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Adsorption-Assisted Desorption and Cross Desorption of CO and H_2 on Nickel Polycrystalline Surfaces

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Synopsis. The rates of adsorption and desorption during co-adsorption process of CO and H_2 on the Ni polycrystalline surface were measured. The desorption rate of CO(a) was enhanced by the presence of CO(g) or H_2(g) in the gas phase. The desorption rate of adsorbed hydrogen was accelerated by CO(g) but not by H_2(g).

A series of our previous works on the adsorption process of CO

$$\mathrm{CO(g)} \underset{v_-}{\overset{v_+}{\rightleftarrows}} \mathrm{CO(a)} \qquad (1)$$

on several group-VIII metal surfaces has shown that the absolute desorption rate v_- is almost proportional to the ambient CO pressure while the adsorption is actually proceeding.[1-6] There is a great enhancing contribution by gas-phase molecules to the desorption rate process—"adsorption-assisted desorption"(AAD)—besides the thermal desorption.

This time we took the same approach for co-adsorption of CO and H_2 on nickel polycrystalline surfaces. Adsorption of CO and H_2 on group-VIII metal surfaces was investigated in relation with the mechanism of methanation etc.[7-14] However there are few cases in which the dynamics of adsorption and desorption were mesured while the adsorption process is actually going on. We studied adsorption–desorption kinetics of the co-adsorption of CO and H_2 on Ni polycrystalline surfaces during the adsorption process.

The adsorption rate v_+ and the desorption rate v_- of CO and H_2 are mathematically divided into 16 components as functions of the surface concentration of CO(a) and H(a), N_{CO} and N_{H}, and the gas-phase pressures P_{CO} and $P_{\mathrm{H_2}}$. For example, the important components of the desorption rate of CO are:

$$\begin{array}{lll} v^{\mathrm{CO}}_- = v^{\mathrm{CO}}_-(N_{\mathrm{CO}}) & : \text{thermal desorption} & \\ \quad + v^{\mathrm{CO}}_-(N_{\mathrm{CO}}, P_{\mathrm{CO}}) & : \text{AAD} & \\ \quad + v^{\mathrm{CO}}_-(N_{\mathrm{CO}}, P_{\mathrm{H_2}}) & : \text{cross desorption by } \mathrm{H_2(g)} & \\ \quad + v^{\mathrm{CO}}_-(N_{\mathrm{CO}}, N_{\mathrm{H}}) & : \text{surface effect by } \mathrm{H(a)} & \\ \quad + \text{(12 other components)} & & (2) \end{array}$$

where each v^{CO}_- (*,*) falls zero when any one of the variables inside parentheses is zero.

The values of those components are obtained by measuring the amounts of the surface species as functions of time. Each component is distinguished by gas-switching technique between corresponding molecules. This technique is the extended version of the "isotope-jump method".[1] The rates are calculated from the change of the surface concentrations of the adsorbates measured by the flash desorption at each point of time. We expected changes in the rate of desorption of H(a) by CO(g), and vice versa, as well as ADD of CO and H_2. We call these phenomena the "cross desorption". It is distinguished from ADD, in which the desorption of the surface species is enhanced by the same species in the gas phase. In this paper we mainly mention about the desorption processes. The adsorption rates were difficult to measures precisely enough in some cases.

Experimental

Experiments were performed in an ultrahigh vacuum apparatus equipped with a mass spectrometer (MS), a sample temperature programmer, an Auger electron spectrometer, etc.[1] Several pieces of Ni foil (0.03 mm thickness, 1.4 $\mathrm{cm^2}$ total area) were used as the samples. The surfaces were cleaned by Ar ion bombardment and annealing. The gas samples were $^{12}\mathrm{C}^{16}\mathrm{O}$, $^{12}\mathrm{C}^{18}\mathrm{O}$, H_2 and D_2 obtained from commercial vessels. The procedures of gas-switching experiments were as follows. Details in calibration and calculation procedures are describe elsewhere.[1]

(1) Clean up the surface by flashing up to 800 K.
(2) Keep the sample at the desired temperature/K.
(3) At time $t=0$, start introducing Gas 1 (the species to leave on the surface) at the desired pressure P_1/Pa.
(4) At time $t=t_1$, stop introducing Gas 1, and, at the same time, start introducing Gas 2 (The gas-phase species) at pressure P_2/Pa.
(5) At time $t=t_1+t_2$, flash the sample and record the flash-desorption trace of the desired species by MS.

