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Tracer Study of the Reactivity of Hydrogen Adsorbed on Nickel in the Hydrogenation Reaction

Toyosaburo TAKEUCHI and Daisaku MIYATANI

Faculty of Literature and Science, Toyama University, Gofuku, Toyama

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The correlation between the bond strength of adsorbed hydrogen and the reactivity of the hydrogen toward ethylene has been investigated by using tritium as a tracer. Hydrogen (or tritium) was adsorbed first on powdered nickel at -78°C; tritium (or hydrogen) was subsequently adsorbed, and then ethylene was added. The total coverage of hydrogen in every experiment was 0.16 or 0.4 for the nickel reduced at 200°C, and 0.06 or 0.4 for the nickel reduced at 400°C. After a certain time, the hydrogen and the mixture of ethane and ethylene were drawn off successively from the reaction vessel and separated. An assay of the tritium in each fraction of the gas was then made. The results on the nickel reduced at 200°C indicate that neither the very-strongly-adsorbed hydrogen nor the weakly-adsorbed hydrogen reacts with ethylene. The results on the nickel reduced at 400°C indicate that the weakly-adsorbed hydrogen does not react with ethylene either. These findings suggest that the very strong sites for the adsorption of hydrogen, which are inactive in the hydrogenation, are diminished by the elevation of the reduction temperature.

Most results of studies[1] of the adsorption of gas by adapting the differential isotope kinetic method have shown that the sites of the metal surface do not adsorb gas equally. However, the correlation between the bond strength of the metal site and the reactivity of the adsorbed gas in the catalytic reaction remains unexplored. In a previous study[2] using tritium as a tracer it was found that the hydrogen adsorbed initially on the reduced nickel is more active in the hydrogenation of ethylene than is that successively adsorbed; it was, therefore, proposed that the strongly-adsorbed hydrogen is more active than the hydrogen adsorbed weakly. In that study, the catalyst used was of a 200°C reduction, and the total coverage of hydrogen on the catalyst was limited to about 0.4.

The nature of the metal surface has been considered to depend upon the temperature of the treatment and on its career. A more detailed study seems, therefore, to be neccessary before we can accept the proposal of the previous study as a general conclusion concerning reduced catalysts. With this in mind, therefore, the present study was undertaken. In addition to this, the dependence of the reactivity of the adsorbed hydrogen upon the coverage was investigated.

Experimental

Extra-pure nickel nitrate was used for the preparation of the catalyst. It was ignited by metal oxide in a furnace at 500°C. 0.5 or 5.0 g of the oxide was used for the reaction. The oxide was reduced at 200°C for three week or at 400°C for one week in an atmosphere of hydrogen, which was replaced several times. Prior to use, the catalyst was evacuated for about three

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[1] N. P. Keier and S. Z. Roginski, *Izvest. Akad. Nauk. U. S. S. R.*, **1**, 27 (1950); J. K. Kummer and P. H. Emmett, *J. Am. Chem. Soc.*, **73**, 2886 (1951); G. C. A. Schuit, Proc. Symposium on the Reactivity of Solids, 1955, p. 571. *Cf.* "Advan. Catalysis," 10 (1958), p. 287; G. C. Bond, *J. Phys. Chem.*, **60**, 702 (1956); K. Hirota, Y. Kobayashi and J. Kiji, This Bulletin, **34**, 1213 (1961); M. Sakaguchi, T. Asano and T. Takeuchi, *Shokubai (Catalyst)*, **4**, 24 (1962).

[2] T. Takeuchi and T. Asano, *Z. physik. Chem.*, *N. F.*, **36**, 1/2, 118 (1963).

hours under a pressure of 10^{-6} mmHg at the temperature of the reduction. The hydrogen used was prepared by the electrolysis of water and was purified by diffusion through a palladium thimble at 150°C. The tritium used was furnished by R. C. C. It was diluted to about $1/10^5$ with normal hydrogen (protium) prepared in the way described above.

