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Effect of Ion Bombardment on Adsorption and Exchange Reaction of Hydrogen by Evaporated Nickel Films

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The effect of an activating treatment of evaporated films of nickel has been investigated by hydrogen adsorption and hydrogen–deuterium equilibration reaction in the pressure range 10^{-6}–10^{-3} Torr at room temperature. Adsorbed hydrogen can be divided into reversible and irreversible parts. The former can be removed easily by pumping at near room temperature, while the latter cannot. A Freundlich isotherm fits the reversible adsorption data while the irreversible adsorption is best described by a Langmuir isotherm (with dissociation). Argon ion bombardment gave drastic increase in hydrogen adsorption, although the surface area of the nickel film measured by xenon adsorption showed no change with either ion bombardment or annealing. The rate of equilibration was found to obey the rate law, $V = kP^{1.3}$ after either ion bombardment and annealing (the values of k were exactly the same on both the films). It is concluded that the rate of the equilibration is controlled by the reaction step, $2\ \mathrm{H(a)}_{\mathrm{irr}} + \mathrm{D_2(a)}_{\mathrm{rev}} = 2\ \mathrm{HD}$, and that only a small part of the dissociative hydrogen which is irreversibly adsorbed appears effective in the equilibration reaction near room temperature. It is also concluded that on these particular sites, there are no effects of bombardment or annealing on the overall rate of the equilibration near room temperature.

INTRODUCTION

Ever since the observation by Eckell (*1*) that catalytic activity of nickel for ethylene hydrogenation was greatly increased by cold-rolling, this phenomenon [which following Duell and Robertson (*7*) will be denoted here as "super activity"] has been studied by many investigators. Some investigators have found similar results (*2–9*) while others have found conflicting results (*10–12*). This kind of increase has been frequently found by such treatments as cold-working, ion bombardment, and quenching from higher temperature. All the treatments mentioned above are well known as methods of introducing defects into crystals. Then catalytic super activity has been considered to be due to the excess defects, following Taylor (*13*) and Cratty and Granato (*14*). Investigation has shown that (a) the increase in frequency factor is about the same order as that of the defect concentration introduced by the treatment mentioned above (*8*), (b) the kinetics of disappearance of super activity by annealing is very similar to the process of annealing out excess defects (*5–7*) and (c) there exists a direct relation between the disappearance of defects and the sudden decrease of super activity (*2–4*). From these results they concluded that the defects act as "super active sites" in catalysis. This conclusion, however, might not be deduced so straightforwardly, because the work was done under relatively poor vacuum conditions (probably above 1 × 10^{-6} Torr) and consequently it is very possible that most of the surface sites were covered by adsorbed residual gases before the measurements were carried out. It is then also possible to interpret the phenomena as a decrease in the degree of contamination, due to the pretreatments mentioned above, and an increase due to the annealing. In order to avoid this ambiguity we have used an evaporated film, which enables us to measure precisely the surface area, the number of sites for adsorption of reactants, and the rate of catalytic reaction on the same sample. If excess defects act as "super active sites" for catalysis, the catalytic activity should be increased by the pretreatments mentioned above. The increase of adsorption sites, however, might not be detected because the concentration of excess defects might not exceed a few percent. This value is within the experimental error of the measurements. On the other hand, when contamination plays a predominant role, the increase in catalytic activity would correspond to a measurable increase in the number of adsorption sites.

In this paper, we describe the effects of argon ion bombardment of clean nickel films on the adsorption of hydrogen and on the rate of the hydrogen–deuterium equilibration reaction and discuss a plausible explanation of them.

EXPERIMENTAL METHODS

Apparatus and Materials

The apparatus for the adsorption measurements was constructed with Pyrex glass and bakable metal valves. A characteristic feature of the apparatus is that it had two pressure measuring parts, each with a precise pressure gauge, and a variable leak valve between them. One part was used for storage and dosing of the adsorbate, and other for measuring the amount of residual adsorbate which was not adsorbed on a sample. The latter part which was denoted as adsorption chamber was capable of being evacuated to 1×10^{-8} Torr by means of a sputter ion pump. An arbitrary amount of the adsorbate could be admitted by controlling the variable leak valve. The hydrogen pressure in the range of 5×10^{-7}–5×10^{-3} Torr could be measured precisely by using a sensitive Pirani gauge. The details of both the apparatus and the Pirani gauge have been described previously (*15*, *16*).

