The Catalytic Activity and Electric Resistance of Evaporated Copper-Nickel Films

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The dependencies of the hydrogenation catalytic activity and electric resistance of copper-nickel films upon the composition of the film were investigated. The film was prepared by the evaporation of copper and nickel metals or their alloys on a substrate cooled by liquid oxygen. Prior to use, the film was treated in a vacuum at 30° or 250°C. The catalytic activity was tested by the hydrogenation reaction of ethylene.

The maximum of activity for the reaction was always found in the alloy region of the film, irrespective of the order of the deposition of the two metals, when the film was treated at 30°C. However, the maximum activity shifted to the pure nickel, when the treatment temperature was raised to 250°C. The electric resistance of 50% nickel film was always maximum. It was also noted that an increase in treatment temperature resulted in a marked decrease in electric resistance, especially on 50% nickel film. The catalytic activity is discussed in view of the change of the amount of the especially unstable lattice imperfections in the film.

I. INTRODUCTION

Since the proposal of the d-band theory by Dowden and Reynolds (*1*) on the catalytic activity of copper-nickel alloys in hydrogenation reactions, many studies (*2–8*) have been carried out in this field using alloy prepared by various methods. However, many experimental results which cannot be applied to their theory have been reported. Dowden and Reynolds, who used foils of copper-nickel, found an activity increase in the alloy region of about 40% nickel and maximum activity in pure nickel. However, Best and Russell (*4*), and Hall and Emmett (*5*), who used powdered alloys, found the maximum activity in the region of the alloy. One of the writers (*6*) found that the sheets of copper-nickel increased in activity simply with an increase in nickel content and powdered alloys were constant even if the nickel content ranged from approximately 10% to 70%.

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The previous study (*2, 3*) by means of electron diffraction and the reaction of hydrogen chloride with the surface of the powdered copper-nickel showed that the composition of the surface is independent of the overall composition of the alloy. These results could explain the discrepancy of the catalytic activity in the same alloy composition. They could not, however, explain the cause of the activity increase found in the alloy region. Hall and Emmett tried to interpret the decrease of activity in the nickel-rich region by the occupation of the d band of the alloy by electrons of the preadsorbed hydrogen. Very recently, the writers (*7*) found that the catalytic activity of evaporated nickel film increased when the film was prepared in a hydrogen atmosphere, which is contrary to the expectations from the report published by Hall and Emmett (*5*). Further study seems to be necessary to clarify the catalytic activity of the alloy.

The present study is concerned with the activity of ethylene hydrogenation on copper-nickel prepared by the evaporation of copper,

nickel, and copper-nickel alloys on the substrate at low temperature. The dependency of the film treatment temperature on the catalytic activity in the hydrogenation of ethylene was observed using films prepared on a cold substrate and treated at various temperatures. The structual factor of the film, of course, is expected to be affected by the temperature of the treatment. The crystallites in such films can be assumed to be defective and to contain many lattice imperfections. It can also be expected that the electrical resistance of such films would change with different treatment temperatures. In this study, the change of the film electrical resistance due to the temperature change in treatment was observed. The results on both the catalytic activity and the electrical resistance are discussed.

II. Experimental

The copper, nickel, and the copper-nickel alloys used were the same as described elsewhere (9, 10). The ethylene used was prepared by the dehydration of ethyl alcohol with sulfuric acid and was purified by vacuum distillation using a liquid nitrogen bath. The hydrogen used was commercially available and it was purified by the diffusion through a palladium thimble.

