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The Work Function as a Monitor for Thermal Desorption Spectroscopy: CO Desorption from Ni Sites on a Ni-Rich (110) Cu–Ni Surface

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A new method for the evaluation of thermal desorption spectra is described. Using this approach, based on the usual assumptions of transition-state theory, the coverage dependence of the Gibbs free activation energy G_D (Θ) of desorption reactions can be determined. As experimental input it suffices to measure any physical property which is proportional to Θ during time-programmed desorption as a function of time and surface temperature. If the isosteric heat and the activation energy of adsorption are known, the activation entropy of desorption and the Arrhenius preexponential factor can be estimated from G_D. Work-function data on CO desorption from Ni-rich (111) Cu–Ni alloy surface are used to discuss this method.

INTRODUCTION

Thermal desorption spectroscopy (TDS) has become a widely used tool in surface chemistry, especially for the study of gas–metal interactions. Information about the adsorbed amount, the number of desorption states, and the kinetic data of the desorption reaction, i.e., reaction order, activation energy, and preexponential factor, can be obtained by TDS. The fundamental concepts of this method have been described by Redhead (*1*), and a recent review on this topic has been given by Menzel (*2*).

The main advantage of thermal desorption spectroscopy is that it can be readily performed, without great experimental effort, in practically all standard ultrahigh vacuum systems as commonly used in surface studies. After adsorption at sufficiently low temperature a thermal desorption spectrum (TDS) is usually obtained by measuring the development of the pressure (or partial pressure of the desorbing species) in the vacuum system during time-programmed heating of the sample.

Most of the methods for quantitative TDS evaluation use only the temperatures of the pressure maxima of a desorption spectrum. In the case of first-order desorption the activation energy of desorption E_D is usually obtained by assuming $k_0 = kT/h \approx 10^{13}\ s^{-1}$ for the preexponential factor. A direct experimental determination of k_0 can be obtained by observing the heating-rate dependence of the desorption maxima (*1, 3*). If E_D is coverage dependent, the maxima evaluation yields only a rough average value of E_D. The coverage dependence of E_D can be obtained from a series of desorption spectra with different initial coverages (*4*). This requires that the TDS maxima are fully resolved and that all spectra of the series have been measured with identical, or accurately known, pumping speeds. In case of overlapping peaks, a fitting procedure is needed to determine the parameters of the desorption reaction, which can lead to considerable ambiguities (*4*).

In recent years several authors (*5–7*) have used the work-function change $\Delta\Phi$ during desorption for monitoring TDS. If $\Delta\Phi$ is a linear function of the adsorbed amount N the maxima of the desorption rate $(\dot{N})$ correspond to the inflection points

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of $\Delta\Phi$. Work-function-monitored TDS can be used to discriminate desorption from the sample and from its holder (*5*), but the main advantage of this method is that the time constant of work-function devices is considerably smaller than that of usual vacuum systems. Therefore a higher resolution can be obtained by $\Delta\Phi$-monitored TDS. This has been shown by Pfnür *et al.* (*7*) by comparing the $(d\Delta\Phi/dt)$ curve gained by analogue differentiation during desorption with the pressure curve. They also demonstrated that work-function monitoring can be used to perform isothermal desorption studies.

During studies of CO adsorption on Cu–Ni surfaces (*8*), we have developed a method for evaluating work-function-monitored TDS that uses not only the positions of the desorption rate maxima, but also the full $\Delta\Phi(T)$ curve measured during desorption. Such a method is especially useful for adsorption studies on alloy surfaces, where it is impossible to measure TDS series or such equilibrium quantities as the isosteric heat of adsorption because of the danger of adsorption-induced changes of the surface composition. In the following sections we describe this method, present preliminary results for CO desorption from the Ni sites of a Ni-rich (110) Cu–Ni surface, and discuss them with respect to results of CO adsorption experiments on pure Ni surfaces.

