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The Catalytic Exchange of Hydrogen-Deuterium on Copper-Nickel Alloy Plates after Various Surface Treatments

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The catalytic activities of nine copper-nickel alloys (5 cm^2 in area) in hydrogen-deuterium exchange were examined at 1.5 Torr partial pressures of hydrogen and deuterium, using an ultra-high vacuum apparatus incorporated with an omegatron mass spectrometer for continuous gas analysis. Without any surface treatment, the activity was greatest on pure nickel, decreased gradually as the content of copper in the alloys increased and virturally vanished in the alloys containing copper more than 70%. The activity of each alloy sample was observed to be extremely enhanced by a slight surface treatment of oxidation-reduction ($P_{O_2}=2.3$ Torr at 500°C for 1 min, $P_{H_2}=16$ Torr at 300°C for 2 hr). The activity of the 85% copper alloy after the oxidation-reduction treatment was greatest, one hundred times that of pure nickel. Annealing for a short time in an ultra-high vacuum subsequent to the oxidation-reduction treatment caused the catalytic activity to decrease abruptly at a critical temperature (425°C). On the bases of the electron microscopic observations and the measurement of the surface roughness changed by the pre-treatments, the nature of active sites on copper-nickel alloys was discussed.

A number of investigations have been undertaken in order to confirm the influence of the electronic structure of alloys, particularly the copper-nickel system, on catalytic activity since the proposal of the *d*-band theory by Dowden and Reynolds.[1,2] In recent investigations of this subject, vacuum evaporated alloy films have frequently been used because they are capable of producing clean surfaces by adaptation to ultra-high vacuum conditions. However, there have been pronounced discrepancies of the catalytic activity patterns in the experimental results reported for copper-nickel alloy catalysts.

A series of papers by Sachtler and his co-workers[3-5] have reported that the activity pattern for benzene hydrogenation showed a constant activity in overall compostion; this is in agreement with the expectation from the work function measurement and also from the thermodynamical fact that the surface compositions of the copper-nickel system should be the same in most of the overall alloy composition region due to the miscibility gap of the system at 200°C. In contrast to these results, many investigators, including Russell,[6] Emmett,[7] and Takeuchi[8] have reported, in similar studies of copper-nickel film catalysts, that the maximum of catalytic activity for the hydrogenation reaction is found in the alloy region, and that it is approximately ten times as active as pure nickel. Particularly, Campbell and Emmett,[7] in their X-ray measurement of film structure, found only one alloy phase containing 60% copper in any case after heating to 500°C in hydrogen; nevertheless they also observed the maximum activity in the alloy region.

These facts suggest that the catalytic activity does not always correspond to the composition of the alloy film. Several possible reasons for the discrepancies in the experimental results for alloy-film catalysts can be considered, as has, for example, been pointed out by Plank and Sachtler.[5]

Many findings have shown that the catalytic activity of film, foil, or metal plate and alloy plate can be greatly influenced by the treatment of their surfaces.

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[1] D. A. Dowden, *J. Chem. Soc.*, **1950**, 242.

[2] D. A. Dowden and P. Reynolds, *Disc. Faraday Soc.*, **8**, 184 (1950).

[3] W. M. H. Sachtler and G. J. H. Dorgelo, *J. Catal.*, **4**, 654 (1965).

[4] W. M. H. Sachtler and R. Jongepier, *ibid.*, **4**, 665, (1965).

[5] P. van der Plank and W. M. H. Sachlter, *ibid.*, **7**, 300, (1967) **12**, 35 (1968).

[6] E. G. Alexander and W. W. Russell, *ibid.*, **4**, 184 (1965).

[7] J. S. Campbell and P. H. Emmett, *ibid.*, **7**, 252 (1967).

[8] T. Takeuchi, Y. Tezuka, and O. Takayasu, *ibid.*, **14**, 126 (1969).

In the study of catalysis by metals and alloys, increased in activity due to deformation with cold-rolling and ion-bombardment have been found. Results have been obtained for nickel[9-12] and silver[13] by plastic deformation, and for nickel,[14,15] platinum,[14] silver,[16] palladium[17] and copper-nickel alloys,[15,18] by ion-bombardment. In these studies, most of the authors have considered that increases in activity may be attributed to the introduction of lattice imperfections by the treatments. In the cases of the catalytic behaviour of alloy films, as reviewed above, lattice imperfections as active sites should be taken into consideration, since it is well known that various imperfections can be produced in films during evaporation.

