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Gas Chromatographic Determination of Reversible Adsorption of Hydrogen

II. The Properties of Reversibly Adsorbed Hydrogen on a Nickel Catalyst

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The nature of the reversible adsorption of hydrogen on nickel, the determination of which was reported for the first time in a preceding paper, has been investigated in terms of heat of adsorption and by the effect of catalyst reduction and the effect of water vapor as a carrier gas impurity. The heat of adsorption was found to be about 2 kcal/mole at low temperature (−195–−100°C) and about 13 kcal/mole at around 0°C (−30–60°C), which indicates two different types of adsorption. The adsorption sites for them appeared to be developed in the early stage of reduction. Adsorbed water is likely to activate another type of hydrogen adsorption.

INTRODUCTION

It was shown in a previous paper (*1*) that the rapid and reversible adsorption of hydrogen over a nickel catalyst could be determined by a gas chromatographic technique using deuterium as a tracer. The amount of adsorption thus measured is the rapid and reversible part of total hydrogen uptake by the catalyst. The nature of adsorbed hydrogen defined by this technique would be important in connection with the catalytic hydrogenation.

Hence the nature of the reversible adsorption was investigated by means of heat of adsorption, effect of catalyst reduction, effect of water vapor as a carrier gas impurity, and effect of cooling the catalyst in vacuum.

EXPERIMENTAL

The catalyst sample was taken from the same batch of nickel catalyst as used in the previously reported work (*1*), i.e., the stabilized nickel catalyst #101 supplied by Nikki-Kagaku Co. which involved kieselguhr (50 wt %) as a support. The amount of catalyst packed in the column was around 6 g. This catalyst was reduced with a hydrogen stream at 300° or 350°C before use, and kept all the time in a hydrogen atmosphere. The surface area of the catalyst was 91 m^2/g and the amount of chemisorption of carbon monoxide at −183°C was 7.6 ml/g, after the reduction at 350°C. The procedure of gas chromatographic measurement was the same as described in the preceding report. Briefly, the retention volume of deuterium relative to helium was measured from the chromatogram. A separate experiment proved that the retention due to kieselguhr was negligible. In the determination of heat of adsorption, the measurements were carried out under reduced pressures. In the examination of the effect of water vapor, the carrier gas was contaminated as follows: The impurity oxygen involved in cylinder hydrogen was converted to water by passing the gas over a platinum catalyst at 300°C. The resulting hydrogen stream contained 1.1 mm Hg of water vapor.

All the measurements, except where particularly mentioned, were made with a stationary state of the adsorption.

RESULTS AND DISCUSSION

1. *Heat of Adsorption*

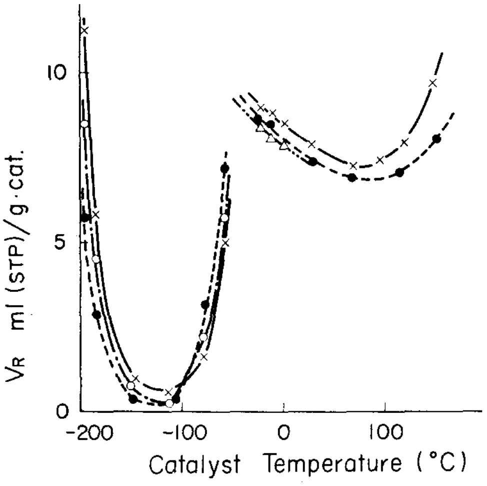

FIG. 1. The retention volumes of deuterium under various pressures. The flow rate is given in the table in ml/min at 0°C and ambient pressure.

—×—	762 mm Hg	32
—-○—-	330 mm Hg	32
---●---	177 mm Hg	37.5
—--△—--	52 mm Hg	121

The retention volumes of the deuterium pulse measured under reduced pressures are plotted against column temperature in Fig. 1.* The catalyst used in this series of experiments was reduced at 300°C and cooled in hydrogen. It is observed in this figure that, in the temperature range in which the retention volume decreases as temperature increases, the lower the hydrogen pressure, the smaller the retention volume. As described in the preceding paper, the retention volume observed in such a case is equal to the amount of reversible adsorption. Hence the variation of the retention volume with temperature is as expected for general adsorption phenomena. Thus the isosteric heat of adsorption (q_{iso}) can be estimated by the following equation:

$$q_{iso} = RT^2(\partial \ln p/\partial T)_{a_r} \qquad (1)$$

where a_r denotes the amount of that part of the adsorbed hydrogen whose adsorption is rapidly reversible. The values of q_{iso} estimated from the data of Fig. 1 are shown in Table 1.

