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Adsorption of Carbon Monoxide on Nickel

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The adsorption of carbon monoxide on evaporated nickel films has been studied by measuring the amount of adsorption and thermal desorption, and observing the change in resistivity of the film. Four different adsorption states (γ_1-, γ_2-, α-, and β-states) were found on the surface at 77 K. Evidence is presented that the γ_2-state is a precursor for both α- and β-state adsorption.

INTRODUCTION

There have been numerous investigations of the interaction of CO with Ni surface over the past few decades (*1*). These investigations have been made with a variety of techniques for single-crystalline and polycrystalline samples, but the characterization of the CO–Ni system is not fully understood. For example, Onchi and Farnsworth (*2*) reported three structures of CO adsorbed on (100) Ni with three different desorption temperatures.

On the other hand, Tracy (*3*) suggested a single type of binding for CO adsorbed on (100) Ni. While two adsorption states for CO on polycrystalline Ni surface were reported by Degras (*4*), Wedler and Papp (*5*) found only a single chemisorbed state on the Ni film. There is some uncertainty in our understanding of CO adsorption on Ni surface. In order to obtain further information on the CO–Ni system, the interaction of CO with nickel surfaces at liquid nitrogen temperature has been studied. This paper reports observations of adsorption and thermal desorption of CO on Ni films, as well as the changes in electrical resistance of the film due to CO adsorption. The results of these experiments are compared with each other, and a model for CO adsorption is proposed, which we believe is consistent with existing data.

EXPERIMENTAL METHODS

The experimental apparatus was evacuated by a Ti getter ion pump after prepumping through metal valves by the usual pumping system, consisting of a three-stage fractionating glass oil diffusion pump, oil rotary pump and a liquid nitrogen trap. After the treatment of bake-out and outgassing of the experimental apparatus, ultimate pressure of 2×10^{-10} Torr was obtained.

The Ni films were prepared by the deposition of a high-purity Ni wire (Materials Research Corp. 99.995%) on the inside wall of a spherical glass cell at the wall temperature of about 310 K with a rate of 5–10 Å/min. The geometrical surface area of the film-covered glass wall was 30 cm². Before the deposition of the Ni film

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TABLE 1

Diffraction Pattern of Ni Film

d (Å)	2σ (degr)	hkl	I/I_1[a] (published)[b]	I/I_1[a] (obsd)
2.03	44.6	111	1.00	1.00
1.76	51.9	200	0.50	0.30
1.25	76.6	220	0.32	Not detected
1.06	93.2	311	0.32	0.30

[a] Intensity ratio normalized with the value of (111) plane.

[b] Data compiled and published by the Joint Committee on Powder Diffraction Standards.

the degassing of the Ni wire was elaborately performed to keep the pressure in the experimental apparatus at least below 10×10^{-10} Torr during the evaporation, because large amounts of gases are usually evolved from the Ni wire (*6*). In our experiments maximum possible contamination on the surface was estimated to be less than 3% of the adsorbed amount of CO by assuming the sticking coefficient of unity. Even if it happens that Ni films are contaminated to a few percent of monolayer with residual gases such as H_2 and CO_2, these gases will be replaced by subsequent CO adsorption and evolved into the gas phase. The evolved gases are detected by an ionization gauge or an omegatron mass spectrometer, as shown in our previous report (*7*). The film was annealed at 420 K just after the deposition. The thickness of the Ni film was of the order of 10^2 Å.

The crystallographical structure of the film was measured by X-ray powder diffraction, using another Ni film prepared in the same way. The observed diffraction pattern using Cu-*K* radiation was consistent with a polycrystalline cubic structure and a lattice parameter of 2.03 Å. The results are summarized in Table 1 with other published data. It was further confirmed that the film surface is microscopically smooth from the observations by means of a scanning electron microscope.