We have previously studied[18] the catalysis for the clean surfaces of copper-nickel alloy plates after argon-ion bombardment in the reaction of ethylene hydrogenation, and found that the maximum activity of the 60% copper alloy was the greatest, fifteen times greater than that of pure nickel; we explained the activity increases in association with the formation of the lattice defects due to the removal of copper atoms, which are nearest neighbors of the nickel atoms.

The purpose of the present study was to obtain more detailed information on the nature of active sites of the copper-nickel alloy surface by means of various experimental techniques, and to compare these information with the results described above.

By using an ultra-high vacuum apparatus, the surfaces of copper-nickel alloy plates have been treated by oxidation-reduction, hydrogen reduction, annealing and so on, and the catalytic activity for hydrogen-deuterium exchange at low pressures has been measured as a function of the copper-nickel alloy composition.

Experimental

Materials. High-purity nickel (>99.9%) and copper (>99.99%), and nine copper-nickel alloys with compositions of 95, 90, 85, 80, 60, 40, 30, 20, and 10 weight per cent copper have been investigated. Each sample was about 0.6 mm in thick and 4.8 cm^2 in total surface area. These samples were polished with metallographic emery paper, an aqueous suspension of alumina, and then with fine cloth in streaming water, and rinsed in distilled water and acetone. Gaseous reactant hydrogen and deuterium of a high purity in a glass cylinder from the Takachiho Chemical CO. were used without further purification. The oxygen and argon gases were prepared by bulb-to-bulb distillation from commerical cylinders at the temperature of liquid nitrogen.

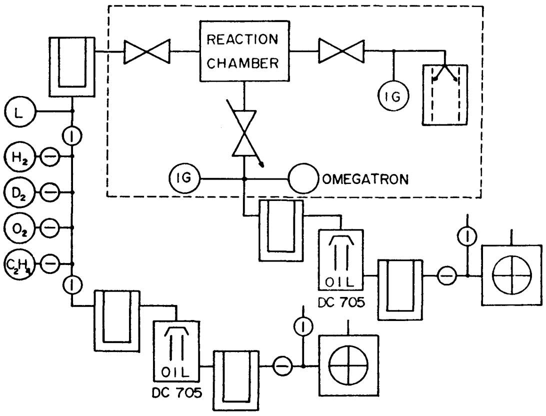

Fig. 1. Ultra-high vacuum apparatus for catalytic measurement (The inside part of dotted line is bakable).

Catalytic Activity. The main features of the vacuum apparatus for catalytic activity measurements are shown schematically in Fig. 1, which has a configuration similar to that used by Farnsworth *et al.*[14,15] The vacuum apparatus consisted of three separate systems—a reaction-chamber, a mass spectrometer, and a gas handling system. These systems could be connected with each other through metal stop cocks and valves. The reaction chamber was a vessel approximately 300 cc in volume, capable of being evacuated to 1×10^{-8} Torr or less by means of a sputter ion pump (8 *l*/sec). The progress of the reaction at low pressures was observed with an omegatron rf. mass spectrometer, which could be evacuated and baked to obtain a residual pressure of 5×10^{-8} Torr or less. The sensitivity and resolution of the omegatron were very satisfactory for tracing the course of the reaction. All the reactant gases were admitted to the reaction chamber through cold traps at the temperature of liquid nitrogen. These gases were mixed at a pressure of 1.5 Torr before they were admitted into the reaction chamber. The pressure in the mass spectrometer was kept at precisely 2×10^{-7} Torr by adjusting the variable leak valve. The reaction rate was determined by using the following equation;[19]

$$k_m = n\cdot\frac{1}{t}\ln\frac{x_e-x_0}{x_e-x_t}\left(\frac{1}{60\cdot A}\right)\ \text{molecules/cm}^2\cdot\text{sec.}$$

where n is the number of molecules in the reaction space and where x_0, x_t, and x_e are the fractions of hydrogen deuteride present at time zero, t, and at equilibrium. A is the geometrical surface area of the samples. The k_m rate is termed the catalytic activity in the present paper.