Figure 1 shows the apparatus used for measuring the rate of equilibration. It

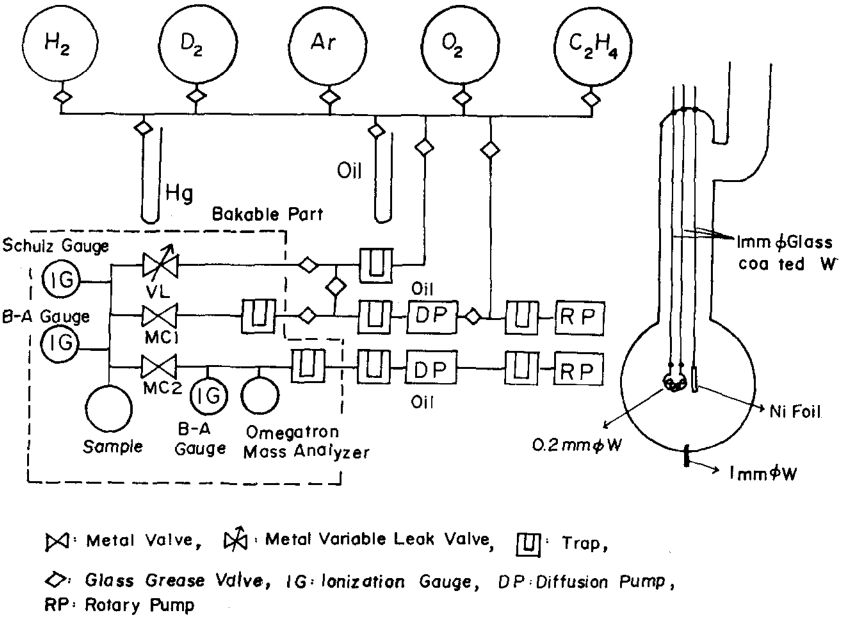

FIG. 1. Block diagram of apparatus.

could be evacuated to 2×10^{-8} Torr by means of an oil diffusion pump with a liquid nitrogen trap and an additional trap consisted of molecular sieves and a titanium getter. The partial pressure of each component in the reaction mixture was determined by an omegatron mass spectrometer. The variable leak valve was used to introduce the mixture at a constant leak rate into the omegatron. A nickel foil for the source of evaporation was prepared by rolling a piece of nickel block of 99.95% purity. The major impurities were Si (0.013%), Fe (0.006%) and a trace amount of Mg. The high purity gases in glass ampoules were supplied from Takachiho Chemicals Ltd., guaranteed as 99.95% for hydrogen, 99.999% for argon and 99.9% for xenon. Argon and xenon were distilled at liquid nitrogen temperature *in vacuo* before use and hydrogen was passed through a liquid nitrogen trap.

Procedure

The nickel foil (80 mg) as the evaporation source was heated by electron bombardment using a tungsten filament. The filament was first rigorously outgassed by electrical resistance heating and the foil was outgassed by slight electron bombardment. Subsequently, nickel was evaporated by increasing the current. No special provision was made for cooling the wall. The residual pressure increased to 5×10^{-6} Torr initially, then decreased quickly and remained at about 1×10^{-7} Torr through the evaporation period of 2 or 3 min. Immediately after the evaporation, the film was annealed at 350°C for several hours until the residual pressure at this temperature decreased to 3×10^{-7} Torr. The films were estimated to be 3–5 μm thick. It was found that three annealing treatments (1 hr each at 450°C) after evaporation were sufficient to give a reproducible surface area measured by xenon adsorption. Before the measurement of adsorption and catalysis, the films were either ion-bombarded with argon with no subsequent annealing or annealed for 1 hr at 450°C following the ion bombardment. A glow discharge of argon at 7×10^{-2} Torr was applied for ion bombardment, with 500 V and 12 mA maintained for 5 min between the filament and film. The measurements of adsorption and activity were begun after the residual pressure had decreased to below 2×10^{-8} Torr. The surface areas of both the bombarded and the annealed films were determined by xenon adsorption (*16*).