The tabulated values clearly show that the heats of adsorption are widely different in the two temperature ranges, (I) −195° to −100°C, and (II) −30° to 60°C. The heat of adsorption for Range I is 2.2 ± 0.5 kcal/mole, which is about ten times the heat of liquefaction of hydrogen. This suggests that the adsorption observed in this region is not a simple physical adsorption. This kind of adsorption at low temperature has frequently been referred to as Type C adsorption. The reported values of heat of adsorption for Type C, obtained by static measurements, are around or more than 5 kcal/mole, as tabulated by Bond (*2*). The somewhat lower value found here could be due to the higher surface coverage under the present experimental conditions, as suggested by the procedure in which the catalyst was equilibrated with hydrogen at 300°C and then cooled in a hydrogen atmosphere.

The heat of adsorption in Range II is 13.5 ± 1.5 kcal/mole, which is in agreement with the value obtained by static measurement at a higher coverage (*3*). This agreement means that the adsorption observed by static measurement is rapid and reversible enough to establish an isotopic equilibrium between adsorbed and gas phases above temperature range II.

Another point to be noticed is the reverse effect of pressure on the retention volume in the transition range between Ranges I and II, i.e., the retention volume increases as the hydrogen pressure decreases. This

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* The data shown here are independent of the direction of temperature variation, as described in the previous (*1*) paper.

TABLE 1
HEAT OF ADSORPTION IN TEMPERATURE RANGES I AND II

Temperature range:	I, −195–−100°C			II, −30–60°C		
Isosteric level of adsorption [(STP) cc/g cat.]	8.50	5.80	1.50	8.64	8.50	8.20
Heat of adsorption (kcal/mole)	2.8	1.7	2.6	14	12	15

peculiar effect may be explained as follows: since the catalyst surface is thermodynamically equilibrated with gaseous hydrogen, giving a stationary state of adsorption, the rate of adsorption must be equal to that of desorption. The rate of desorption would be proportional to the hydrogen coverage at the stationary state. However, as suggested by the effect of pressure on the retention volume in Range II,* the coverage is less sensitive to pressure, i.e., a few percent change is caused by the pressure change from 52 to 762 mm Hg. Hence one may expect little effect of pressure on the coverage and thus on the rate of desorption† even in the transition range. On the other hand, the retention volume in the transition range depends on the rate of isotopic equilibration between gaseous deuterium and adsorbed hydrogen, although this is not the case in Range II with a sufficiently fast equilibration. Thus the faster the rate of isotopic equilibration, the larger the part of adsorbed hydrogen to be observed as "reversible" in the transition range. This rate of isotopic equilibration must be determined by the rate of desorption, and thus is hardly dependent on the hydrogen pressure. However, the apparent rate of equilibration, expressed by the time required for the equilibration, must be faster when the hydrogen pressure is lower, because the number of molecules to be equilibrated in a unit volume of the column is proportional to the pressure. Hence when the hydrogen pressure decreases, the temperature at which the retention volume curve reaches the situation of Range II, i.e., a state of sufficiently fast equilibration, would become lower. This means that the reversible part of the adsorbed hydrogen in the transition range apparently increases as the hydrogen pressure decreases.

2. Development of Adsorption Site in the Course of Catalyst Reduction

As shown above, at least two kinds of states were found for the hydrogen adsorbed on the nickel catalyst. It was of interest to see how the adsorption sites come out and develop in the course of catalyst reduction. Thus the variation of deuterium retention with the extent of catalyst reduction was measured at temperatures from −195° to 350°C and is shown in Fig. 2. The degree of reduction was determined by the amount of recovered water caused by the reduction of catalyst, referring to the state reached after 12 hr of reduction at 350°C.

The sample catalyst before reduction did not show deuterium retention at any temperature below room temperature. At a degree of reduction as low as 8.7%, deuterium retention was observed at −195°C. The retention in Range II was first observed at 37% reduction and increased with the extent of reduction to a plateau obtained at 60% reduction.