The main part of the apparatus and the reaction vessel are shown in Fig. 1. The 140-ml vessel was made with Hario (K 250) glass and was used for the hydrogenation reaction. Three tungsten wires of 1 mm in diameter were sealed at the top of the vessel. Under the wires, two filaments similar to those used in 200-W electric bulbs were welded as is shown in the figure. A similar type of vessel was used for the film electrical resistance measurement. In this case, another pair of 1-mm diameter tungsten wires were sealed on both sides of the vessel wall. One of the filaments was used for the evaporation of copper-nickel alloy. Two filaments were used for the successive evaporation of copper and nickel. The total amount of these metals was 6 mg. Prior to evaporation of the metals, the vessel was heated in the electric furnace at 250°C. Then about 200 torr of hydrogen was introduced in order to reduce the metals, and they were kept in a hydrogen
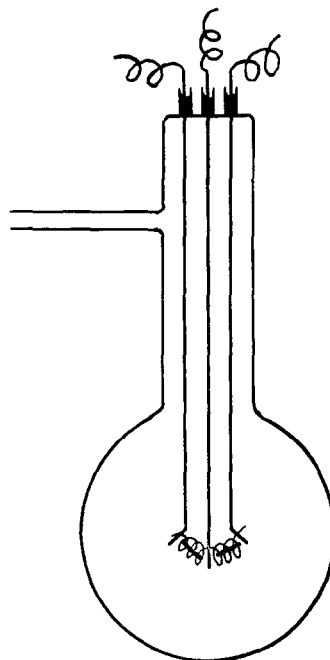

Fig. 1. The reaction vessel.

environment for 48 hr. The temperature of the filaments was then raised by increasing the electric current until the filaments showed red brilliance and this temperature was maintained for 1 hr. After reduction, the vessel was evacuated and kept under the pressure of 10^{-6} torr for about 3 hr. Then the vessel was placed into a liquid oxygen bath. The current of one filament was increased gradually until the metal was completely evaporated. The metal in the other filament was evaporated in the same way. The bath of liquid oxygen was replaced by an electric furnace again and the temperature raised gradually to 30°C and kept at this temperature for 24 hr in order to stabilize the film by sintering. It had earlier been found that the resistance of the fresh film formed at −183°C was very changeable.

The mixture of ethylene and hydrogen in a volume ratio of 1:1 and a total pressure of 24 torr was admitted into the reaction vessel. The reaction was carried out at 30°, 20°, and 10°C. The decrease in pressure was measured by using a U-type manometer of Apiezon oil. Care was taken not to con-

taminate the film with Apiezon oil by using a U-type trap. It was placed between the reaction vessel and the manometer and was cooled in a Dry Ice bath. After the hydrogenation reaction of the film treated at 30°C had been studied, the BET area was measured using ethylene at −183°C, as had been done by Wooten and Brown (11). Then the ethylene was evacuated; meanwhile the temperature increased gradually to 250°C. This temperature was kept for 24 hr in order to advance the sintering. Then the temperature was lowered to 60°, 80°, or 90°C and the activity test was made.

The electrical resistance of the film was measured using a Wheatstone bridge. The accuracy of the measurement was ±1 Ω.

The first measurement of the electrical resistance was made at −183°C, 30 min after the film had been prepared. Then the temperature of the vessel was raised to 30° or 250°C for 12 hr in order to sinter the film, and then the temperature was lowered to −78°C, and the second or third measurement was carried out.

III. RESULTS

The relation of the logarithm of the reaction rate to time was approximately represented by linear lines on all films treated at 30° or 250°C except for the film of pure copper. Pure copper was practically inactive for the reaction irrespective of the temperature of treatment.

Figure 2 shows the results of the film treated at 30°C. The figure shows that the films prepared from the alloy (FI) and those prepared from nickel on copper (FII) give the maximum activity at the composition of about 50% nickel. A very similar relation was reported by Campbell and Emmett (12), who had found two large activities in the alloy region on films prepared by the evaporation of copper on nickel (FIII). The activity measurements of films FIII were not made within 48 hr after the evaporation of the metals because the activities of these films, within 24 hr after the evaporation, were very small. Most of the results on the films FIII indicate that the activities in the alloy region are greater than that in pure nickel.
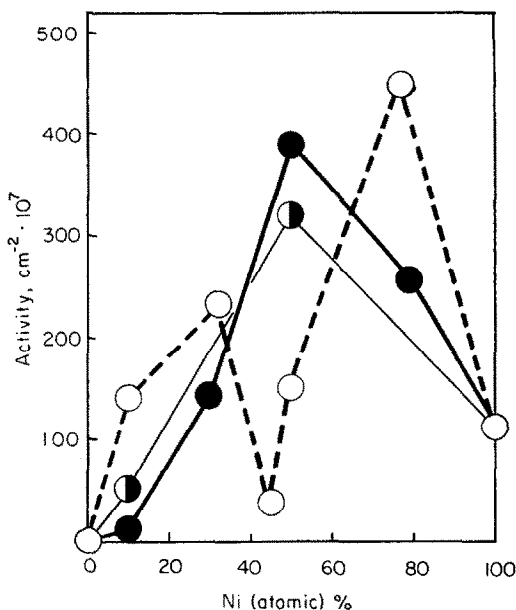
Figure 3 shows the results on the films