Adsorption of CO on Ni film at liquid nitrogen temperature was performed by two different procedures; in the first process (a) the adsorption was performed in succession just after the saturation of the adsorption at room temperature, and in the second process (b) CO was adsorbed on the surface kept at liquid nitrogen temperature throughout the process. The adsorbed amount of CO (Q) was measured by means of the Knudsen capillary technique (*8*). The amount was calculated by using the equation,

$$Q = \int^{\Delta t} c(P_1 - P_2)dt,$$

where c is the conductance of the capillary (50 cm³/sec), P_2 is the pressure in the measuring cell and P_1 is the pressure of gas introducing system. In our experiments, P_2 was varied in the course of adsorption with keeping P_1 constant during the measurement, both of which were measured by each ionization gauge.

After the completion of CO adsorption at liquid nitrogen temperature, CO in the gas phase was pumped out and then the desorption spectra were measured. For the desorption measurement, the cell was allowed to warm up spontaneously to room temperature. Above room temperature, the cell was heated by a kind of oven,

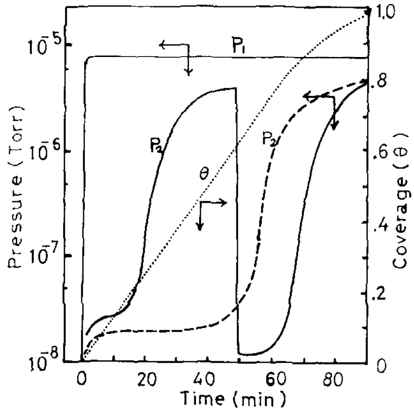

FIG. 1. Variation of pressure in the gas adsorption cell (P_2) at room temperature and liquid nitrogen temperature as a function of time with constant pressure of the gas introducing system (P_1). Process (a); (– – –) process (b); (· · ·) surface coverage vs time for process (b).

which was made to fit the measuring cell and give the cell a homogeneous heating.

Resultant desorption spectra were obtained by measuring the change of pressure as a function of time by the ionization gauge. The variation of the film temperature was measured by a Chromel–Alumel thermocouple sealed in the inside wall of the glass cell and was approximately linear with the time (typical heating rate, 1.5 K/sec). After the measurement of one desorption spectrum the cell was exchanged with a new one, and next measurement with different amounts of adsorbed CO was performed on a freshly prepared film. The composition in the gas phase was monitored by the omegatron throughout the experiments.

In addition to the above measurements, the change of the electrical resistance of the film due to the CO adsorption was measured by a Wheatstone bridge. Two Pt foil electrodes were sealed at the opposite position in the inside wall of the glass cell.

Blank experiments were also performed to measure the magnitude of CO adsorption on the glass cell without Ni film. The amount of CO adsorbed on the glass cell was 2.4 × 10^{12} molecules/cm^2. The peaks of CO desorption from the glass surface were observed in the temperature region of 70–100 K, and, to a lesser extent, at the region of over 500 K. The CO desorption at 70–100 K was estimated to contribute at most 4% of the desorbed amount from the Ni film surface in the corresponding temperature region.

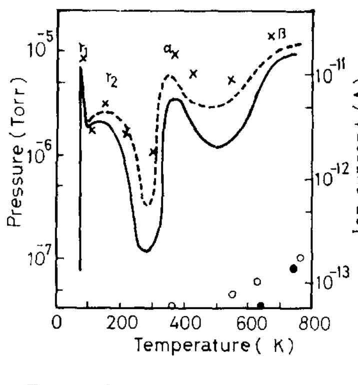

FIG. 2. Desorption spectra for saturated coverage of CO on Ni film at liquid nitrogen temperature for two adsorption processes. (——) Process (a); (– – –) process (b). The γ_1 peak of (– – –) overlaps with that of (——). (×) Ion currents of CO$^+$; (○) those of H_2^+, and (●) those of CO$_2^+$.

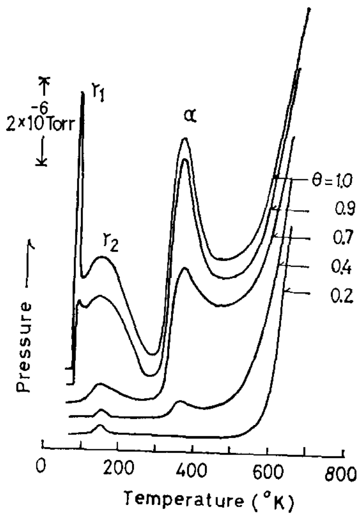

FIG. 3. Desorption spectra for CO on Ni surface as a parameter of the coverage in process (b). The zero levels of the curves are shifted to prevent overlap.