For each pair of Gases 1 and 2, measurements were done at various T, P_1, P_2, t_1, and t_2, and the surface concentrations of Gases 1 and 2 (N_{CO} and $N_{\mathrm{H}}/N_{\mathrm{D}}$/molecules·$\mathrm{cm^{-2}}$) were obtained from the peak ares of flash desorption in (5).

The obtained surface concentrations N's were plotted as functions of t_2 with fixed T, P, and t_1. These t_2–N curves were numerically curve-fitted to exponential functions, and the differerential conefficients at $t=t_1+0$ were calculated. These differential coefficients i.e. the slopes of the tangents at the right side of t_1 are the rates of adsorption of the "Gas 2" species, and the rates of desorption (negatively signed) of the "Gas 1" species. In some cases precise determination of adsorption rate was not possible because of the background gas pressure. We mainly focussed on the desorption rates.

Results and Discussion

1. Gas 1=$^{12}\mathrm{C}^{18}\mathrm{O}$, Gas 2=$^{12}\mathrm{C}^{16}\mathrm{O}$ $\{v^{\mathrm{CO}}_\pm(N_{\mathrm{CO}}, P_{\mathrm{CO}})\}$. The kinetics of absorption of CO without H_2(g) were examined. We can measure the absolute rates of adsorption and desorption of CO by distinguishing Gases 1 and 2 using isotope-labelled molcules. The absolute rates of adsorption and desorption are dependent on the surface concentration N_{CO} and the gas-phase pressure P_{CO}.[4] The absolute adsorption rate $v^{CO}{}_{+}$ is a nonlinear function of N_{CO} and proportional to P_{CO}. The initial adsorption rate ($v^{CO}{}_{+}$ when $N_{CO}=0$) is independent of the temperature T between 329 K and 394 K. The desorption rate $v^{CO}{}_{-}$ is greatly affected by the gas-phase pressure of CO:

$$v^{CO}{}_{-} = \mu_{CO}N_{CO} = (\mu_{CO}{}^{0} + k_{CO}P_{CO})N_{CO}. \tag{3}$$

Figure 1 shows the rate constant μ_{CO} as a function of P_{CO} and T. The rate constant at $P_{CO}=0$, $\mu_{CO}{}^{0}$, corresponds to the thermal desorption process, the pressure-dependent part of the rate constant is proportional to P_{CO}. We call this kind of kinetics "adsorption-assisted desorption (AAD)".[1-6] So far we have proposed several models to elucidate the mechanism of acceleration of the desorption by the effect of the gas phase.[14]

2. Gas $1=D_2$, Gas $2=H_2\{v^{H_2}{}_{\pm}(N_H, P_{H_2})\}$. Whether AAD is applicable for gases other than CO is an attractive question.[15,16] The absolute rates of adsorption and desorption of H_2 only were measured in the same manner as CO by using H_2 and D_2. The species desorbed by flash desorption procedure are H_2, HD, and D_2. The amounts of H(a) and D(a) were calculated by summing the areas of those three peaks. The absolute adsorption rate $v^{H_2}{}_{+}$ was a nonlinear function of N_D and proportional to P_{H_2}. It decreased with increasing temperature T. Figure 2 shows the absolute desorption rate $v^{D}{}_{-}$ as a function of N_D and P_{H_2}. It is approximately proporitional to $(N_D)^2$ in the high coverage region. $v^{D}{}_{-}$ did not change when the pressure P_{H_2} changed. Namely, AAD did not occur in the case of H_2 on Ni.

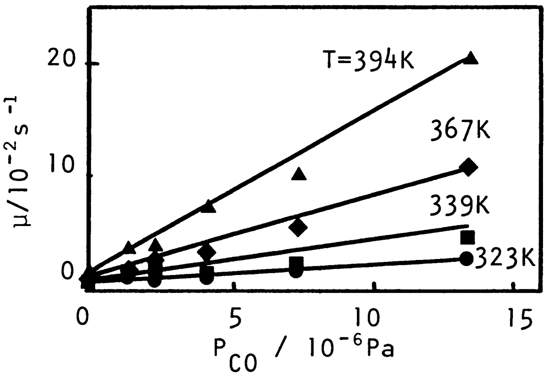

Fig. 1. The absolute desorption rate constant of CO, μ, as a function of pressure P_{CO} and temperature T.