FIG. 2. Catalytic activities of hydrogenation reaction of ethylene at 30°C on the copper-nickel evaporated films treated at 30°C: —●—, FI, —◑—, FII, --○-- , FIII.

treated at 250°C. The reaction temperature on these films was higher than that for the film treated at 30°C because the reaction rate decrease caused by the increase of the sintering temperature was very great. The figure indicates that the distinct decrease in activity occurred especially in the alloy region of about 50% nickel and the maximum activity shifted to the pure nickel.

In order to compare the rates of the reaction at the same temperature of 30°C on the films treated at different temperatures, the rates of the reaction at 30°C on two kinds of films formed by alloys were obtained by the calculation using the activation energies of the reaction. The result is shown in Fig. 4.

The relation between the activation energies of the reaction and the composition of the FI films treated at 30° and 250°C are shown in Fig. 5. The figure shows that the activation energy decreases inversely with the increase in nickel content and increases again with pure nickel.

The electrical resistance of the film decreased gradually over several days if the fresh film was allowed to stand at the preparation temperature (−183°C). How-
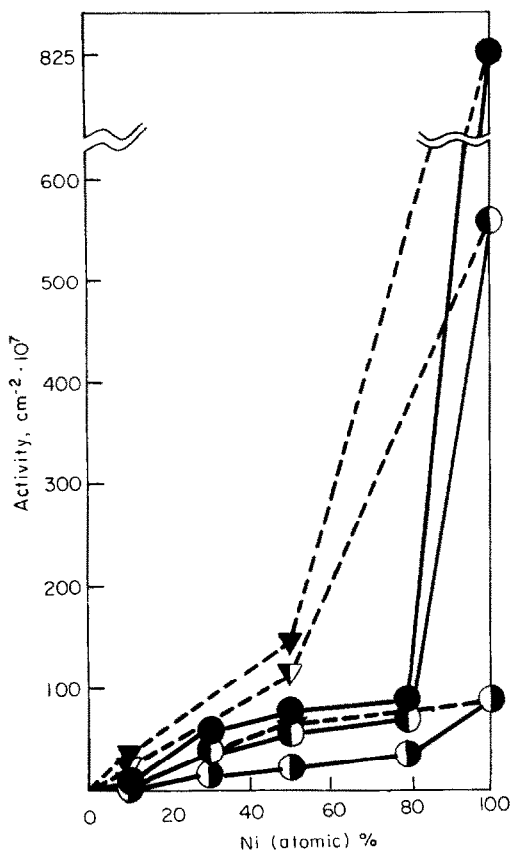
Fig. 3. Catalytic activities of hydrogenation reaction of ethylene on the copper-nickel evaporated films treated at 250°C. FI: —●—, reaction temp. is 90°C; —◐—, 80°C; —◑—, 60°C. FII: ▼ , 90°C; ▽ , 80°C; ⩔ , 60°C.

ever, it became constant within about 20 min after the temperature of the vessel was raised to 30° or 250°C. The relationship between the electrical resistance and the composition of the film is shown in Fig. 6. This relationship is very different from that of the massive alloy (26). Also, the maximum film resistance is in the alloy region of approximately 50%
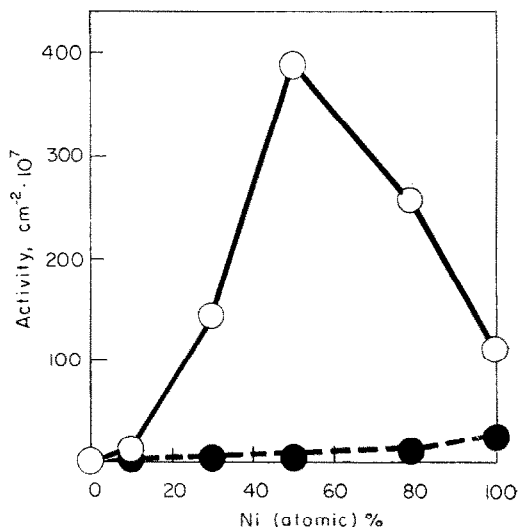

