Heats of Adsorption of Hydrogen and Catalytic Activities of Hydrogenation of Ethylene on Powdered Copper-Nickel Alloys

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A previous paper[1] on copper-nickel alloys prepared from copper and nickel nitrates demonstrated that the heat of adsorption of hydrogen and the catalytic activity of the hydrogenation of ethylene are closely related to the composition of alloys. In this note we are concerned with the correlation of the heat of adsorption of hydrogen to the rate of hydrogenation of ethylene and the activation energy, which were not discussed in the previous paper.

The correlation may be represented on the basis of the data in the previous paper as in Fig. 1, where the rates of reaction and the activation energies are plotted against the heats of adsorption of hydrogen at a sparse coverage of the corresponding alloy. The activation energies were obtained from further study at various reaction temperatures (100—160°C), study which was carried out in order to supply the deficiency in the previous study. The composition (Ni%) to which each point corresponds is indicated in the figure. Of particular interest is the fact that the correlation of the rate to the heat of the adsorption of hydrogen can be represented as a straight

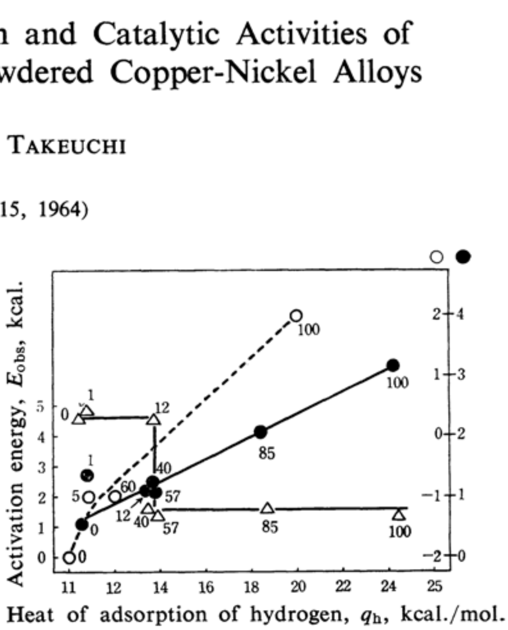

Fig. 1. Relations of the heat of hydrogen adsorption to the rate of catalytic hydrogenation of ethylene and the activation energy of the reaction.

—△— Activation energy.
—●— Rate of hydrogenation of ethylene (120°C) K/min.cm$^2\times 10^7$ outside scale of ordinate
—○— Rate of p-hydrogen interconversion (−196°C) log K inside scale of ordinate (Russell et. al.[4,5])

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[1] T. Takeuchi, M. Sakaguchi, I. Miyoshi and T. Takabatake, This Bulletin, 35, 1390 (1962).

line, and that the rate increases with an increase in the heats of adsorption, unlike the results on pure metals obtained by Beeck[2] and Schuit.[3] A similar correlation has, however, been obtained by Russell and his co-workers[4,5] from their study of the reaction of *p*-hydrogen interconversion and that of the heat of the adsorption of hydrogen on the same type of catalyst.

Since the observed activation energy in our study did not change continuously, notwithstanding the continuous change in the heat of adsorption of hydrogen, the correlation between the rate and the heat of adsorption can not be explained by the following equation obtained from the Langmuir-Hinshelwood kinetics:

$$E_{\mathrm{obs}}=E_{\mathrm{true}}-q_{\mathrm{h}}-q_{\mathrm{e}}$$

where E_{obs} is the observed activation energy, E_{true}, the true activation energy, and q_{h} and q_{e}, the heats of adsorption of hydrogen and ethylene respectively.