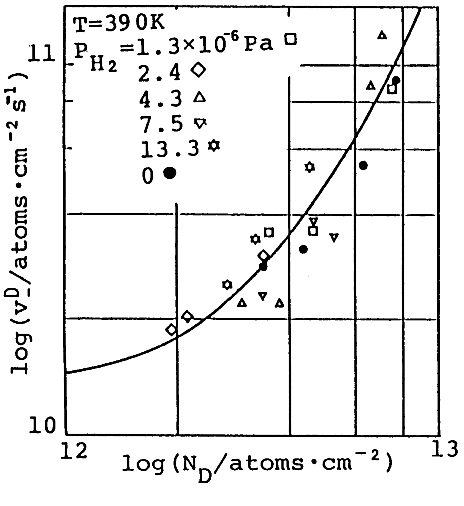

Fig. 2. The absolute desorption rate of D(a), $v^{D}{}_{-}$, as a function of the surface concentration N_D and pressure P_{H_2}.

3. Gas $1=CO$, Gas $2=H_2\{v^{H_2}{}_{+}(N_{CO}, P_{H_2})$ and $v^{CO}{}_{-}(N_{CO}, P_{H_2})\}$. If Gas 2 is a different chemical species from Gas 1, we see the effects of the adlayer of Gas 1 on the adsorption of Gas 2, and the effects of Gas 2 in the gas phase on the desorption from the adlayer of Gas 1. Replacement of the adsorbates in the equilibrium condition is trivial and well recognized. We observe the effects of the gas phase molecules on the desorption kinetics. In the present case the gas-phase species is H_2, and the adlayer species is CO. It was difficult to calculate $v^{H_2}{}_{+}$ precisely, as the amount of H(a) was suppressed by coexistence fo CO. The adsorption step of H_2(g) ($v^{H_2}{}_{+}$) was strongly poisoned by CO(a).

The desorption of CO(a) was weakly enhanced by H_2(g). Figure 3 shows CO(a) (N_{CO}) decreasing after the gas phase was switched to H_2. It decreased a little bit faster at $P_{H_2}=1.3\mathrm{X}10^{-4}$ Pa than a $P_{H_2}=0$, i.e. $v^{CO}{}_{-}(N_{CO}, P_{H_2})>0$. The "cross desorption" of CO(a) by H_2(g) was demonstrated in this experiment.

4. Gas $1=D_2$, Gas $2=CO\{v^{CO}{}_{+}(N_D, P_{CO})$ and $v_{-}(N_D, P_{CO})\}$. The reverse case of 3. was examined. The adsorption rate of CO was almost indifferent of the surface concentration of D(a) at temperatures higher than 329 K. The result was almost the same as the data of the absolute adsorption rate.[5]

Figure 4 shows the desorption rate of D, $v^{D}{}_{-}$, as a function of N_D and P_{CO}. In Fig. 4, $v^{D}{}_{-}$ is fitted to second-order functions of N_D, that is,

$$v^{D}{}_{-} = \mu_D(N_D)^2 \tag{4}$$

Cross desorption of D(a) by CO(g) is obvious in this

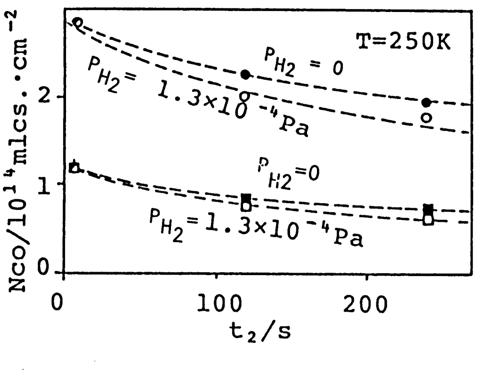

Fig. 3. The surface concentration of CO(a), N_{CO}, as a function of time t_2 with ambient H_2 molecules at pressure P_{H_2} for two initial N_{CO}'s.