Figure 1 shows the apparatus used for the reaction and for the assay of tritium. Most of the apparatus was the same as that used in a previous study,[2] except for the vessels, S_i, which were used for the storage of hydrogen drawn off from the catalyst after the reaction. A is the reaction vessel, with a volume of about 300 cc, including a McLeod gauge, M_1. B and C are U-tubes, cooled by a dry-ice bath and a liquid nitrogen bath respectively. D_1 and D_2 are diffusion pumps. E is a U-tube cooled by a dry-ice bath for the protection of the counting tube from contamination by the vapor of the grease. L is a gas burette, and G is a gas-counting tube with a volume of about 50 cc. After the catalyst had been evacuated, the temperature of the reaction vessel was lowered to the reaction temperature of −78°C, protium (or tritium) was introduced first so that its coverage was 0.1; tritium (or protium) was subsequently introduced so that the total coverage was twice the initial coverage. Ethylene was then admitted so that the amount (in moles) was half of the hydrogen in the vessel.

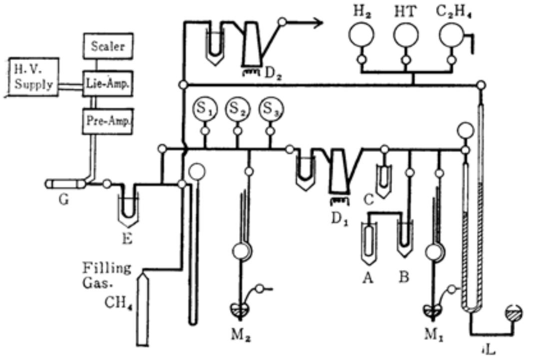

Fig. 1. Apparatus of reaction and assay of tritium.

In the case of the catalyst reduced at 400°C, two series of experiments at different coverage were carried out; *i. e.*, the coverage of hydrogen in one series was 0.03, while that in the other series was 0.20. The mole ratio of ethylene to hydrogen was the same as that in the case of the reduction at 200°C. The coverages of hydrogen were estimated on the assumption that the hydrogen dissociated in adsorption, giving two atoms, each occupying a single site of the metal.

After a certain time, a mixture of ethylene and ethane was collected in the U-tube, C, by opening the stop cock before the reaction vessel; the hydrogen was expanded into one of the reservoirs, and then into the other, meanwhile measuring the pressure. When the pressure of vessel became less than 10^{-3} mmHg, the temperature of the vessel was raised in order to make the desorption of gas proceed readily, step by step, from −78 up to 200 or 400°C. The hydrogen and the condensates were then collected separately according to the evacuation temperature. The details of the assay of the tritium in every fraction were the same as have been presented elsewhere.[3] The surface areas were obtained by the BET method, using ethylene at −183°C, as was attemped by Wooten,[4] after the evacuation of gas had been finished.

Results and Discussion

The relations between the amount of every fraction of gas collected by evacuation and the respective counting value, cpm per 10^{-10} mol, are shown in Figs. 2 to 5. Figure 3 is reproduced

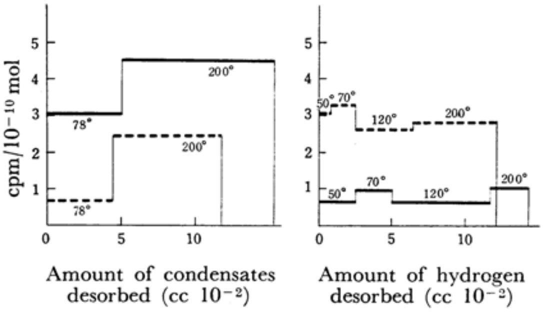

Fig. 2. Counting values of each fraction of gas after the reaction.

—— (1A), Protium adsorbed first and ethylene admitted 5 min after the admission of tritium. Reaction lasted 15 min.

- - - (1B), Tritium adsorbed first and ethylene admitted 5 min after the admission of protium. Reaction lasted 15 min.