RESULTS AND DISCUSSION

The adsorption curves of CO are shown in Fig. 1. The solid curve corresponds to process (a) and the broken curve to process (b). In process (a) the adsorbed amount of CO at the saturation at room temperature is 1.1 × 10^{15} molecules/cm^2 and the adsorbed amount at liquid nitrogen temperature after presaturation at room temperature is 1.2 × 10^{15} molecules/cm^2; the total amount of adsorbed CO (Q_a) is 2.3 × 10^{15} molecules/cm^2. On the other hand the total amount of adsorbed CO in process (b) (Q_b is 3.0 × 10^{15} molecules/cm^2 and exceeds Q_a by 0.7 × 10^{15} molecules/cm^2.

The desorption spectra are shown in Fig. 2. The solid curve is obtained from process (a) and the broken curve is obtained from process (b). Ion current of CO$^+$

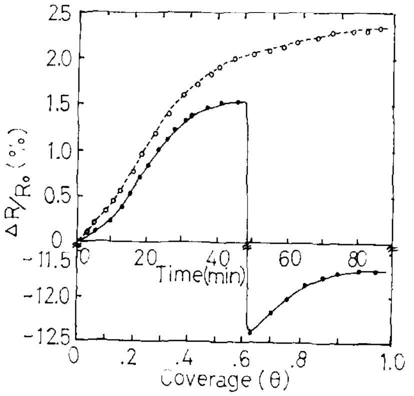

FIG. 4. Change of electrical resistance of Ni film due to CO adsorption for the two adsorption processes. (——) Process (a); (- - -) process (b). R_0 is the initial electrical resistance of Ni film and ΔR is the increase of the film resistance from the one. (——) Does not refer to the coverage (θ) abscissa.

($M/e = 28$) was traced during the course of the thermal desorption with a fixed resonance frequency of the omegatron, to assure that the reading by ionization gauge corresponded to that of CO pressure. The ion currents of CO^+, H_2^+, and CO_2^+ are also shown in Fig. 2.

Both desorption spectra in Fig. 2 show four maximum desorption rates. The temperatures of the maximum desorption rates are 80, 130, 350, and 750–770 K, respectively. In this report the four states are designated as γ_1, γ_2, α, and β in the order of the temperature increase. It is shown in Fig. 2 that the increase of the adsorbed amount in process (b) results in the increase of the population in the γ_2-, α-, and β-states. In process (a), the adsorbed amount at liquid nitrogen temperature exceeds that of the presaturation at room temperature by 0.1×10^{15} molecules/cm^2. On the other hand, the total desorbed amount of the γ_1- and γ_2-states is apparently less than the sum of the desorbed amount of the α- and β-states. This fact suggests that there remain vacant sites for the α- and β-state adsorption in spite of the apparent saturation at room temperature.

Desorption spectra with a parameter of the coverage (θ) of CO are shown in Fig. 3 for process (b). The fractional coverage is normalized with the maximum adsorbed amount at liquid nitrogen temperature. These measurements were successfully possible in the present experiments, since the clean, large and reproducible surface has been prepared. Figure 3 clearly manifests how the four states are formed with the coverage. Most of the β-state CO are occupied until $\theta = 0.4$. It is remarkable that CO in the γ_2-state is detected at a small coverage ($\theta = 0.2$), where the α-state CO is not detected. However, most of the γ_2-state CO seems to be formed at the final stage of the adsorption ($0.7 < \theta < 0.9$). The α-state CO is principally observed at the middle stage of the adsorption ($0.4 < \theta < 0.7$).

