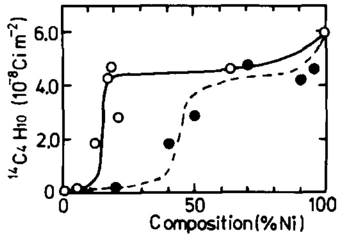

FIG. 6. The amount of ^{14}C-butane produced by ethylene on Fe–Ni. (—O—) For bulk. (--●--) For surface.

Unfortunately, the change in composition at the depth of more than 100 layers could not be clarified because of the short penetration range of β-rays. It is possible to assume, however, that the internal concentration of Ni is greater than that of the average, and that the change of the concentration is expressed as a sigmoid type shown in Fig. 7. The greater the average concentration of Ni is, the greater that of the interior, approximately proportional to average concentration, though the surface concentration of Ni did not vary with the average concentration.

Cu–Ni alloys have a fcc structure at all alloy compositions. No correlation was found between the physical properties of alloy and the catalytic activity of alloy expressed by the surface composition, but a remarkable activity value was found in the alloy of more than 40% Ni, which has para-

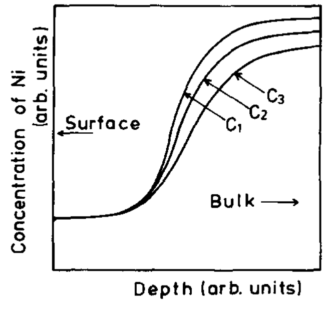

FIG. 7. The schematic representation of the correlation between Ni concentration and depth of alloy particle. Average composition $C_1 > C_2 > C_3$.

magnetic property when the activity was expressed by the average composition. This phenomenon is favorable to the *d*-band theory proposed by Dowden (*4*). The correlation between hydrogen atom and *d*-band of metals is discussed elsewhere (*28*).

The hydrogenation of ethylene on powdered Cu–Ni alloys impregnated previously with tritium by ^{6}Li $(n, \alpha)^3$H reaction indicates that the rate of the reaction increased in proportion to the amount of tritium released from alloys (*29, 30*), which suggests that the reaction is related to the movable hydrogen in the alloy.

Most studies on the effect of dissolved or preadsorbed hydrogen on the catalytic activity have concluded that hydrogen acts as poison for pure metals of the VIII group, the holes in the *d*-band of metals being occupied by the *s*-electron of hydrogen (*3, 31–36*), and that the only incomplete occupation of *d*-band is favorable for the catalytic reactions (*37–39*).

It has been pointed out in earlier findings (*35, 36*) of the promotion of hydrogen in the catalytic reactions that the activity of Cu–Ni alloys for the hydrogenation reaction of ethylene increases with the pretreatment with hydrogen while that of pure Ni decreases. There are analogous results in the reactions on Pd–Ag (*40*) and Pd–Au (*41*). In the hydrogenation reaction on Raney Ni alloy, the removal of hydrogen from the alloy decreases the catalytic activity (*42*).

The positive action in binary alloys including Fe–Ni and Co–Ni would be interpreted by other factors which relate to the amount of movable hydrogen in these alloys as was suggested by the tracer study on Cu–Ni (*29, 30*).

The activity of the hydrogenation on Fe–Ni increased in two steps at the following bulk structures, which are assumed from the average composition.

$$\text{bcc} < \text{bcc} + \text{fcc} < \text{fcc}.$$

In regard of the correlation between hydrogen and the alloy composition of Fe–Ni, the diffusivity and solubility of hydrogen varies with the crystal structure of the alloy; in fcc region the former is small, while the latter is great (*43, 44*) as shown in Fig. 4. These facts reveal that the hydrogen accumulating in bulk promotes the catalytic activity.

The sequence of hydrogen solubility for pure metals is written as the following (*45*)

$$\text{Ni} > \text{Fe} = \text{Co} > \text{Cu}.$$

The solubility for Ni is 10 times greater than that for Co in the vicinity of the reaction temperature used in our study. Unfortunately, the solubility for Co–Ni alloys is not clear in the present situation. It is assumed, however, that the region of fcc is superior to hcp in the dissolution of hydrogen, because the diffusion constant for Co of fcc structure is greater than that of hcp, and the activation energy of diffusion for α-Co(fcc) is lower than that for ε-Co (hcp) (*46*). Indeed, the formation of the hydride, Ni–Co–H, was found in the region of more than 60% Ni (*47*), which suggests that the dissolution of hydrogen occurs readily in the Ni-rich region.

The difference in the catalytic activities between pure Co and Ni is not so great, regardless of the difference in the crystal structure. However, it will be noted that the activity in fcc region is greater than that of hcp in both expressions of surface and bulk. The marked increase in the activity at the narrow region of more than 90% Ni of bulk composition could be interpreted in terms of the abrupt decrease in the particle size. The surface area of this region was three times greater than the other region. The decrease of the particle size will increase the amount of hydrogen in bulk because of the increase in the lattice imperfections.

The diffusivity and the solubility of hydrogen in metals is strongly affected by the lattice imperfections (*48*). Grain and subgrain boundaries serve as trap sites and act as short circuit for diffusion paths, which are abundant in powdered alloys. The "miscible gap" of alloys proposed by Sachtler and Jongepier (*13*) would contain abundant dislocations. Therefore, it is concluded that fcc region of powdered Ni alloys surpasses other regions with regard to the dissolution and the diffusivity of hydrogen. The alloy of fcc structure behaves as the hydrogen reservoir as was found in the reaction on $LaNi_5H_n$ (*49*). Hydrogen is supplied from the interior of the catalyst if it is insufficient in the gas phase, when the activity of alloy is influenced by the bulk structure rather than by the surface. However, the activity relates to the surface composition, when the supply of hydrogen from bulk to insufficient. The diffusion of hydrogen between gas phase and bulk would be weakened if the surface is contaminated or the quality of lattice imperfections is changed (*35*), even through the concentration of Ni on the surface is fixed.

The preferential formation of dimer at the fcc region of Fe–Ni alloy and pure nickel suggests that the dimerization reaction occurred on the same sites for the hydrogenation reaction. The marked increase in the dimer formation on pure Ni suggests the increase in the amount of carbonaceous products of the polymer, which related to the contamination of active sites. Saeki *et al.* (*50*) have found recently by the tracer method that the amount of irreversibly adsorbed ^{14}C-products on pure Ni was three times greater than that of 90% Ni of Cu alloy and four times greater than that of 50% Ni. The decrease of activity at Ni-rich region of each alloy used in the present study can be attributed to the contamination of active sites by the carbonaceous products.

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