The reaction rate of the equilibration was measured in a gas-flow system. The initial mixture consisting of approximately equal parts of hydrogen and deuterium was stored behind MC I in Fig. 1 at 5–20 Torr. A constant flow of the mixture into the reaction vessel was established through the variable leak valve. By properly adjusting this valve as well as MC I and MC II, the pumping speed could be varied while the pressure was kept constant. Thus the time factor ($1/SP$) could be changed under conditions of constant pressure and the rate V of the equilibration reaction could be evaluated from the following equation,

$$Vt = -\ln (X_e - X) + C, \qquad (1)$$

$$X = \frac{P_{\mathrm{HD}}}{P_{\mathrm{H_2}} + P_{\mathrm{D_2}} + P_{\mathrm{HD}}},$$

t	$1/SP$ (sec/Torr · liter)
X_e	equilibrium concentration
S	pumping speed (liters/sec)
C	constant
V	rate of equilibration (Torr · liters/sec)

The concentration X was measured at a constant total pressure of 5×10^{-7} Torr in the omegatron. The equilibrium concentration X_e was measured by taking the time factor at least 20 times greater than the one used for measuring the rate. As the omegatron had a background peak of $M/e = 3$ when only hydrogen or deuterium was introduced, it was carefully calibrated for both hydrogen and deuterium at least once a week.

Results

The surface area measurements determined that the roughness factor of a film was about 13 immediately after evaporation. This was decreased to about half the value by annealing at 450°C for 1 hr and an additional annealing resulted in a

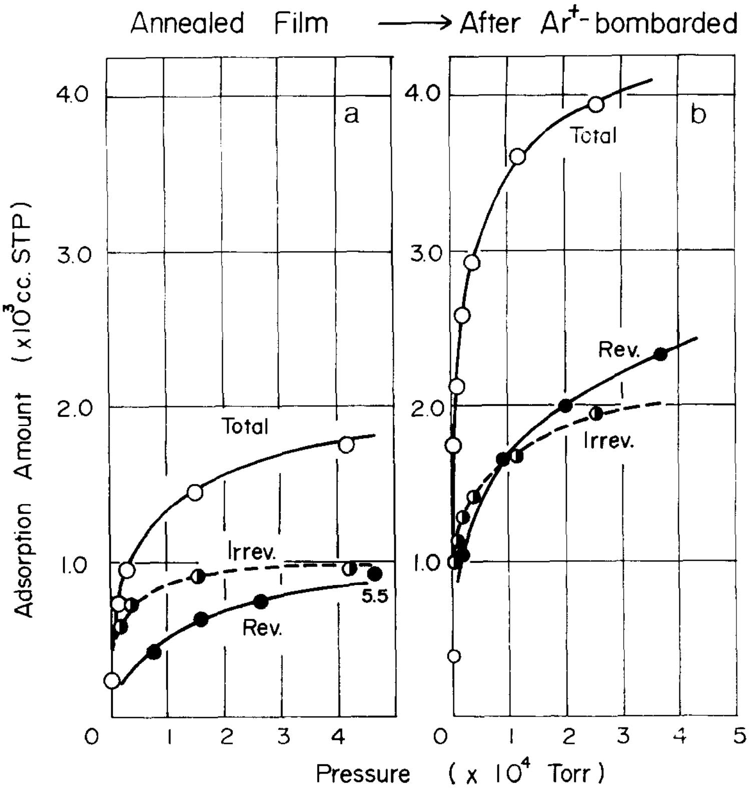

FIG. 2. Adsorption isotherms of hydrogen at 23.5°C. (a) Annealed film; (b) bombarded film.

nearly constant value of the roughness factor (about 3 to 4), which showed no more decrease with further annealing. In spite of the high annealing temperature in this work, the ultimate roughness factor was still somewhat high. This is probably due to the relatively high roughness of the glass substrate used in the present work (*17*).

Figure 2a shows the adsorption isotherm of hydrogen at 23.5°C on an annealed film. The upper line was obtained by dosing hydrogen on a bare surface and the lower solid line by dosing the same surface (following evacuation to 3×10^{-7} Torr) subsequently after measuring the last point on the upper isotherm. Almost the same pattern was obtained on the bombarded film (Fig. 2b), but in this case the amount of adsorption was approximately twice that of the annealed film. Adsorption on glass walls was found to be negligibly small (about 5×10^{-5} ccSTP at 6×10^{-4} Torr).