Fig. 4. The catalytic activities of hydrogenation reaction of ethylene at 30°C on the films treated at 30° and 250°C: —○— , films treated at 30°C; —●— , films treated at 250°C.

nickel irrespective of the treatment temperature. The decrease in electrical resistance with an increase in treatment temperature is shown in Table 1. The table indicates that the decrease with 50% nickel film is greatest through every change of the temperature.
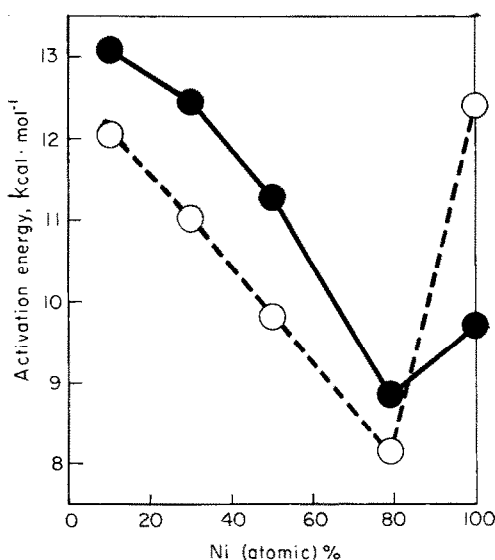

Fig. 5. Activation energies of hydrogenation reaction of ethylene on the evaporated films prepared from copper-nickel alloy; —●—, treated at 30°C; —○—, treated at 250°C.
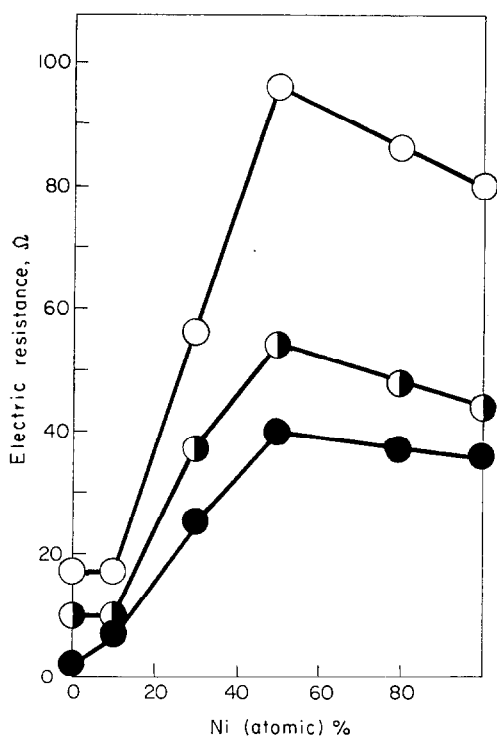
TABLE 1

THE TEMPERATURE DEPENDENCY UPON THE ELECTRICAL RESISTANCE OF Cu-Ni FILMS

Temp. treated (°C)	$\Delta\Omega$		
	Cu	50% Ni	Ni
−183° } 30° }	7	42	36
250° }	7	14	8

FIG. 6. The electrical resistance of the copper-nickel films prepared from Cu-Ni alloy: —○—, films treated at $-183°C$, measured at $-183°C$; —◐—, films treated at $30°C$, measured at $-78°C$; —●—, films treated at $250°C$, measured at $-78°C$.

