August, 1980] © *1980 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *53*, *2123—2127 (1980)* 2123

Thermal Desorption of Hydrogen Adsorbed on Copper Surface

Isao Kojima,* Makoto Kiyomiya, and Iwao Yasumori
Department of Chemistry, Tokyo Institute of Technology, Meguro-ku, O-okayama, Tokyo 152

(Received October 6, 1979)

The thermal desorption of hydrogen adsorbed on a clean surface of polycrystalline copper foil was studied under ultra high vacuum conditions. The presence of chemisorbed hydrogen in a dissociated state was verified in a temperature range between 193 and 573 K. During the desorption process, the adsorbed hydrogen atoms recombined into molecules; this follows second order kinetics. The activation energy for desorption was 68.6 ± 8.0 kJ mol^{-1} and remained nearly constant in the range of surface coverage up to 1.6×10^{14} atom cm^{-2}. The isotope effect on the desorption of deuterium was found to be straightforward. These findings showed a good agreement with the results obtained from the analysis of H_2–D_2 equilibration on copper powder catalyst. In addition, the necessary conditions to obtain the exact desorption spectra were inspected with the aid of computer simulation.

Studies on the elementary processes of adsorption and desorption are important in understanding the catalytic reaction on solid surfaces. Although there have been many investigations of the adsorption of hydrogen on copper surfaces,[1–7)] the mechanism has not been well established. An activated process for adsorption is the consensus in most of reports,[2,5,6)] but they do not give concordant values for the activation energy and the heat of adsorption.

In our previous study,[8)] it was shown that H_2–D_2 equilibration on reduced copper powder can be interpreted in terms of the Bonhoeffer-Farkas mechanism, which involves the dissociative adsorption of hydrogen and the surface recombination of adsorbed hydrogen atoms in the reaction pathway. From the analysis of the reaction time course, kinetic parameters of adsorption and desorption were evaluated. In a subsequent work,[9)] these results were found to accord well with those of the classical trajectory calculations for the dissociative adsorption on a model (100) copper surface.

Thermal desorption (TD) gives direct information on the adsorbed states, the fraction of coverage, and the kinetics of desorption. A TD measurement, using a conventional high vacuum system, was applied to the hydrogen adsorbed on copper powder and the formation of HD together with H_2 and D_2 was successfully observed by heating the surface covered with hydrogen and deuterium. The estimated value for the activation energy of desorption was, however, about a half of that obtained from the analysis of the reaction kinetics.[10)] Accordingly, the present study aimed to solve this contradiction between these experimental results and, further, to make clear the adsorbed state of hydrogen on a copper surface. To attain this purpose, we paid special attention to finding the optimum situation for pursuing the desorption process and designed a desorption system which is operated with high pumping speed in the range of ultra high vacuum (UHV). The desorption spectra obtained by using the system were analyzed in detail. The adsorbed state of hydrogen, the activation energy of desorption, and its dependence on the coverage of adsorbed hydrogen were determined, and the isotope effect on desorption was also inspected. Further, the obtained results were compared with those derived from the study of H_2–D_2 equilibration on copper catalyst.

Experimental

A schematic representation of the apparatus employed is shown in Fig. 1. The experiments were performed in a pyrex glass UHV system. The adsorption–desorption system with a volume of 410 cm^3 consisted of a desorption cell, a pressure gauge, a greaseless glass valve, and an ion getter pump. A 3-stage mercury diffusion pump was connected to the system through a liquid nitrogen cold trap and a bakeable metal valve and used for initial pumpdown to about 10^{-6} Torr (1 Torr= 133.3 Pa). After the bakeout of the system at 530 K for 24 h, a vacuum of about 5×10^{-10} Torr was readily attained by using the ion getter pump.