The adsorption from the second dose indicates clearly that there is weakly adsorbed hydrogen on the surface which can be readily pumped off at the given temperature. This is denoted here as "reversible adsorption." The difference between the amounts of adsorption in the two doses is due to another type of adsorbed hydrogen which is bound to the surface more tightly and cannot be pumped away easily. This second type of adsorption is denoted here as "irreversible adsorption." From Fig. 2a and b, it can be seen that ion bombardment increases both types of adsorption. It should be mentioned that the films of 2a and b had virtually the same surface areas (436 and 464 cm^2, respectively) in spite of the different treatments. In general, the surface areas of the films were not changed by ion bombardment and annealing.

Figure 3a shows Langmuir plots for the irreversible adsorption data in Fig. 2. The linearity is good on both the annealed and

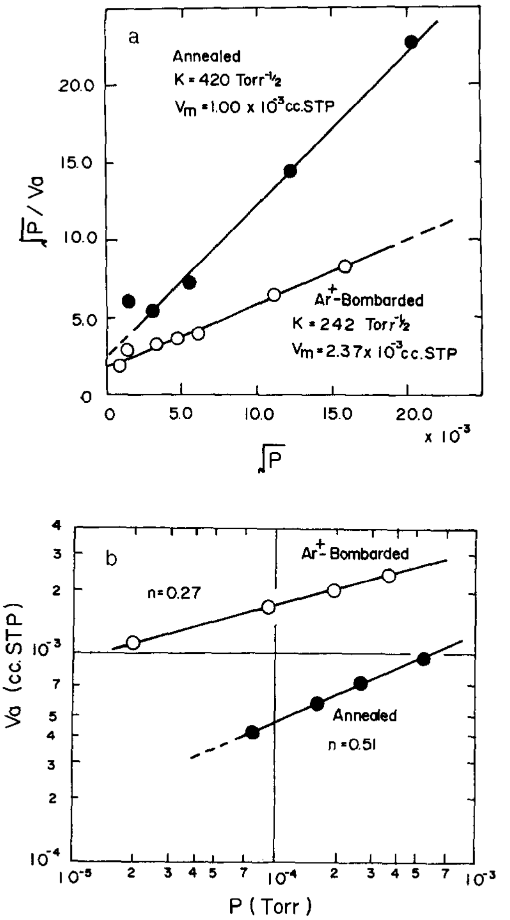

FIG. 3. (a) Langmuir plots for the irreversible adsorption of hydrogen. (b) Freundlich plots for the reversible adsorption of hydrogen.

the bombarded films. The monolayer capacity for the irreversible adsorption was increased about 2.4 times by the bombardment. The equilibrium constant for the irreversible adsorption was $242/(\mathrm{Torr})^{1/2}$ for the bombarded film and $420/(\mathrm{Torr})^{1/2}$ for the annealed film. Figure 3b shows the Freundlich plots for the reversible adsorption shown in Fig. 2. It can be seen that the reversible adsorption data fit the Freundlich equation well.

Sample plots of the H_2–D_2 equilibration data are shown in Fig. 4. The rates calculated from these data are linear when plotted against the total pressure on a full logarithmic scale as shown in Fig. 5. The straight line indicates that the pressure dependence of the rate is $V = kP^{1.3}$. In contrast to its effect on the adsorption, ion bombardment apparently had no effect on the rate of equilibration near room temperature.

DISCUSSION

It was found that the roughness factors of the well annealed films were about 3 to 4 which were not changed either by ion bombardment or additional annealing, although the roughness factors of freshly deposited films were about 10 or more, indicating that the films were extremely porous immediately after the deposition. Thus it is concluded that the relatively mild ion bombardment (500 V, 27 μA/cm^2) does not change the pore structure of the well annealed films. On the other hand, the measurements of hydrogen adsorption showed enhanced adsorption on the bombarded films. In the present work, the monolayer capacity of hydrogen was 1.2–3.0 × 10^{14} molecules/cm^2 on the annealed films and 3.0–5.0 × 10^{14} molecules/cm^2 on the bombarded films at 25°C. These values were calculated from the extrapolated saturation values of the isotherms of hydrogen at 25°C and surface areas obtained by xenon adsorption. As the isotherms of hydrogen obtained by descending equilibrium pressures coincided fairly well with those obtained by ascending pressures, it is concluded that there is a negligibly small absorption of hydrogen into the films in the present study. Although the monolayer capacities of both films agree fairly well with those reported by several authors (*18–20*), the values on the bombarded films were about twice those of the annealed films. The lower values on the latter would be due to the enhanced contaminations introduced by annealing (*21*, *22*).