IV. DISCUSSION

In the case of binary alloy M_{A-B} evaporation, the ratio of the evaporation rates of each atom of M_A and M_B is represented by Raoult's law as $\gamma_A P_A M_A / \gamma_B P_B M_B$, where γ represents activity and P and M the vapor pressure and the atomic weight, respectively, of each metal. When γ_A and γ_B are postulated to be unity and the temperature of the evaporation is $1500°C$, as assumed by the brilliancy of the tungsten filament, P_{Cu} and P_{Ni} are 10^{-3} and 10^{-4} torr, respectively. Therefore, copper evaporates more readily than nickel. As a result, the surface of the film should be more rich in nickel than in copper. However, the very similar relation between catalytic activity and alloy composition (i.e., the relation which gives the maximum activity in the region of the alloy) indicates that the surface compositions of

the films, FI and FII, do not differ greatly from one another if the overall composition is the same. Therefore, it may be suggested that the mutual diffusion of copper and nickel atoms occurred readily except for the case of FIII, after the formation of the film, and the distribution of both atoms in the film approached homogenity. In the case of FIII, more time was required to homogenize the film. The occurrence of nonuniformity of the film due to the order of the deposition of metals had been reported by Moss and Thomas (27), who studied palladium-silver films by means of X-ray. The diffraction pattern of these films showed that little or no alloying had taken place when the deposition of palladium was first and a considerable amount of alloying occurred when the deposition of silver was first. The mutual diffusion mechanism of copper and nickel atoms has been proposed by Fisher and Rudman (28). They used a mixture of copper and nickel particles and concluded that, prior to interdiffusion, nickel particles are enveloped by copper because of the rapid surface diffusion of copper. The mutual diffusion mechanism of evaporated films prepared on cold substrate seems to be more complicated than the case with particles. Mizushima and Ochi (13) had concluded that the microcrystals of the evaporated film are liable to form lattice imperfections if the crystals grow on the cold substrate. Laksmanan (14), who studied the film of nickel-chromium by means of X-ray diffraction, reported that the mutual diffusion is promoted by the existence of lattice imperfections. These reports confirm our assumptions of the possibility of an abundance of lattice imperfections and the mutual diffusion in the alloy film which was formed on the cold substrate.

The correlation between the apparent activation energy and the alloy composition does not agree with the reports by Best (4) and Hall (5). The correlation is not markedly affected by the treatment temperature, being different from the case of the reaction rate, as is shown in Fig. 5. It was found that the compensation effect can be applied to both alloys, as is shown in Fig. 7.

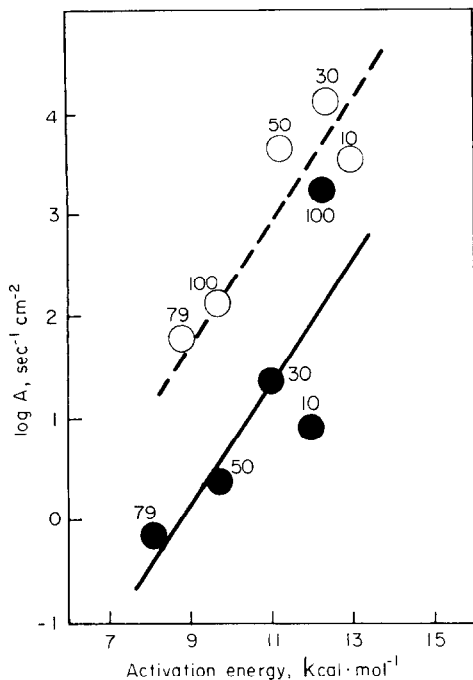The electronic theory for alloy catalysts

FIG. 7. Compensation effect on the films prepared from copper-nickel alloy: --O--, treated at 30°C; --●--, treated at 250°C. (Each number shows Ni % in the alloy.)

proposed by Dowden and Reynolds (1) concludes that the catalytic activity in the hydrogenation reaction on copper-nickel alloy should increase in the region of more than 40% nickel. However, our results did not agree with the results obtained by Dowden and Reynolds irrespective of the treatment temperatures. The results of the films treated at 30°C are very similar to those reported by Best and Russell (4), and Emmett and co-workers (5, 12, 15), who used powder and an evaporated film of copper-nickel. They found the maximum activity of hydrogenating ethylene and benzene in the alloy region. Our results on the films treated at 250°C are very similar to those obtained by Schwab and Brennecke (8) for the hydrogenation of cinnamic acid and the results obtained by the writers in the hydrogenation of ethylene (9, 10). The catalyst used in the former study was powdered alloy and, in the latter, was sheet prepared by melting the metals completely in a furnace.