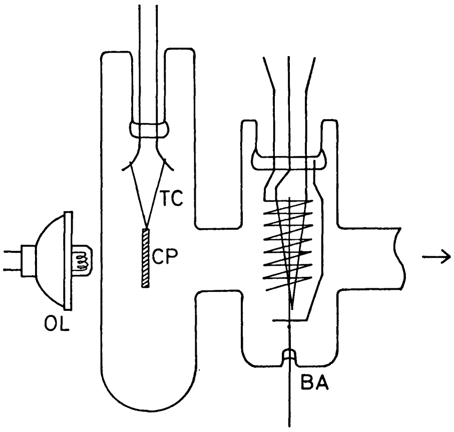

Fig. 1. A schematic representation of desorption system. BA: Bayard-Alpert gauge, CP: copper plate, OL: halogen lamp, TC: Pt–Pt/Rh13% thermocouple.

The desorption spectra were recorded by means of a Bayard-Alpert gauge, through which the desorbed gas was evacuated. This allowed us to measure directly the density of desorbed molecules related to the desorption rate. A polycrystalline plate of copper with a surface area of 4.2 cm^2 was used as the adsorbent. The sample was spot-welded to the junction point of Pt–Pt/Rh13% thermocouple wire, 0.05 mm in diameter, and was hung down in the desorption cell by the wire so as to minimize the temperature fluctuation and the desorption from the thermocouple. The sample after the bakeout was reduced in a flow of hydrogen of pressures between 10^{-3}—10^{-4} Torr at 570—670 K for 48 h and then outgassed at 773 K until no further gas evolution could be detected. The surface cleanliness was judged by the reproducibility of measurements after the reduction-outgas cycle. The surface with a constant activity could then be obtained by reducing and outgassing several times at 773 K *in vacuo* better than 5×10^{-10} Torr. To avoid the wall effect, the sample was heated directly by infrared irradiation supplied from a halogen reflector lamp, Osram Model 15V 150W. The infrared light beam was dispersed on the copper plate. The heating rate was adjusted in a range 0.2—4 K s^{-1} using a constant-current power supply. Hydrogen pressures measured by the ion gauge were calibrated with nitrogen of equivalent pressures using the published value of the sensitivity ratio, $S_{H2}/S_{N2}=0.44$.[11] After the copper surface was exposed to hydrogen of 1×10^{-5}—1×10^{-8} Torr for 45 minutes at room temperature and was evacuated to 5—10×10^{-10} Torr at 193 K, the surface temperature was raised linearly with time up to 570 K.

Results

Since the detailed discussions on the basis for determining kinetic parameters from desorption spectra have already been given,[12,13] only the salient features will be outlined here.

An accurate knowledge of the effective pumping speed is necessary to determine the absolute values of kinetic parameters for desorption. From the following procedure, the pumping speed, S ($cm^3\ s^{-1}$), was determined for hydrogen. The mass balance of gases present in a vacuum system requires the following equation to hold:

$$V\frac{dP}{dt} = Q - S\Delta P \tag{1}$$

$$\text{and}\quad \Delta P = P - P_0,$$

where P and P_0 are the operating and background pressures in the system, respectively, V is the volume of the system, and Q is the external influx of gases (in Torr $cm^{-3}\ s^{-1}$). Accordingly, by introducing hydrogen gas into the closed vacuum system at a constant rate, the influx was evaluated from the increasing rate of pressure:

$$Q = V\frac{dP}{dt}. \tag{2}$$

Then the system was evacuated and after the pressure attained an equilibrium value, P_{eq}, S was determined by using the relation

$$S = (P_{eq} - P_0)/Q. \tag{3}$$

From the measurements stated above, S was evaluated to be $2.3\times10^3\ cm^3\ s^{-1}$ in a pressure range between 10^{-8} and 10^{-6} Torr.

Figure 2 illustrates the typical desorption spectra of hydrogen and deuterium adsorbed at the same fraction of coverage on a surface. Only one peak was observed in each spectrum; the peak of D_2 appeared at the temperature higher than that of H_2 by about 10 K. The temperature at peak maximum shifted to the lower temperature side with increased amount of adsorption under a constant rate of temperature increase and showed the same trend of shift with a decrease of the rate of temperature rise under a constant amount of adsorption. The increase of surface coverage, for example from 1.4×10^{13} to 2.0×10^{14} atom cm^{-2} of hydrogen, shifted the peak maximum from 355 to 327 K at the rate of temperature rise of 1.2 K s^{-1}, and the increase in the rate from 0.17 to 3.2 K s^{-1} brought about the increase in the peak temperature from 330 to 368 K at the constant coverage of 1.8×10^{13} H-atom cm^{-2}.