In contrast to the adsorption results, the rate of H_2–D_2 equilibration was unaltered by either bombardment or annealing. The rate in either case is given by the equation $V = kP^{1.3}$, indicating no change in either the catalytic activity or the reaction mechanism. It is concluded that excess defects induced by the bombardment play no significant role in the catalytic reaction. The

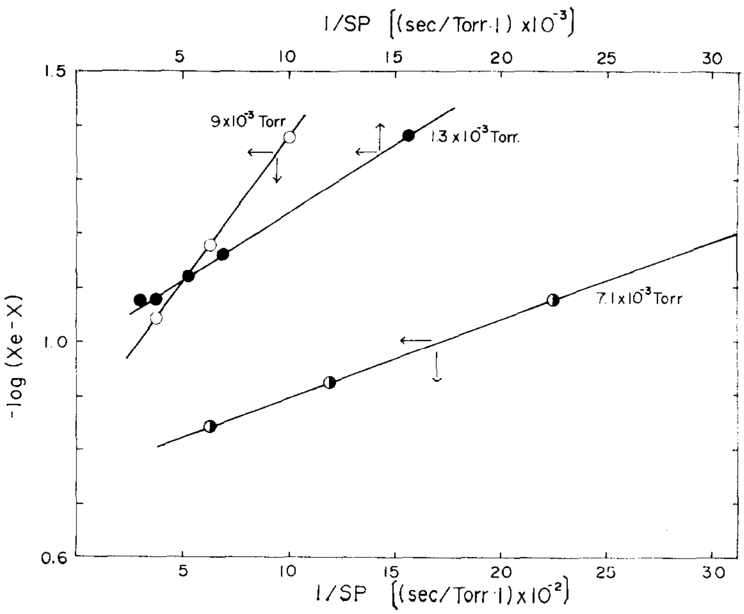

FIG. 4. Examples of kinetic data for H_2–D_2 equilibration by means of omegatron mass spectrometer.

results of adsorption and catalysis might indicate that there is no proportional relation between the number of adsorption sites and the catalytic activity and that a relatively small fraction of the adsorption sites are effective on the catalysis.

In light of the results of adsorption, the rate expression can be valid for only two mechanisms:

$$H_2(a)_{rev} + D_2(g) = 2HD, \qquad (2)$$

$$V = k'(kP^{0.3})P,$$

$$2H(a)_{irr} + D_2(a)_{rev} = 2HD, \qquad (3)$$

$$V = k'\left(\frac{KP^{1/2}}{1 + KP^{1/2}}\right)^2 kP^{0.3}.$$

In mechanism (2), the rate expression has the exact form of $V = kP^{1.3}$. In mechanism (3), however, it is an approximation for the low pressure region only; it is not applicable above 10^{-5} or 10^{-4} Torr, if the equilibrium constants of irreversible adsorption are taken as $4 \times 10^2/(\text{Torr})^{1/2}$ and $2 \times 10^2/(\text{Torr})^{1/2}$ (the values obtained from the adsorption measurement on annealed films and bombarded films, respectively). The experimental results, however, show fairly good linearity in the 10^{-3} Torr range for log V vs log P plots. This might indicate that only a small part of the irreversibly adsorbed hydrogen could be actually associated with the equilibration reaction near room temperature.

In order to find the mechanism, we measured the reactivity of the irreversibly ad-

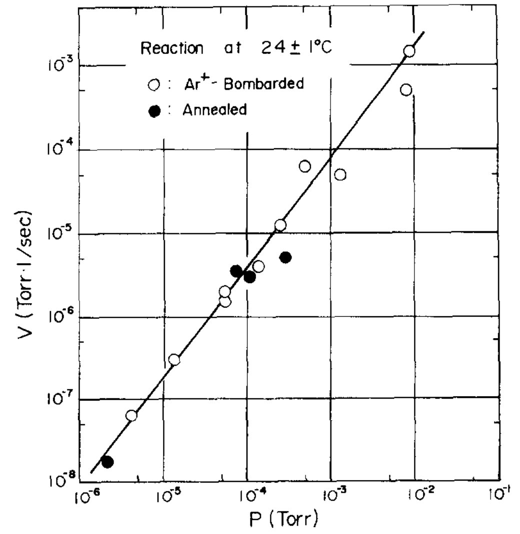

FIG. 5. Catalytic activity of nickel films as a function of reaction pressure.