It is to be noted that an abnormal retention was observed on the measurement above 70°C in the course of reduction. In an extreme case at 37% reduction, no deuterium peak was observed above 70°C. This would be because the deuterium sample was transformed to water and strongly adsorbed on the catalyst. Beyond 60% reduction, the retention volume was observable although the peak shape was very broad, and it decreased with the extent of reduction at any temperature above 70°C. A sudden decrease of the retention volume was noticed between 90% and 97.5% reduction, while no change in the retention was observed for Range II. This change would be due to the higher

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* It has been proved in the previous report (*1*) that the reversibility of adsorbed hydrogen approaches unity in Range II.

† The effect on the activation energy for desorption would also be small.

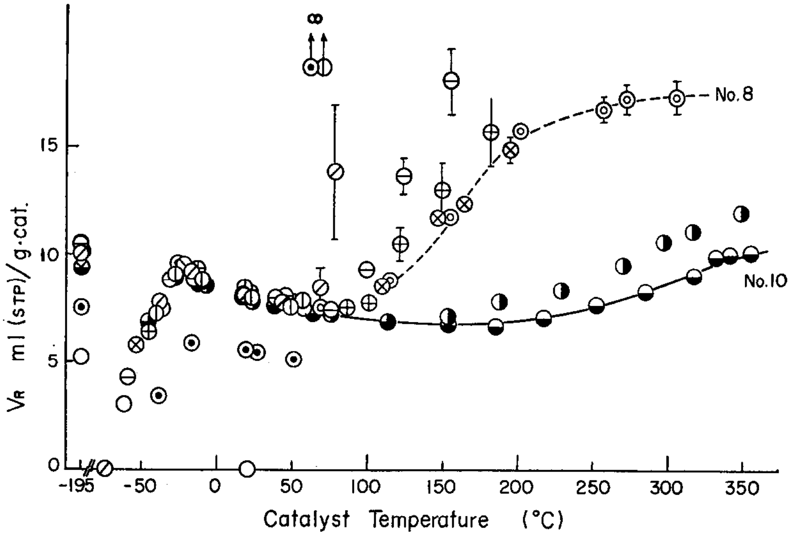

FIG. 2. The variation of deuterium retention with the extent of catalyst reduction at 1 atm.

No.	Key	Reduction temp. (°C)	Time (hrs)	Degree of reduction (%)
1	○	100	1.0	8.7
2	⊙	150	1.0	37.2
3	⦶	200	1.0	60.8
4	∅	250	1.0	69.2
5	⊖	300	1.0	74.3
6	⊕	300	3.1	83.7
7	⊗	300	5.0	88.4
8	◎	300	9.3	90.3
9	◑	350	5.5	97.5
10	◒	350	6.5	100.0

reduction temperature. Line No. 10 in Fig. 2 represents the variation of retention volume with the column temperature for the catalyst fully reduced at 350°C.

In summary, the sites for the reversible adsorption of hydrogen in temperature ranges I and II were developed in the early stage of reduction and were unaffected by further reduction, beyond 60%, while the apparent retention volume above 70°C was significantly affected by the higher reduction. Since the retention volume might result from not only reversible adsorption but also exchange with surface hydrogen such as hydroxyl, and since the lower the reduction, the more the surface hydroxyl, the decrease of retention volume with the reduction could be attributable to the decrease of surface hydroxyl.

3. *Effect of Water Vapor as a Carrier Gas Impurity*

It was observed in a preliminary experiment, in which a rubber tubing was used as a part of the carrier gas line, that the retention volume rapidly increased with column temperature above 50°C to reach a maximum at about 100°C; this increase disappeared from the experiment of Fig. 1, obtained with an all glass system. This anomaly was proved to be caused by the presence of water vapor which diffused into the carrier gas line from the atmosphere through the rubber tube. It would be of interest to see how and why this anomaly takes place. Thus the experiments at 1 atm were carried out with a carrier gas contaminated with water.

The course of the retention volume with

time at 120°C after the addition of 1.1 mm Hg of water vapor to the carrier gas is exemplified in Fig. 3. The catalyst was completely reduced and equilibrated with pure hydrogen prior to the experiments. It is shown in this figure that the presence of water vapor in the carrier gas gradually increased the retention volume of deuterium.

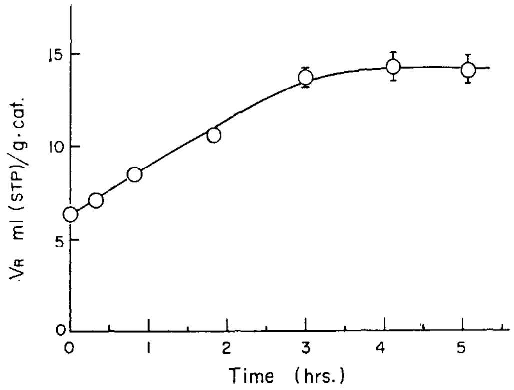

FIG. 3. A variation with time of retention volume at 120°C after the addition of water vapor to the carrier gas.