Figure 4 shows that the activity decrease is most pronounced in the alloy region of 50% nickel. The decrease for 50% nickel is about 5 times greater than that for pure nickel. It may be deduced from this fact that the catalytic activities are of the sigmoid type, which is similar to the result given by Dowden and Reynolds, if the films are treated at a temperature between 30° and 250°C.

The relation between lattice imperfections and electrical resistance of metal has been studied by many scientists. These results show that the increase in resistivity with an increase of lattice imperfections is approximately 2 μohm-cm for the point defect and the interstitial atom of copper or nickel (16), 0.3 μohm-cm for the dislocation of nickel, and 0.06 μohm-cm for that of copper (17). In view of these conceptions, the great difference found in film resistivity of different compositions and the change of resistivity by the treatment temperature change in this study cannot be attributed entirely to the lattice imperfections changed in the film. It would be rational to explain most of the resistivity change by relating it to the incompleteness of the linkages of the microcrystals or the crystallites which aggregate in the state of the film. The growth of crystals and their linkages would be incomplete if the temperature of the substrate and that of the treatment are low because the migration rate of the atoms or the agglomeration of crystallites is very small (18, 19, 20). The resistivity of the film would decrease relative to the tightness linkage as a result of the contact area increase of the microcrystals. The facts that the resistivity of the film of 50% nickel treated at 30°C was greatest and the rate of the resistivity decrease with an increase in treatment temperature was also greatest suggest that the growth rate of the crystallites of 50% nickel is particularly small and the activation energy of the crystal growth is relatively great. Unfortunately, the size of the film crystallite was not measured in this study. However, such an assumption may be supported by the BET area of the powdered copper-nickel (4, 10) though it was prepared from a mixed solution of

nitrates of copper and nickel. The maximum area was given with the about 50% nickel powder. It can be assumed that the smaller the growth rate, the greater the amount of lattice imperfections when the deposition is made on the cold substratum.

The relation between the catalytic activity and the composition of the films treated at 250°C was very similar to that of the massive alloys, i.e., the maximum activity is in the alloy region of 50% nickel; however, both relations between electrical resistance and film composition and of the massive alloy were not similar to one another. A considerable number of film lattice imperfections seem to remain even after the treatment at 250°C in comparison with the massive alloy. Such a contradiction would suggest that the lattice imperfections do not act equally in their catalytic role, and that the lattice imperfections which are more heat-unstable are more active for the catalytic reaction.

Recently, Yamashina and Farnsworth (21) reported that the catalytic activity of the alloy sheets of copper-nickel in the hydrogenation of ethylene increases simply with the increase in nickel content and, however, that the change of activity occurs with a bombardment of argon ions, especially in the region of the alloy, and that the maximum activity is found in the alloy region of 60% nickel. The result is very similar to that for the evaporated film sintered at 30°C. They explained the activity increase in connection with the formation of the lattice defects due to the removal of copper atoms which exist closest to the nickel atoms.

Uhara and co-workers (22, 23) claimed recently that the catalytic activity of cold-worked nickel varies in two ranges of the annealing temperature, which correspond to the disappearance of vacancies and dislocations. Unfortunately the amount of lattice imperfections cannot be qualitatively discussed in our study. However, we may conclude that the alloy activity cannot be represented simply in connection with its composition and that the activity should be explained by taking the lattice imperfections into consideration. Very recently, Sachtler and Dorgelo (24, 25) found that the surface

composition of the evaporated copper-nickel alloy is not coincident with the overall composition. From experimental data they showed a constant value in a very wide region of the alloy, as had been found in our previous study (6) on powdered copper-nickel. Our results on the catalytic activity on both alloy series treated at different temperatures do not agree with their results. They deposited the metals on the substrate at room temperature. However, it can be concluded in this situation that the discrepancy of the composition of the alloy in both studies might depend upon the difference of the temperature of the substrate.

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