In view of this situation, we attempted to explain the occurrence of the discrepancy of the correlation between alloys and pure metals on the basis of the following hypothesis. If the surface of the catalyst is assumed to be nonuniform with respect to the adsorption of hydrogen and if the distribution of the bond strength of the adsorbed hydrogen against the coverage can be represented as the two cases shown in Fig. 2, and if, moreover, the bond strength of the hydrogen available for the reaction is restricted in the $E \sim E+dE$ range, the available amount of hydrogen on catalyst B in case 1 will be greater than that on catalyst A, when the greater inclination of the distribution curve can be given by the catalyst with the greater initial heat of adsorption. On the other hand, if the inclination is represented as in case 2, the available amount of hydrogen on catalyst A* will be greater than that on B*. Inasmuch as the available amount of hydrogen rules the rate of hydrogenation as well as that of *p*-hydrogen interconversion, it may suffice to say, consequently, that the reaction on pure metals and that on copper-nickel alloys correspond to those in case 1 and case 2 respectively. It was found in the study[6] using tritium as a tracer that the hydrogen adsorbed very strongly and/or very weakly on nickel did not react readily with ethylene. Unfortunately, we have no positive evidence that the heats of adsorption of hydrogen on the alloys can be given as case 2, for the measurement was made only on the sparse coverage. However, the heats on pure metals measured by Beeck[2] may be regarded to be approximately as in case 1.

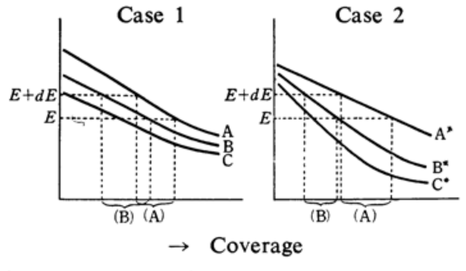

Fig. 2. Possible forms for the variation of bond strength (E) of adsorbed hydrogen.

The activation energies can be represented by the distinct series of different values, i. e., about 4.5 kcal. and 1.5 kcal. respectively. Such a discontinuous variation in activation energy is very similar to that found by Couper and Eley[7] in the *p*-hydrogen interconversion on palladium-gold alloys, if the expression of the axis of the abscissa can be replaced by the concentration of nickel on the surface of the alloy. Our previous studies[8,9] indicated that the concentration of nickel on the surface of the powdered copper-nickel alloy differed from that in the interior. It would be possible, however, to assume that the concentration of nickel on the surface increases with an increase in the average concentration of alloy and that the increase in the concentration increases the heat of adsorption of hydrogen. The figure shows that the composition which changed the activation energy is in the range from 12 to 40% nickel. Such a composition is approximately in accord with that to be expected from the proposal by Dowden and Reynolds,[10] even though the compositions indicated in the figure do not mean those of the surface. The activation energies in our study are quite small compared with those which have been reported by many other researchers.[11-16] No

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[2] O. Beeck, *Discussions Faraday Soc.*, **8**, 118 (1950).

[3] G. C. A. Schuit, ibid., **8**, 205 (1950).

[4] P. B. Shallcross and W. W. Russell, *J. Am. Chem. Soc.*, **81**, 4132 (1959).

[5] L. S. Shield and W. W. Russell, *J. Phys. Chem.*, **64**, 1592 (1960).

[6] D. Miyatani, R. Yamaguchi and T. Takeuchi, 1st Symposium on Isotopes, Japan (1964); to be published shortly.

[7] A. Couper and D. D. Eley, *Discussions Faraday Soc.*, **8**, 172 (1950).

[8] S. Yamaguchi and T. Takeuchi, *Z. anorg. u. allgem. Chem.*, **294**, 254 (1958).

[9] T. Takeuchi, F. Shibata and M. Sakaguchi, *Z. physik. Chem., N. F.*, **14**, 339 (1958).

[10] D. A. Dowden and P. W. Reynolds, *Discussions Faraday Soc.*, **8**, 184 (1950).

[11] E. K. Rideal, *J. Chem. Soc.*, **121**, 309 (1922).

[12] O. Toyama, *Rev. Phys. Chem., Japan*, **11**, 153 (1937).

[13] O. Beeck, *Rev. Mod. Phys*, **17**, 61 (1945).

[14] R. J. Best and W. W. Russell, *J. Am. Chem. Soc.*, **76**, 838 (1954).

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

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

confident explanation for this occurrence of small values can be offered. It can be recalled, however, that the rate of the hydrogenation of ethylene has an optimum at the temperature range of about 150°C.(17) The reaction temperature of our study includes this transition range. This might give the small activation energies.

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(17) H. Zur Strassen, *Z. physik. Chem.*, **A169**, 81 (1934); cf. G. C. Bond, "Catalysis by Metals," Academic Press, New York (1962), p. 243.