Surface Area. Changes in the surface area (roughness factor of sample plates with various treatments could be detected precisely by the rapid measurement method for a small surface area.[20]

Results

Catalytic Activity of Copper-Nickel Alloys after Oxidation-reduction Treatments. Figures 2 and 3 show the catalytic activity curves after various surface treatments for the hydrogen-deuterium exchange reaction as a function of the alloy composition. In all the cases shown in the figures, the reaction temperature was 100°C and the initial pressures of both hydrogen and

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[9] J. Eckell, *Z. Elektrochem.*, **46**, 433 (1933).

[10] G. Rienäcker, *ibid.*, **46**, 369 (1940).

[11] I. Uhara, T. Hikino, Y. Numata, H. Hamada, and Y. Kageyama, *J. Phys. Chem.*, **66**, 1374 (1962) and their many papers.

[12] E. Miyazaki, T. Fukushima, K. Kawasaki, and K. Nakada, This Bulletin **44**, 291 (1971).

[13] I. Uhara, S. Kishimoto, Y. Yoshida, and T. Hikino, *J. Phys. Chem.*, **69**, 880 (1965).

[14] H. E. Farnsworth and R. E. Woodcock, *Advan. Catal.*, **9**, 123 (1957), *Ind. Eng. Chem.*, **49**, 258 (1957).

[15] J. Tuul and H. E. Farnsworth, *J. Amer. Chem. Soc.*, **83**, 2247 (1961).

[16] H. M. C. Sosnovsky, *J. Phys. Chem. Soilds*, **10**, 304 (1959),

[17] Y. Inoue and I. Yasumori, *J. Phys. Chem.*, **73**, 1618 (1969).

[18] T. Yamashina and H. E. Farnsworth, *Ind. Eng. Chem. Prod. Res. Develop.*, **2**, 34 (1963).

[19] D.D. Eley and P.R. Norton, *Dis. Faraday Soc.*, **41**, 135 (1966).

[20] K. Watanabe and T. Yamashina, *J. Catal.*, **17**, 257 (1970).

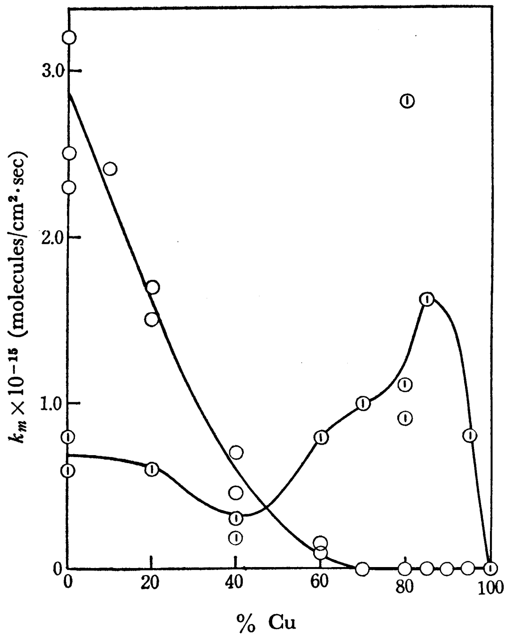

Fig. 2. Catalytic activity pattern for hydrogen-deuterium exchange reaction at 100°C.
○: Treatment (1) (Non-treatment)
⦶: Treatment (2) (Hydrogen-treatment)