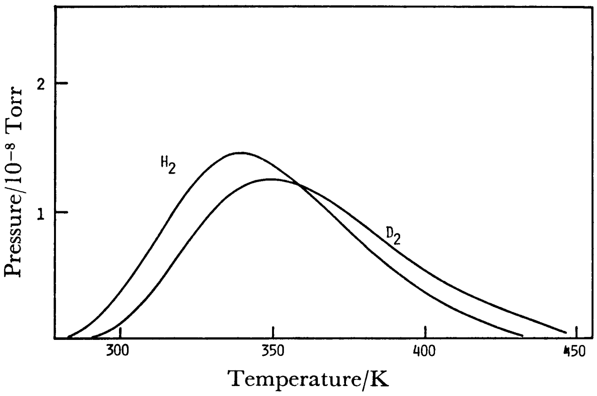

Fig. 2. Thermal desorption spectra of hydrogen and deuterium on copper surface.

Mass balance during the desorption requires that Q in Eq. 1 is replaced by the rate of desorption from the surface:

$$V\frac{dP}{dt} = \frac{A}{C}\frac{dN}{dt} - S\Delta P, \tag{4}$$

where N is the number of desorbing molecules per unit area, A is the surface area and, C is a conversion factor in a unit of molecule K $Torr^{-1}\ cm^{-3}$, which is equal to 3.2×10^{16} at 300 K. In the normal UHV system with large pumping speed, the ratio V/S is negligibly small and therefore the desorption rate becomes approximately proportional to the pressure increase:

$$\frac{dN}{dt} = \frac{C}{A}S\Delta P. \tag{5}$$

The amount of adsorbed hydrogen, N_0 (molecule cm^{-2}) is given by

$$N_0 = \frac{CS}{A}\int_0^\infty \Delta P\, dt. \tag{6}$$

The value of the integral in the right hand side of Eq. 6 is proportional to the area of the desorption peak.

The desorption rate per unit surface area is expressed as

$$R_d = \frac{dN}{dt} = \nu \exp(-E_d/RT)n^x, \tag{7}$$

where ν is the pre-exponential factor, E_d is the activation energy of desorption, n is the number of adsorbed atoms per unit area, and x is the reaction order with respect to the adsorbed species. The desorption was operated in a linear temperature rise with time, *i.e.*, $T=T_0+\beta t$, where β is a coefficient of temperature rise. The differentiation of Eq. 7 with temperature shows that the temperature, T_m, at which the desorption spectrum gives a peak maximum can be correlated with the factors ν, E_d, β, and x by the following equation:

$$E_d/RT_m^2 = (x\, n_m^{x-1}\nu/\beta)\exp(-E_d/RT_m) \tag{8}$$

where n_m is the number of adsorbed particles remaining at T_m. Then, it is found that

$$\log(T_m^2/\beta) = \frac{E_d}{2.303\,RT_m} + \log\frac{E_d}{R\nu x n_m^{x-1}}. \tag{9}$$

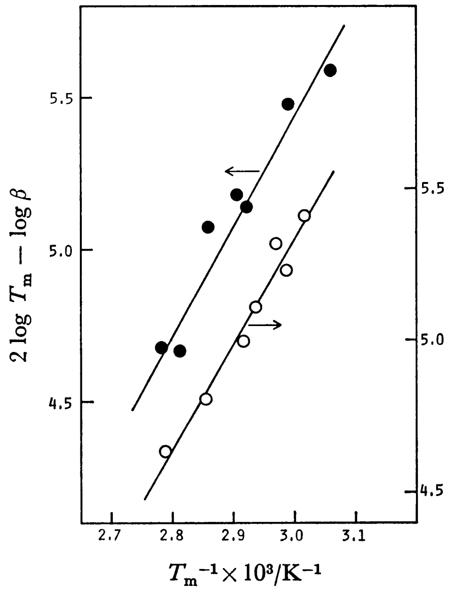

Fig. 3. Plots of ($2 \log T_m - \log \beta$) *vs.* T_m^{-1}.
○: H_2, ●: D_2.