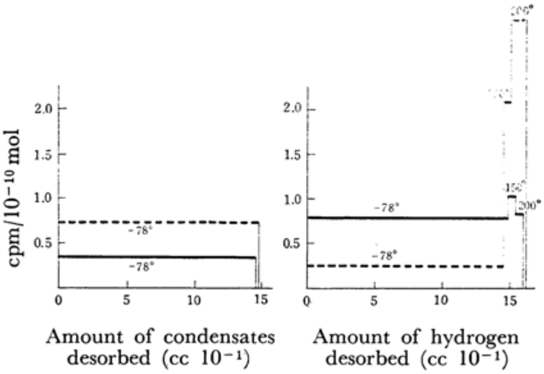

Fig. 3. Counting values of each fraction of gas after the reaction.

—— (2A), Protium adsorbed first and ethylene admitted 3 minutes after the admission of tritium. Reaction lasted 60 min.

- - - (2B), Tritium adsorbed first and ethylene admitted 3 min after the admission of protium. Reaction lasted 60 min.

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[3] M. Sakaguchi, I. Motoki and T. Takeuchi, Proc. 3rd Conf. on Radioisotopes Japan, 1959, p. 455.

[4] L. A. Wooten and C. Brown, *J. Am. Chem. Soc.*, **65**, 113 (1943).

TABLE 1. DISTRIBUTION OF TRITIUM
(Nickel reduced at 200°C)

Exp. No.	1(A)	1(B)	2(A)	2(B)
Surface area, M^2	6.6	6.6	1.7	1.7
Hydrogen admitted first, cc (STP)	Protium 0.147	Tritium 0.115	Protium 0.136	Tritium 0.125
Hydrogen admitted second, cc (STP)	Tritium 0.173	Protium 0.127	Tritium 2.17	Protium 2.25
Coverage in every time	0.08	0.08	0.20	0.20
$C_{\text{calc.}}$ cpm/10^{-10} mol	2.87	2.14	0.81	0.74
$C_{\text{cond.}}/C_{\text{calc.}}$	1.46	0.88	0.50	2.20
$C_{H_2}/C_{\text{calc.}}$	0.30	1.10	1.10	0.70

TABLE 2. DISTRIBUTION OF TRITIUM
(Nickel reduced at 400°C)

Exp. No.	3(A)	3(B)	4(A)	4(B)
Surface area, M^2	8.0	8.0	4.4	4.4
Hydrogen admitted first, cc (STP)	Protium 0.061	Tritium 0.043	Protium 0.114	Tritium 0.151
Hydrogen admitted second, cc (STP)	Tritium 0.057	Protium 0.042	Tritium 0.765	Protium 0.888
Coverage in every time	0.03	0.03	0.20	0.20
$C_{\text{calc.}}$ cpm/10^{-10} mol	4.60	4.80	1.10	1.11
$C_{\text{cond.}}/C_{\text{calc.}}$	0.84	1.28	0.20	1.30
$C_{H_2}/C_{\text{calc.}}$	—	—	1.40	0.60

from a previous paper,²⁾ only changing the expression for convenience of comparison. The evacuation temperature used for each fraction is indicated in the figure. The cpm of condensates desorbed at the later stage is found always to increase, while that of hydrogen is found sometimes to increase and sometimes to decrease. In order to understand clearly how the tritium is distributed, the ratios of the mean counting values of the condensates, $C_{\text{cond.}}$, and those of hydrogen, C_{H_2}, to the calculated values of hydrogen $C_{\text{calc.}}$, were calculated. $C_{\text{calc.}}$ was obtained by assuming that tritium and protium were mixed uniformly in the reaction vessel. If all the hydrogen adsorbed on nickel behaves indiscriminately in relation to ethylene and if, moreover, the isotope effect for the reaction is disregarded, the $C_{H_2}/C_{\text{calc.}}$ ratios, are given as 1.