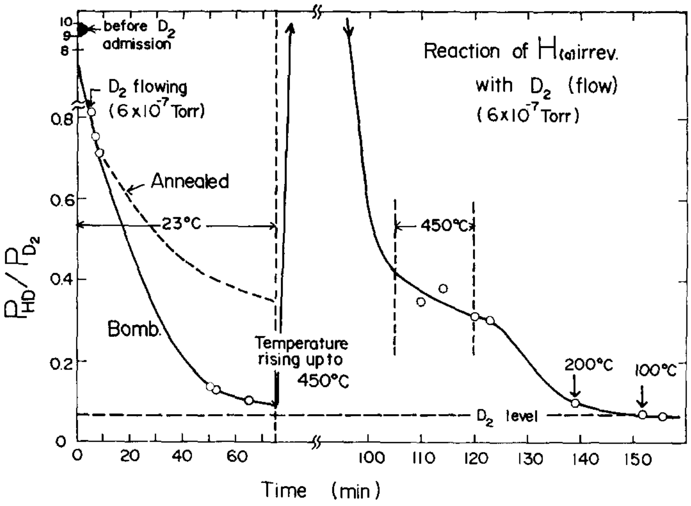

FIG. 6. Reaction process of the irreversibly adsorbed hydrogen $H(a)_{irr}$ with deuterium.

sorbed hydrogen as follows; the film was exposed to hydrogen at about 1 Torr for 1 hr at 25.0°C, the adsorption chamber was then evacuated to 3×10^{-7} Torr at the same temperature and deuterium was passed continuously over the film at a constant pressure of 6×10^{-7} Torr. Mechanism (2) predicts that there will be no HD formation by this procedure, while mechanism (3) predicts there will be appreciable HD formation. The results on a bombarded film are shown in Fig. 6. HD formation was found and the ratio of HD/D_2 in the mass spectra decreased with the reaction time, approaching the ratio for pure D_2. However, when the film temperature was raised, a large amount of HD was again observed, even at 450°C. Almost the same results were obtained on the annealed film.

For an annealed film, the approximate expression $V = kP^{1.3}$ is also applicable at 10^{-6}–10^{-4} Torr. The reason could be that the equilibrium constant of the irreversibly adsorbed hydrogen effective in catalysis is about $20/(\text{Torr})^{1/2}$ on the annealed films, (on the bombarded films it is calculated to be the order of $1/(\text{Torr})^{1/2}$) and then the approximation of

$$\left(\frac{KP^{1/2}}{1 + KP^{1/2}}\right)^2 = k''P^{0.8}$$

is valid in the stated pressure range. From the assumption above, we can obtain the approximate expression $V = kP^{1.3}$ for the annealed films.

It can be concluded that the reaction proceeds by mechanism (3) on both films. In addition, it is clear that only a small part of the irreversibly adsorbed hydrogen is involved in the equilibration reaction near room temperature. This coincides well with the results shown in Fig. 5, and the proposal of Gasser, Robert and Stevens (*20*).

SUMMARY

The treatment with argon ion bombardment was found to change the extent of hydrogen adsorption at 25°C on evaporated nickel films, that is, it resulted in an increase in the amount of adsorption, a decrease in the equilibrium constant of irreversible adsorption, and a decrease in the pressure exponent of reversible adsorption. In contrast to the adsorption results, no changes were found in the rate of the equilibration reaction, which has the rate expression of $V = kP^{1.3}$ on both the annealed films and the bombarded films. It was found that the exact expression is considered to be $k'[KP^{1/2}/(1 + KP^{1/2})]^2kP^n$ where $n = 0.3$ on the bombarded films and

$n = 0.5$ on the annealed films. The equilibration reaction proceeds by interaction between the irreversibly adsorbed dissociative hydrogen and the reversibly adsorbed molecular hydrogen as $2H(a)_{irr} + D_2(a) = 2HD$. It was also found that only a small fraction of irreversibly adsorbed hydrogen is involved in the equilibration reaction near room temperature and there is no direct relation between the adsorption of hydrogen and the rate of the equilibration reaction. On these particular sites, no effects were found from bombardment and annealing on the overall rate of equilibration near room temperature.

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