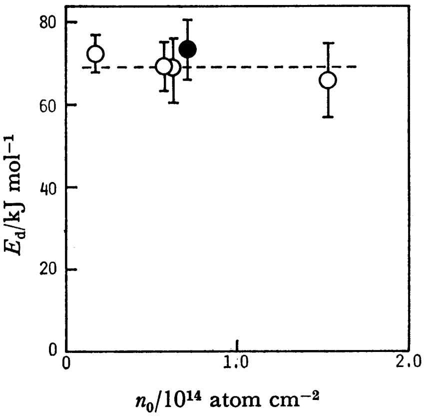

Fig. 4. Invariance of activation energy of desorption with surface concentration.
○: H_2, ●: D_2.

For a constant initial coverage, E_d and n_m would be unchanged even if β is varied. A plot of log (T_m^2/β) *versus* $1/T_m$ gives a straight line with slope of $E_d/2.303\,R$. This relationship is shown in Fig. 3 for adsorbed hydrogen and deuterium at the initial coverages of $6.4 \pm 0.2 \times 10^{13}$ H-atom cm^{-2} and $7.2 \pm 0.3 \times 10^{13}$ D-atom cm^{-2}, respectively. Figure 4 summarizes the activation energy of desorption as a function of the amount of desorption: Values of E_d for H_2, as shown by open circles, were constant at 68.6 ± 8.0 kJ mol^{-1} up to a surface concentration of 1.6×10^{14} atom cm^{-2}. The filled circle in Fig. 4 shows the activation energy of desorption for D_2. The obtained value of the energy was 73.6 ± 8.0 kJ mol^{-1}, which is slightly greater than that for H_2.

When the thermal desorption is carried out at constant β, the shifts of T_m shown in Fig. 2 lead to the determination of reaction order. Equation 8 can be rearranged to

$$2 \log T_m - \frac{E_d}{2.303\,RT_m} = (1-x) \log n_m + \log \frac{\beta E_d}{x\nu R}. \quad (10)$$

Because E_d is constant with coverage, as seen from Fig. 4, a plot of ($2 \log T_m - E_d/2.303\,RT_m$) *versus* log n_m gives a straight line with a slope of $1-x$, where n_m is given by

$$n_m = \frac{CS}{A}\int_{t(T_m)}^{\infty} \Delta P\,dt. \quad (11)$$

The results are shown in Fig. 5. From the slope, the desorption order , x was evaluated to be 2.0 ± 0.2.

The values of E_d and x permitted us to calculate the frequency factor of desorption from the intercept of Fig. 2. This value of ν was found to be $1.0 \pm 0.5 \times 10^{-4}$.

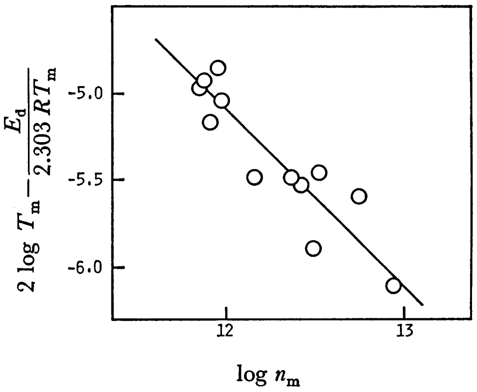

Fig. 5. A plot of $\left(2 \log T_m - \frac{E_d}{2.303\,RT_m}\right)$ *vs.* log n_m.