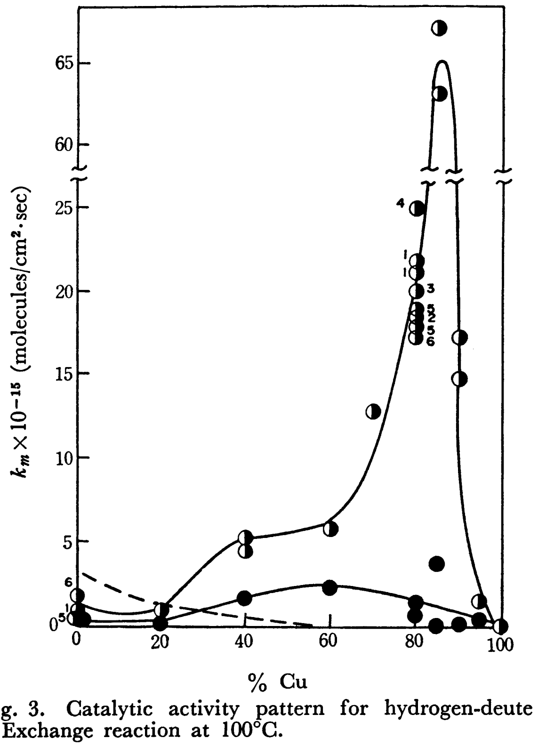

Fig. 3. Catalytic activity pattern for hydrogen-deuterium Exchange reaction at 100°C.
◑: Treatment (3) (Oxidation-reduction treatment)
●: Treatment (4) (Annealing-treatment)
Dotted line: Treatment (1)
Number of each activity point of 80% copper alloy signifies different oxidation condition as follows;

Number	O-R treatment	
	Oxidation (1 min)	Reduction (2 hr)
1	$P_{O_2}=2.3$ Torr	$P_{H_2}=16$ Torr
2	0.175	16
3	0.135	16
4	0.068	16
5	0.024	16
6	0.017 (2 min)	16

deuterium were 1.5 Torr. The number of each curve on the figures indicates the order of surface treatment procedure as follows:

(1) Non-treatment: Mechanically-polished with metallographic emery paper and alumina powder, and then with fine cloth in a stream of water.

(2) Hydrogen-treatment: Heated in hydrogen (16 Torr) at 300°C for 1 hr subsequent to the (1) treatment.

(3) Oxidation-reduction Treatment: Deoxidized by hydrogen (16 Torr) at 300°C for 2 hr after oxidation with oxygen (2.3 Torr) at 500°C for 1 min subsequent to the (1) and (2) treatments (in that order) (hereinafter referred to as the O–R treatment).

(4) Annealing-treatment: Vacuum-annealed under below 5×10^{-8} Torr at 500°C for 0.5 hr subsequent to the (1), (2), and (3) treatments (in that order).

In the case of the (1) treatment, the activity was observed to be greatest on pure nickel, to decrease gradually as the content of copper in the alloys increases, and virtually to vanish in the alloys containing more than 70% copper. After the (2) treatment, however, the activity of pure nickel decreased while catalytic activity appeared in the range of copper-rich compositions.[21] Besides, after the O–R treatment, the activity curve appeared to be quite different from the others, as may be seen in Fig. 3, in which the catalytic activity of copper-nickel alloys may be seen to be much greater than that of pure nickel; in particular, the activity of the 85% copper alloy was found to be greater than that of pure nickel, after the same treatment, by a factor of one hundred. Of particular interest in Fig. 3 is the very narrow range of composition around the 85% copper alloy. Such a high activity was found to remain unchanged even after several days and several reaction runs. When the catalysts activated by the O–R treatment were annealed, the catalytic activity was decreased drastically, as is shown in Fig. 3(4); the activity values were nearly the same regardless of the alloy composition.

Effect of Vacuum Annealing. In order to examine the nature of the active sites produced by the O–R treatment, the deactivation process of the catalytic activity due to thermal annealing *in vacuo* was examined.

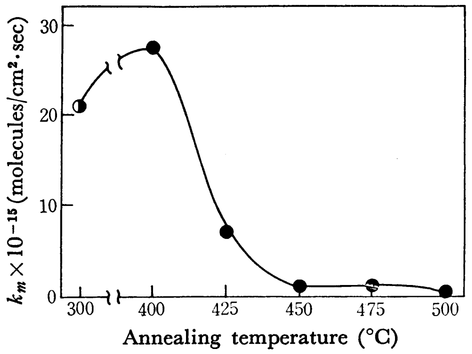

Fig. 4. Effect of annealing on catalytic activity of 80% copper alloy for hydrogen-deuterium exchange reaction at 100°C (Annealing time, 10 min).