No. 1A in Table 1 indicates that the cpm of the condensates is greater than $C_{\text{calc.}}$, while that of hydrogen is smaller than $C_{\text{calc.}}$, when the catalyst was reduced at 200°C, and that protium was adsorbed first. No. 1B shows that the reverse is true when tritium is adsorbed first. These results reveal that ethylene is inclined to react readily with the hydrogen adsorbed successively; *i. e.*, ethylene reacts more readily with hydrogen adsorbed weakly than with that adsorbed strongly. Such a conclusion is the very reverse of that of the previous study, shown in No. 2A and 2B, a study which was made with a total coverage of about 0.4.

No. 3A in Table 2 shows the findings on the catalyst reduced at 400°C. The coverage of hydrogen in this case was 0.03. In this experiment, no hydrogen could be detected after the reaction, though the evacuation was carried out by raising the temperature to 400°C. This is because the amount of hydrogen introduced into the reaction vessel was very small, *i. e.*, about half of that in the cases of No. 1A and 1B, and about 1/10 of

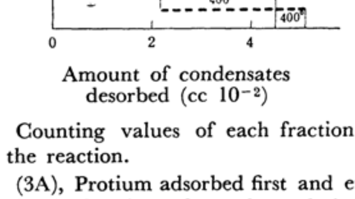

Fig. 4. Counting values of each fraction of gas after the reaction.
—— (3A), Protium adsorbed first and ethylene admitted 3 min after the admission of tritium. Reaction lasted 3 min.
- - - (3B), Tritium adsorbed first and ethylene admitted 3 min after the admission of protium. Reaction lasted 3 min.

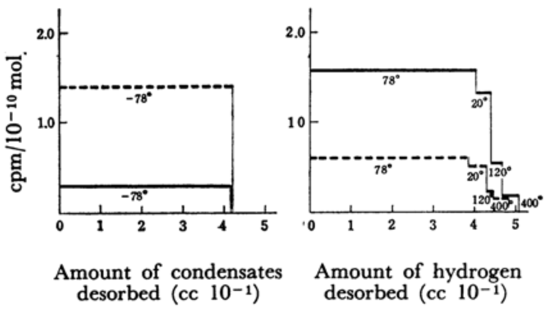

Fig. 5. Counting values of each fraction of gas after the raction.

—— (4A), Protium adsorbed first and ethylene admitted 60 min after the admission of tritium. Reaction lasted 30 min.

---- (4B), Tritium adsorbed first and ethylene admitted 60 min after the admission of protium. Reaction lasted 30 min.

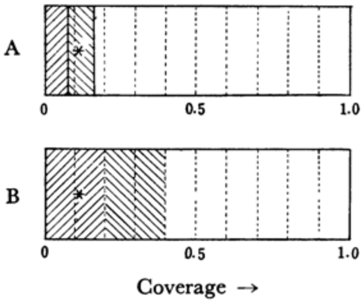

Fig. 6. Schematic representation of the surface occupied by hydrogen.

that in the cases of No. 4A and 4B. In addition, a part of the hydrogen might dissolve into the interior of the metal during the evacuation at the elevated temperature. It should be noticed, however, that the cpm of the condensates is smaller than that of $C_{\mathrm{calc.}}$ when protium is adsorbed first.

No. 4A and 4B show the results of the study of the catalyst reduced at 400°C and covered with hydrogen so that its coverage is 0.2. The cpm of the condensates is far less, and that of hydrogen is far greater than $C_{\mathrm{calc.}}$, when protium is adsorbed first, the reverse of the case when tritium is adsorbed first. The findings on both catalysts reduced at 400°C reveal that the hydrogen adsorbed strongly is inclined to react readily with ethylene.