Discussion

The present study proves that the thermal desorption is a useful method for determining the desorption kinetics. However, in typical adsorption systems many complicated situations occur;[14] there may be several different adsorbed states even for a single adsorbed species. In addition, the activation energy of desorption may depend on the concentration of adsorbed species and on the structures of surfaces. Transition metals such as W, Ni, Pt *etc.* have been found to show complicated desorption spectra of hydrogen because of superposed peaks.[14,15] It is, therefore, desirable to use more simple systems in order to perform the precise analysis of the desorption mechanism. In the present study, the desorption spectra on copper showed a single peak which shifted to the higher temperature side with the decreased coverage of surface. The activation energy of desorption was unchanged up to the surface concentration of 1.6×10^{14} atom cm^{-2} or $\theta_H = 0.6$ when the saturated amount was estimated at 2.8×10^{14} atom cm^{-2} [8] (Fig. 4) and the desorption order was given by integer number as 2 (Fig. 5). All of these findings lead us to conclude that the chemisorption of hydrogen takes place dissociatively on a copper surface and that the interaction among adsorbed hydrogen atoms is quite weak.

In the previous studies of hydrogen adsorption and H_2–D_2 equilibration, it was found that the isothermal adsorption of hydrogen on a copper surface can be interpreted in terms of the Langmuir equation for dissociative adsorption.[8,9] This behavior of adsorption was also verified by TD measurements. The activation energy of desorption evaluated by TD agreed well with that obtained from the kinetic measurement, 71 ± 4 kJ mol^{-1}. Further, the desorption rate constant at 287 K was evaluated by using the values of activation energy and the frequency factor as $3.3 \pm 2.0 \times 10^{-17}$ cm^2 molecule^{-1} s^{-1}, which is also consistent with the value $7.9 \pm 6.0 \times 10^{-17}$ obtained in the previous study. In the desorption of deuterium, T_m was higher than that of H_2 for the same fraction of coverage and E_d was also greater than that for H_2, indicating the presence of a normal isotope effect on desorption. The value of E_d for D_2 agreed with the previously obtained value within the experimental error.

In the analysis of the desorption spectrum, the magnitude of the evolution rate, relative to the changing rate of the accumulation in the system, takes an essential role is determining whether Eq. 5 exactly reflects the desorption process or not. When the difference between these two rates is not so large, Eq. 5 is not valid and its use would result in a lower value for the activation energy of desorption than the true one. In order to make the above situation clear, an exact simulation of Eqs. 4 and 7 for the second order desorption was performed by using a computer. As is seen from Figs. 6 and 7, the position of peak maximum shifted to the higher temperature side with the decrease of the pumping speed. The analysis of desorption spectra by using Eq. 9 resulted in the decrease of the apparent activation energy to 40.5 kJ mol^{-1} at 10 cm^3 s^{-1}. Such a depression of the energy seems to be the main reason why an incorrect energy value was obtained by using the usual high vacuum system with low evacuation conductance.[10] The desorption spectrum simulated at the speed of 2300 cm^3 s^{-1} accorded with that calculated from Eq. 5 within 0.1 K. This large difference of the two rates in the present study permitted us to determine exactly the kinetic parameters and mechanism of the desorption. In addition, the pressure gauge was located directly in front of the source of gas evolution; thus the pressure inside the cell and its change on heating was accurately followed and recorded by the gauge. It is to be noted that the same caution should be used for the gas chromatographic TD measurement with respect to the magnitude of the flow rate of the carrier.

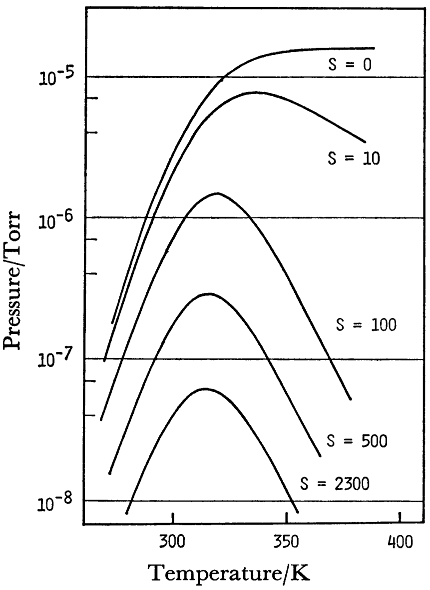

Fig. 6. Effect of pumping speed on desorption spectra. The spectra were simulated for different pumping speed, S (cm^3 s^{-1}) by using Eqs. 4 and 7 in the text.
E_d: 68.6 kJ mol^{-1}, ν: 1×10^{-4}, β: 1 K s^{-1}, n_0: 1×10^{14} atom cm^{-2}, A: 4.2 cm^2, V: 410 cm^3.