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[21] It should be noted that the fluctuation in the activity data was found to be quite large after the (2) treatment.

Figure 4 shows the effect of the annealing temperature on the catalytic activity of the 80% copper alloy after the O–R treatment, where each sample was annealed under below 5×10^{-8} Torr for 10 min at various temperatures. The reaction temperature for the hydrogen-deuterium exchange was 100°C.

The catalytic activity is found not to be changed after annealing at 300°C and to increase slightly after annealing at 400°C, while it decreases abruptly at temperatures above 425°C. Figure 5 shows the effect of the annealing time on the catalytic activity. It is seen that, at 300°C, the activity remained nearly the same even after 8 hrs' annealing, and that at 400°C, the maximum activity was found to be twice that before annealing, but at 500°C a rapid decrease of activity for the initial few minutes was observed. It should be noted that there was a critical temperature at which the activity decreased drastically.

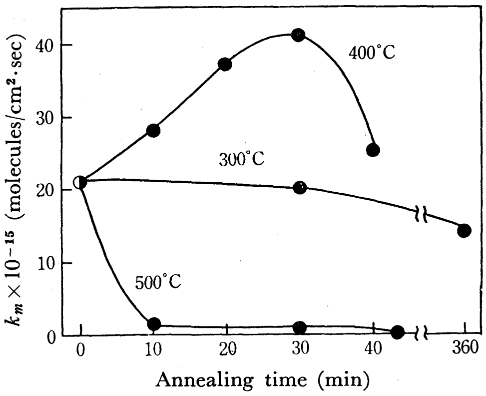

Fig. 5. Effect of annealing time on catalytic activity of 80% copper alloy for hydrogen-deuterium exchange reaction at 100°C.

Observation of the Surface State. Figure 6 represents the results of the electron-microscopic observation of the surface of the 80% copper alloy after each treatment, (1) to (4), as is shown above. As may be seen in the figure, the surface became smooth after the hydrogen treatment (2), many pits on the surface appeared after the O–R treatment (3), and the surface was invisibly changed by the annealing treatment (4). The values of the roughness factor (the ratio of the true surface area to the geometric surface area), as estimated by means of the above method,[20] are also shown in Fig. 6. The roughness factor of the surface was increased about twice by the O–R treatment, but no change was found in the values between those after the O–R treatment and the subsequent annealing treatment. It should also be emphasized that changes in the roughness factor with the surface treatment were not related to changes in the catalytic activity shown in Fig. 3.

Discussion

As has descrived above, the catalytic activities of copper-nickel alloy plates were extremely enhanced by the O–R treatment; the activity was greatest after the O–R treatment in the very narrow range of alloy composition lying around 85% copper. On the contrary, pure metals, copper, and nickel were not activated by the treatment.