The distribution of the adsorbed hydrogen and the sites of the various bonding powers of the catalyst may be expressed schematically as in Fig. 6, because the bonding power for the chemisorption of hydrogen decreases with the increase in the coverage; molecules or atoms adsorb on strong sites first, and then on less strong sites. In the figures, the section occupied by hydrogen atoms is indicated with the striped shadow. A and B are the cases where the coverages are 2×0.08 and 2×0.2 respectively. The figures suggest both that the hydrogen adsorbing very strongly and that adsorbing weakly on the catalyst reduced at 200°C react with ethylene only with difficulty, and that only a part of the hydrogen adsorbing with an appropriate power is effective for the catalytic reaction. Hence, the section of the effective bonding power for the catalytic reaction is indicated with a star. The findings on the catalyst reduced at 400°C reveal that the bonding power of all the strong sites which fix the hydrogen as incapable of hydrogenation is weakend by the elevation of the temperature of the reduction.

Many theories about the active site of the catalyst have been reported hitherto.[5] A specific crystal plain, the intersection of the surface plain, a point defect and dislocation, and an impurity on the surface have been proposed as active in the reaction. Recently, Sweet and Rideal[6] have found that the heat of the adsorption of hydrogen on nickel film rises markedly in the range near zero coverage ($\theta < 0.02$), while the differential entropy of adsorbed hydrogen falls in the same range. They proposed the "trap sites" as had Wortman *et al.*[7] as the result of an adsorption study using a nickel field-emitter. Horiuti and Toya[8] attempted to interpret theoretically the decrease of entropy at near zero coverage with relation to lattice imperfections. It is difficult at present to present a definite conclusion on the structures of very strong sites and active sites. It can be said, however, that the elevation of the temperature of reduction causes the growth of a special crystal facet by the migration of atoms, a decrease in the imperfect structure, and the appearance or disappearance of impurities on the surface.

The variation in cpm found in every fraction of the condensates and that of hydrogen should be explained not only by the non-uniformity of the catalyst sites, but also by the isotope effects in the reaction and the desorption of gases. It has been reported by many researchers[9] that the rates of the reaction of ethylene with protium are greater than those with deuterium. Boreskov and Vassilevitch[10] have found that the rate of the adsorption of tritium is far smaller than that of other hydrogen isotopes. Peter and Lomas[11] reported that

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[5] H. S. Taylor, *Discussions Faraday Soc.*, **8**, 9 (1950); B. M. W. Trapnell, "Advan. Catalysis," 3 (1951), p. 1; I. Uhara *et al.*, *J. Phys. Chem.*, **66**, 2691 (1962); *ibid.*, **67**, 996 (1963).

[6] F. Sweet and E. Rideal, Act. Deux. Congr. Intern. Catalysis Paris 1960, p. 175.

[7] R. Wortman, R. Gomer and R. Rundy, *J. Chem. Phys.*, **27**, 1099 (1957).

[8] J. Horiuti and T. Toya, *J. Research Inst. Catalysis, Hokkaido Univ.*, **11**, 174 (1964).

[9] S. S. Roginski, "Theoritische Grundlagen der Isotopen Chemie," Ver Deutscher Verlag der Vissenschaften, Berlin (1962), p. 358.

[10] G. K. Boreskov and A. A. Vassilevitch, Act. Deux. Congr. Intern. Catalysis, Paris, 1960, p. 1095.

[11] K. Peters and W. Lomas, *Z. phys. Chem.*, **A183**, 51 (1937).

the rate of the desorption of protium is greater than that of deuterium. We may assume from these facts that the tritium on the surface will be gradually concentrated during the reaction, even if tritium exsists on the strong sites, as the tritium used was prepared by diluting it with normal hydrogen. Moreover, protium will desorb more rapidly than tritium when the gas is evacuated after the reaction. The cpm of the condensates which are desorbed at the later stage will become greater, because ethylene will react or exchange its hydrogen with the more concentrated tritium. When the hydrogen on the effective sites is transported from the sites by the reaction, other hydrogen or ethylene, adsorbing on less strong sites, will migrate to the vacancies. As has been stated above, the behavior of gas on the surface can be considered to be complicated and to be related to the isotope effect. However, the qualitative explanation of the variation of cpm in every fraction of gas desorbed remains as a problem for future study.

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