It took 4 hr to get a stationary state. The stationary values of the retention volume are plotted against column temperature in Fig. 4. The measurements at temperatures lower than −20°C were performed in the pure hydrogen stream after the saturation with water at 50°C because the water vapor was found to condense at the inlet of the column. The water did not affect the retention volume in Range II, i.e., the retention volume was in agreement with that obtained with pure hydrogen carrier, which is denoted as the base line in Fig. 4.

On the other hand, it remarkably increased above 60°C, giving a maximum around 100°C. The peak shape observed at 60°C had a tail that was so big as to make the retention volume meaningless. The broadness of the peaks is shown by vertical bars in Fig. 4. Such a variation in peak shape had been observed in the transition from Range I to II as shown in the previous paper (*1*). Thus it may be supposed that the positive effect of water on the retention volume near 100°C indicates the activation of another state of hydrogen adsorption. However, the retention of the deuterium pulse might have resulted from the exchange reaction with water adsorbed on the nickel catalyst. If the retention was caused exclusively by the exchange, the retention volume should not exceed the amount of adsorbed water, which must be less than the amount of water carried into the column. In the case of Fig. 3, the increase in retention volume due to water addition amounted to 7.7 ml/g or 0.35 mmole/g for the first 3 hr, during which only 0.98 mg/g or 0.055 mmole/g of water was introduced into the column. Thus the larger part of the observed increase in retention volume seems to be due to an increase of the reversible adsorption of hydrogen by added water. However there is another

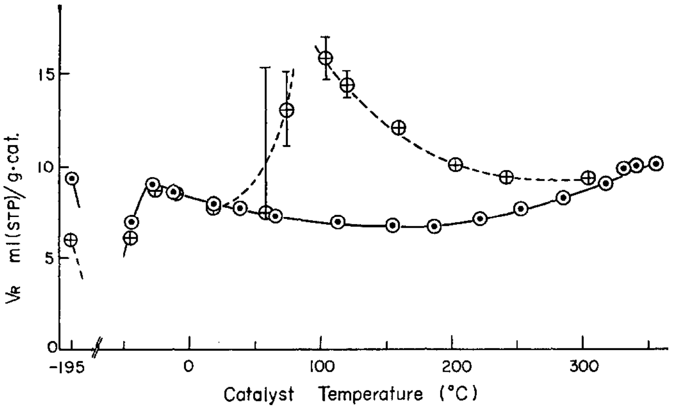

FIG. 4. The retention volume of deuterium in the presence of water vapor: ——⊙——, base line, ——⊕——, 1.1 mmHg H_2O.

interpretation—that the hydrogen exchange takes place with the hydroxyl group of the kieselguhr surface with the aid of added water, i.e., the deuterium pulse first reacts with adsorbed water to give heavy water which successively exchanges its hydrogen with the surface hydroxyl.* In this case the amount of exchangeable hydrogen would be much larger than that of added water. But the amount of surface hydroxyl other than that produced by the added water should be independent of temperature below 350°C at which the catalyst was reduced and thus dried with flowing hydrogen. The observed decrease in the retention volume from 100° to 250°C would again suggest the increase of reversible adsorption of hydrogen by added water. A minor part of the increase would be due to the exchange with adsorbed water.

The negative effect of water observed at −195°C is rather trivial and not so extensive.

Very little effect of water on the reversible adsorption in Range II would be more important in relation to the catalytic activity, and would be consistent with the finding that the reversible adsorption in Range II is more easily developed by reduction.

4. Reversible Adsorption on the Catalyst Cooled in Vacuum

In the experiments described above, the catalyst was always in contact with hydrogen after reduction at 350°C. On the other hand, in conventional static adsorption, the catalyst is to be cooled in vacuum to the adsorption temperature after evacuation at a higher temperature. It has been known that for promoted iron and nickel the strongly chemisorbed hydrogen acts as a poison for hydrogen equilibration (*4*).

In this connection the effect of cooling in vacuum was examined. After evacuation at 300°C for 5 hr, the reduced catalyst was cooled in vacuum down to −195°C, at which the carrier gas hydrogen was admitted to the catalyst column. After that the retention volume was measured at increasing temperatures up to near 300°C, and then at decreasing temperatures.