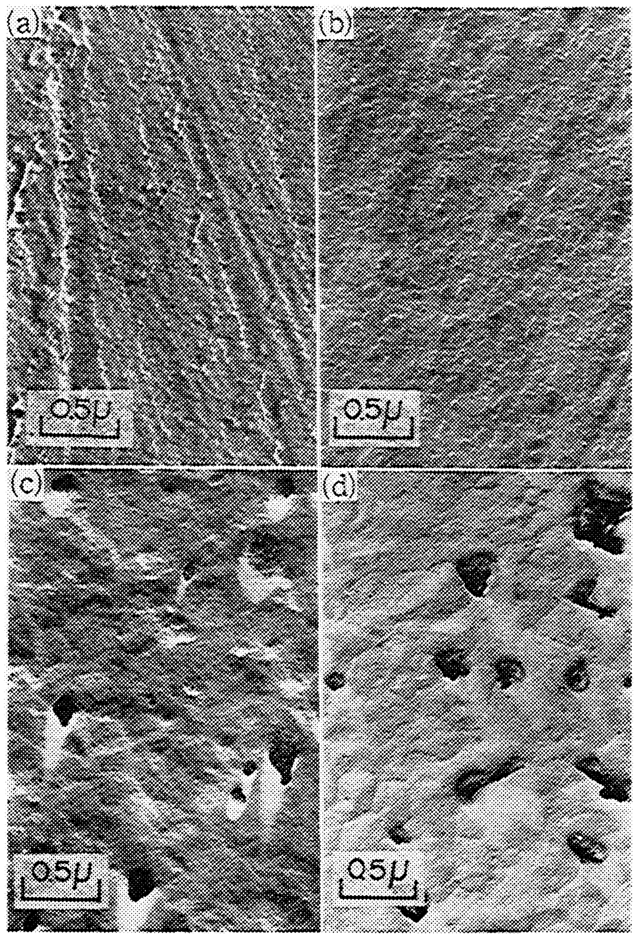

Fig. 6. Electron micrographs and roughness factor of 80% copper alloy surface after various treatments.

(a): Non-treatment (1), Roughness factor 3.1
(b): Hydrogen-treatment (2), Roughness factor 3.1
(c): Oxidation-reduction treatment (3), Roughness factor 5.7
(d): Annealing-treatment (4), Roughness factor 5.6

The thickness of the surface layer which was oxidized and deoxidized by the O–R treatment was estimated by means of a tortional microbalance with high sensibility. The results from this experiment, after treatment under different oxidation conditions, are shown in Table 1. In each case, the oxide layer was observed to be completely deoxidized by the reduction treatment. From these results, it should be pointed out that the very thin layer (a few monolayers) on the alloy surface is possibly closely related to the catalytic phenomena.

Two possible reasons for the enhancement in catalytic activity after the treatment may be considered to be :
(a) an increase in the surface area (the roughness factor) of the catalyst, and (b) a production of new active sites after the O–R treatment. Measurement of the changes in the surface area indicated that the roughness factor was increased only about twice after the O–R treatment; it did not correspond to the catalytic activity. Consequently, it is possible to conclude that the origin of the remarkable enhancement of activity is the production of new active sites by the

TABLE 1. RESULTS OF GRAVIMETRIC MEASUREMENT WITH SURFACE TREATMENT

Treatment		Mass Gain after Oxidation	Thickness of oxide layer	Roughness factor after reduction	Catalytic activity ($H_2+D_2=2HD$)
Oxidation	Reduction				
$P_{O_2}=0.017$ Torr 2 min, 500°C	$P_{H_2}=16$ Torr 2 hr, 300°C	9.7×10^{-8} g/cm^2	15—20 Å	5.5	1.6×10^{16} molecules/cm^2·sec
$P_{O_2}=2.3$ Torr 1 min, 500°C	$P_{H_2}=16$ Torr 2 hr, 300°C	1.9×10^{-6} g/cm^2	300 Å	5.7	2.1×10^{16} molecules/cm^2·sec

treatment.

In our previous study[18] of the effect of ion bombardment on the catalytic activity of copper-nickel alloys, a result similar to that of the present work was obtained; we found the composition of the copper-nickel alloy which gives the maximum activity, fifteen times that of pure nickel. Measurement of the annealing effect of alloy catalysts after ion bombardment also showed that, for the copper-nickel alloys, the critical temperatures at which the activity began suddenly to decrease were observed to be between 300 and 500°C. When we compare the activity pattern and deactivation process after the ion bombardment with those after the O–R treatment, many similar general tendencies can be found.

To account for the enhancement of activity after the treatments, it is assumed that lattice defects resulting from the O–R treatment or the ion bombardment contribute to the greatly-enhanced catalytic activity. According to the study of the effect of ion bombardment on the surface of silver by Sosnovsky,[16] the catalytic activity of silver is increased in the order of several tens of times by the treatment; it was concluded on the basis of the evidence by Ogilvie[22] that ion bombardment produces disoriented regions bounded by stable arrays of dislocations, that the reaction occurs at sites where dislocation lines intersect the surface. Takeuchi *et al.*[8] also concluded that the activity of copper-nickel alloy films can be explained by taking the unstable lattice imperfections into considerations. Similarly, large numbers of structural defects of various kinds were found in thin oxide films on copper, nickel, and alloys.[23] It seems likely that same structural defects in oxide films, especially dislocation, remain even after the hydrogen reduction of the oxide in the temperature range below 300°C. Uhara and his co-workers[11] pointed out that the catalytic activity of cold-worked metals was decreased in two temperature ranges during annealing; those ranges correspond to the disappearance of vacancies (>200°C) and dislocations (>400°C).