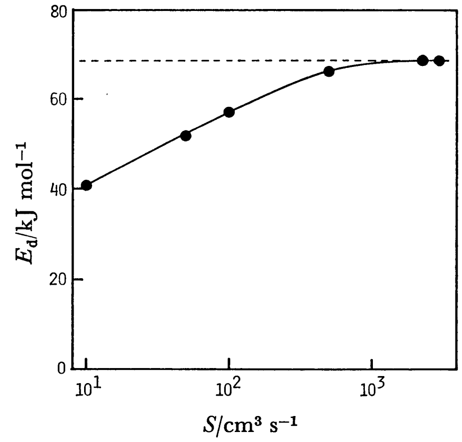

Fig. 7. Calculated activation energy of desorption as a function of pumping speed. Parameters used in the calculation were the same as those of Fig. 6 except that β is changed from 0.2 to 2 K s^{-1}. A dashed line shows the true value of activation energy of desorption.

Balooch *et al.* found that the activation energy for the adsorption of hydrogen on a copper surface depends on the crystallographic planes, as shown in the sequence $E_a(111) \gtrsim E_a(100) > E_a(113)$.[6] The present study cannot tell whether the desorption rate depends on the lattice planes or not. However, a single adsorbed state was observed on the polycrystalline copper used, and it is likely that the annealed surface exposed preferentially the (100) plane on which hydrogen is mainly adsorbed.

Classical trajectory calculations were applied to the adsorption of hydrogen on copper[9,16] and made possible the microscopic analysis of the process of dissociative adsorption. The desorption of the molecule from the surface is also interesting in view of the energy transfer from the lattice vibration to the vibration of adsorbed atoms and to the motion of molecules released from the surface. The results obtained here will be available for such microscopic descriptions of the behavior of adsorbed atoms. Trajectory calculation studies for the desorption of hydrogen from a copper surface are now in progress and will be published elsewhere.

References

1) D. O. Hayward and B. M. W. Trapnell, "Chemisorption," Butterworths, London (1964).
2) T. Kwan, *Adv. Catal.*, **6**, 67 (1954).
3) D. D. Eley and D. R. Rossington, "Chemisorption,"

Butterworths, London (1957).

4) J. Pritchard and F. C. Tompkins, *Trans. Faraday Soc.*, **56**, 540 (1960).

5) C. S. Alexander and J. Pritchard, *J. Chem. Soc., Faraday Trans.* 1, **68**, 202 (1972).

6) M. Balooch and R. E. Stickney, *Surf. Sci.*, **44**, 310 (1974).

7) D. A. Cadenhead and N. J. Wagner, *J. Catal.*, **21**, 312 (1971).

8) M. Kiyomiya, N. Momma, and I. Yasumori, *Bull. Chem. Soc. Jpn.*, **47**, 1852 (1974).

9) I. Yasumori, N. Momma, and M. Kiyomiya, *Jpn. J. Appl. Phys. Suppl.* 2, *Pt. 2*, 485 (1974).

10) N. Momma, Ph. D. Thesis, Tokyo Institute of Technology, 1972.

11) Z. Oda, *Shinku*, **3**, 240 (1960).

12) G. Ehrlich, *J. Appl. Phys.*, **32**, 4 (1961).

13) P. A. Redhead, *Vacuum*, **12**, 203 (1962).

14) D. Menzel, "Interactions of Metal Surfaces," Springer-Verlag, New York (1975).

15) I. Toyoshima and G. A. Somorjai, *Catal. Rev. -Sci. Eng.*, **19**, 105 (1979).

16) A. Gelb and M. Cardillo, *Surf. Sci.*, **59**, 128 (1976); **64**, 197 (1977).