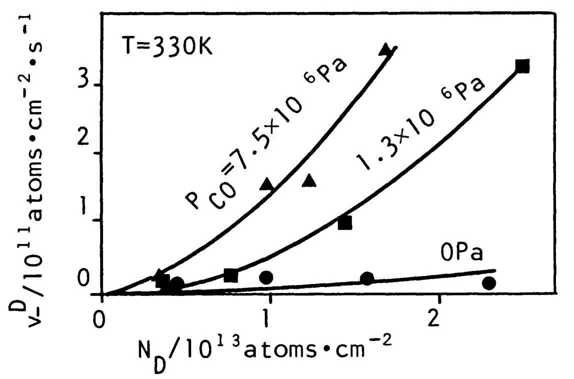

Fig. 4. The desorption rate of D(a), v^D_-, as a function of the surface concentration of D(a), N_D, and pressure of CO, P_{CO}.

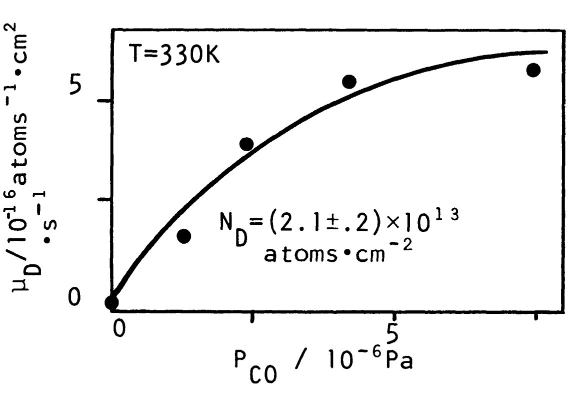

Fig. 5. The 2nd-order rate constant of D(a), μ_D, as a function of CO pressure P_{CO}.

case. Figure 5 shows P_{CO}-dependence of the second-order rate constant μ_D of v^D_-. It is curve fitted to

$$\mu_D = \mu_D^0 + k_{D,CO}P_{CO}^{0.74}. \tag{5}$$

The heat of adsorption of CO is larger than that of H_2.[17] If there is a direct energy-transfer process between adsorbates upon adsorption of CO, desorption of H(a) can be accelerated by CO, but not by H_2.

5. Gas 1=D_2 and CO, Gas 2=Vacuum {$v^D_-(N_D, N_{CO})$ and $v^{CO}_-(N_D, N_{CO})$}. This experiment was done to distinguish the effect of the gas-phase molecules from that of the adsorbed molecules. The desorption of molecules into vacuum indicates the effects of one adsorbed species to the other adsorbed species. Figure 6 shows the second-order rate constant μ_D of D(a) when N_D was constant and N_{CO} was varied. μ_D was not significantly changed by N_{CO}, namely, the desorption of CO did not depend on the surface concentration of D(a) at the same temperature.

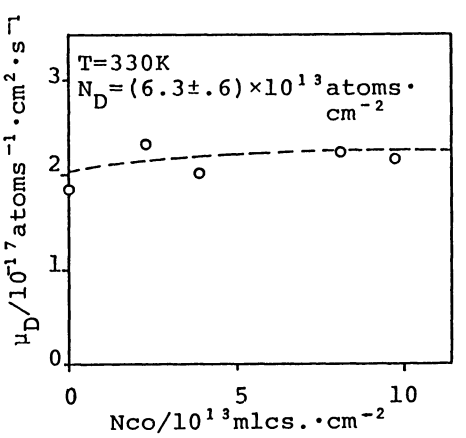

Fig. 6. The 2nd-order desorption rate constant of D(a), μ_D, as a function of the surface concentration of CO(a), N_{CO}. This measurement was done without ambient gas molecules.

To summarize, we observed the acceleration of desorption of a surface species by the same species in the gas phase—adsorption-assited desorption— of CO but not of H_2. The adsorption of CO(g) is indifferent of the presence of H_2(g) or H(a), and desorption of CO(a) is weakly promoted by H_2(g). Adsorption of H_2 is poisoned by CO(a), and desorption of H(a) is accelerated by CO(g). The acceleration of desorption of H(a) is not due to the surface interaction with CO(a), but to the interaction between CO(g) and H(a) when CO reaches the surface.

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