In another series of experiments, the catalyst was cooled in a nitrogen atmosphere from 300°C to room temperature. The catalyst column was then evacuated at room temperature for 2 hr and the nitrogen replaced by hydrogen, in which the catalyst was cooled to −195°C.

The results obtained in both series of experiments were in agreement with each other, as shown in Fig. 5. It should be noted in this figure that an important difference from the base line is found in the increasing temperature series of experiments, i.e., a little lower value of retention volumes in Range II, while a little higher value in the range from 60° to 250°C, revealing as a whole a new maximum of retention volume. This maximum disappeared in the decreasing temperature series in which the retention volumes agreed with the base line. Hence disappearance of the new maximum should be due to the hydrogen adsorbed at higher temperature. This adsorbed hydrogen might be dissolved hydrogen. In any case, the hydrogen taken up at 300°C seems to cause the decrease in the amount of reversible adsorption in the temperature range 70° to 250°C.

Another point of the results to be noted is the temperature range in which the promotion of reversible adsorption was observed for the catalyst cooled in vacuum. This temperature range coincides with that in which the promotion of retention volume by water vapor was observed. This suggests the presence of a third type of reversible adsorption besides the first and second ones which are characterized by the temperature ranges I and II, respectively. This would correspond to the three states of hydrogen adsorption on Ni found by Suhrmann *et al.* (*5*). The promoting action of water would be to reduce the work function of the nickel surface which is favorable for the H^- or $H\cdot$ type of adsorption. On the other hand the strongly chemisorbed hydrogen would fix the catalyst electron, resulting in an increase in the work function. Its negative effect on the third type would be reasonable on this ground.

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* A direct exchange between deuterium and hydroxyl would need a higher temperature, as shown by Hall *et al.* (*7*).

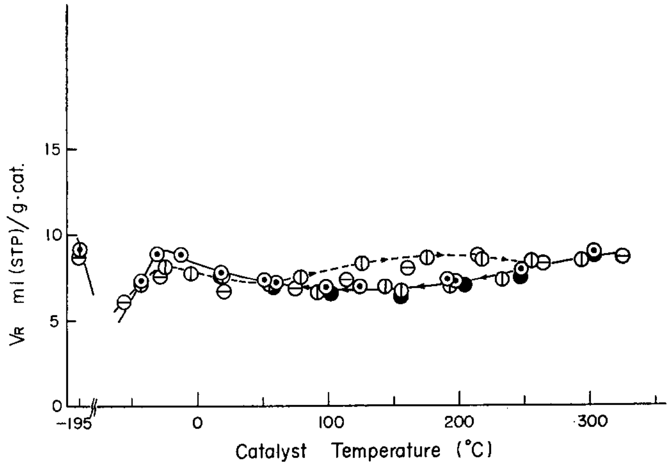

FIG. 5. The retention volume by the catalyst cooled in vacuum: ⊙ ●, base line (before and after the measurement, respectively), ⦶, cooled in vacuum, ⊖, cooled in nitrogen.

5. *The Effects on the Catalytic Activity*

It would be most important to examine the correlation between the catalytic activity and the type of adsorption characterized by reversible adsorption. The variation of exchange activity in the course of catalyst reduction was as follows:

% Reduction:	8.7	37.2	60.8	74.3	83.7	88.4
% HD in effluent pulse at −195°C	0	18.5	51.5	84.6	100	100

While the reversible adsorption at −195°C was already observed at 8.7% reduction and attained a plateau value at 60% reduction, the exchange reaction was likely to require a higher degree of reduction, as indicated by this result.

The catalytic activity in the hydrogenation of ethylene was examined by a pulse flow technique in the course of catalyst reduction. At 8.7% reduction, the conversion of ethylene to ethane at 20°C was negligible whereas it was 100% at 37.2% and above. This suggests that the activity in hydrogenation at room temperature is related with the reversible adsorption in Range II because they are both developed in an early stage of reduction. Since the reversible adsorption in Range I was also developed in an early stage of reduction, the activation of catalyst by reduction would be common for the reversible adsorption and for the catalytic activity. However the active site for the exchange reaction at −195°C seems to be outside the scope of the present technique of adsorption, because the site might be heterogeneous and of very low concentration over the surface, as indicated by Gundry's work (*6*).

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