Considering these results, it can be concluded that the active sites produced by the O–R treatment may be related to surface dislocations of a particular type on copper-nickel alloys. Otherwise after the O–R treatment the active sites seem to be associated with a heterogeneous surface in alloy composition. Kubaschewsky and his co-workers[24] have shown that the miscibility gap forms a phase separation in copper-nickel alloys at temperatures lower than 322°C. On the other hand, Hall and Emmett[25] in their study of powder catalysts of copper-nickel alloys, found activity pattern in the effect of hydrogen pre-adsorption quite similar to that of the O–R treatment (Fig. 3) in the present study. The effect of pre-adsorbed hydrogen by alloy surfaces is probably important in accounting for the remarkable enhancement of the catalytic activity.

As has been described in the Introduction, a number of papers on the catalysis of copper-nickel alloy films have been published. Sachtler *et al.*[3–5] have shown that particular copper-nickel alloys in copper-rich appear to be formed preferentially after heating at 200°C; they also revealed, by calculations, that the free energy of the formation of an alloy containing 80% copper at 200°C appears to be favored as a result of a wide miscibility gap of the alloy system, and suggested on the basis of experiments on the CO adsorption, that the 80% copper alloy must exist in the surface layer. In similar experiments, Campbell and Emmett[7] found that when alloy films were homogenized by heating to 500°C in hydrogen from an alloy containing about 60% copper (bulk composition), the excess of

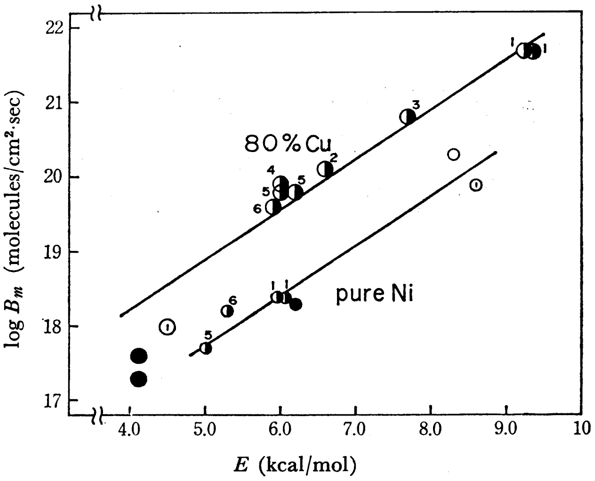

Fig. 7. Plot of the activation energy against the log B_m for nickel and 80% copper alloy, for hydrogen-deuterium exchange reaction.
Smaller circle: pure nickel
Larger circle: 80% copper alloy
○: Treatment (1), ◑: Treatment (3),
⦶: Treatment (2), ●: Treatment (4).
Number of each activity point of 80% copper alloy signifies different oxidation condition as same as in Fig. 3.

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22) G. J. Ogilvie, *J. Phys. Chem. Soilds*, **10**, 222 (1959).

23) J. V. Cathcart, G. F. Petersen, and C. J. Spanks, *Proc. Cagamore Army Master Res. Confer.*, **13**, 333 (1967).

24) L. Elford, F. Müller and O. Kubaschewski, *Ber. Bunsenges.*, **73**, 601 (1969).

25) W. K. Hall and P. H. Emmett, *J. Phys. Chem.*, **63**, 1102 (1959).

nickel or copper present gives the X-ray diffraction pattern of the pure metals. The activity patterns obtained by Sachtler *et al.*[3-5] showed a constant value over these films with an equal surface composition, while that obtained by Campbell and Emmett[7] showed a promoting effect, increasing to a value of from five to fifteen times as great as for pure nickel in spite of the wide miscibility gap. The structure and surface phenomena of alloy films might be very complicated in comparison with the plates of the alloys used in the present work.

Finally, plots of the logarithm of the pre-exponential B_m factor against the energy of activation are shown in Fig. 7. It appears that the tendency for increased energies of activation to be compensated for by an increase in the pre-exponential factor was found to be separable in pure nickel and in the copper-nickel alloy.