The relative change of the film resistance due to CO adsorption was observed in Fig. 4 which is plotted against the adsorption time. The coverage normalized with the maximum amount of CO adsorbed in process (b) is also given in the abscissa of Fig. 4. The solid curve shows the results for process (a) and the broken one for process (b). The result in Fig. 4 is consistent with the results in Figs. 1, 2, and 3. First, the rapid increase of the electrical resistance in process (b), compared to that in process (a), corresponds to the fact of $Q_b > Q_a$ and indicates that the sites of α- and β-states are efficiently occupied in the case of process (b).

Second, the change of the film resistance is reasonably interpreted with the results shown in Fig. 3. In the region of $\theta < 0.4$, the electrical resistance shows a drastic change with CO adsorption. This change is due to the adsorption of CO in the β-state. The β-state CO with highest desorption temperature is expected to be most tightly bound. The resistance change in the range from $\theta = 0.4$ to 0.7 seems to occur by the adsorption of CO in the α-state. There is a slight change of the resistance at the final stage of CO adsorption where the γ_2-state is formed. The adsorbed CO in the γ_1-state in the range of $\theta > 0.8$. does not cause the resistance change as shown in Fig. 4.

Some kinetic data of CO adsorbed on the Ni surface are summarized in Table 2. The activation energy for desorption, E, was calculated by assuming the first-order rate equation for the CO desorption and using the analysis by Redhead (*9*). The pre-exponential factor in the rate equation is assumed to be 10^{-13} $\sec^{-1}$. The obtained values of E and the variation of E with the coverage are in agreement with the results from the calorimetric measurements of CO adsorption (*10*, *11*). When the pressure in the measuring cell at the adsorption stage increased above 1×10^{-5} Torr, the peak of the γ_1-state increased while other states were not affected. Therefore, the γ_1-state can be identified as a physically adsorbed state. The γ_2-state seems to be a chemisorbed state held weakly on the surface, considering the observed change of the resistance and the magnitude of E. The α- and β-states may be interpreted as linear and bridged bonded CO; the two types of binding state have been proposed by many authors and confirmed by the recent measurements of infrared spectra and saturation magnetization (*12*). Confirmative information may be expected from the measurements of adsorbate binding energies by the technique such as ultraviolet photoemission spectroscopy (*13*).

The presence of the γ_2-state at low coverage as shown in Fig. 3 indicates that the γ_2-state will play the role of a precursor state. The results in Figs. 1 and 2 are reasonably interpreted by the idea; the existence of the γ_2-state at low temperature explains the facts that $Q_a < Q_b$, and that the adsorbed amount in γ_2-, α-, and β-states differs between processes (a) and (b). The model that chemisorption on a transition metal takes place via a weak precursor state which acts as a feeder for the more strongly bound adsorption state has been suggested by many authors (*4*, *14*). Degras (*4*) adopted the model in the analysis of the results obtained from his study of CO adsorbed on Ni surface. However, the experimental evidence showing the existence of such a precursor state has not been reported.

TABLE 2

Kinetic Data Obtained from Desorption Spectra

State	Desorption peak temp (K)	E (kcal/mole)	Adsorbed amount (molecules/cm^2)
γ_1	80	4	0.7×10^{14}
γ_2	130	9	4×10^{14}
α	350	27	6×10^{14}
β	750–770	50	18×10^{14}

The number of the chemisorbed states observed by our measurements is different from Wedler and Papp's results (*5*). The discrepancy may be attributed to the difference of the conditions of the film deposition and the effect of residual gases on the film. The existence of three states on the single-crystalline Ni surface covered with CO below room temperature has been reported in works using thermal desorption method (*15*).

CONCLUSION

Four states are observed for the CO adsorption on the Ni surface at liquid nitrogen temperature: The total amount of adsorbed CO as well as the population in the individual state depends on the way that the CO has been introduced on the surface [process (a) or (b)]. Three adsorbed states (γ_2, α, β) are identified to be chemisorbed states and the other (γ_1) to be physisorbed state. It is shown that there remain many empty sites for the α- and β-states at room temperature adsorption in spite of its apparent saturation.

The γ_2-state is observed to exist even at an early stage of the CO adsorption at liquid nitrogen temperature. It is concluded that the γ_2-state may fulfill a role of a precursor for the α- and β-states adsorption, the existence of which has been proposed by many investigators.

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