METHOD

Using the Eyring–Polanyi equation for the rate constant, the rate of an *n*th-order desorption can be given as

$$\dot{N} = -N^n(kT/h)\exp(-G_D/RT), \quad (1)$$

where G_D is the Gibbs free energy of activation for the desorption reaction, i.e., the difference of Gibbs free energy between the transition state and the adsorbed state. We assume that a physical quantity φ which is proportional to the adsorbed amount N can be measured as a function of time t during desorption, and its time derivative $\dot{\varphi}$ can be obtained by digital or analogue differentiation:

$$\varphi = \varphi(t) = cN(t) \quad \text{and} \quad \dot{\varphi} = d\varphi/dt = c\dot{N}(t). \quad (2)$$

Then G_D can be determined for every time t during desorption by means of (1) from $\varphi(t)$, $\dot{\varphi}(t)$, and the temperature $T(t)$ measured during desorption. Thereby G_D is formally obtained as a function of time, but for every t the relative coverage Θ can be evaluated according to

$$\Theta(t) = N(t)/N_0 = \varphi(t)/\varphi_0, \quad (3)$$

where N_0 is the adsorbed amount at saturation and φ_0 the respective value of φ. Thus G_D can be determined from a single TDS as a function of Θ, and in the case of first-order desorption not even knowledge of the constant c in Eq. (2) is required.

To compare G_D obtained by our method with other results we can use the relation

$$H_D = H_{iso} + E_a - RT \quad (4)$$

to calculate the activation enthalpy of desorption $H_D(\Theta)$ from known values of the isosteric heat of adsorption $H_{iso}(\Theta)$ and the activation energy of adsorption E_a. $H_D(\Theta)$ in turn can be taken to estimate the activation entropy of desorption $S_D(\Theta)$, or the Arrhenius preexponential $k_0 = kT/h \exp(S_D/R)$, from our $G_D(\Theta)$.

EXPERIMENTAL

Our experiments were carried out in a standard stainless-steel ultrahigh vacuum system with a base pressure below 10^{-8} Pa. The sample was a disk (12 mm diameter, 2 mm thick) with a (110) surface. It had been prepared from a Cu–Ni single crystal with 17% bulk Cu content (Materials Research Corp., 99.999% purity) in the usual way, namely, orientation by means by X-ray diffraction, cutting by spark erosion, mechanical and electropolishing, after which a mirror-like finish was achieved. The sample was spot-welded between two parallel Mo rods connected to a liquid nitrogen reservoir on a movable and rotatable sample holder. Cooling of the sample could be achieved by filling the reservoir with liquid nitrogen; heating was carried out by passing a current through the rods. The temperature of the sample was monitored by a copper–constantan thermocouple spotwelded to the edge of the sample between the two rods.

Under the vacuum the sample was cleaned by several cycles of heating, Ar-ion sputtering, and oxygen adsorption and desorption. The purity was monitored by means of Auger electron spectra obtained by a cylindrical mirror analyzer (Riber, Paris) with an integrated electron gun. After the cleaning procedure no traces of contaminants could be detected. Different compositions of the surface were obtained by using sputtering for Ni surface enrichment, and subsequent annealing for Cu enrichment (*8*, *9*, *11*). Special care was taken to minimize the surface defect concentration caused during this procedure by sputtering at elevated temperature (750 K), annealing the sample at the same temperature for at least 15 min after sputtering, and cooling down to room temperature slowly. After this the surfaces showed a bright and sharp (1 × 1) LEED structure with a dark background, and the LEED pattern did not improve during longer annealing. The actual surface composition obtained in this way was determined from the relative intensities of the 100-eV MVV Auger lines of Cu and of Ni, using a relative sensitivity factor determined from pure samples of these metals. It has to be stressed that these concentration values can only give a rough estimation of the surface composition because the 100-eV Auger electrons have an escape depth corresponding to a few atomic layers, and the sample has an unknown composition gradient within these layers due to our preparation procedure (*8*, *11*).

An extractor-type ionization gauge (IM 50—Leybold-Heraeus) was used for total pressure measurements, and a quadrupole mass spectrometer (Riber—QS 100) for residual gas analyses and controlling the thermal desorption spectra. Work-function changes during adsorption and desorption were measured by means of a self-compensating Kelvin bridge with a vibrating reference electrode made of gold-covered stainless-steel mesh spot-welded to a stainless-steel ring (5 mm diameter).

RESULTS

It has been shown (*8*, *9*) that different CO adsorption sites can be distinguished in TDS on (110) Cu–Ni surfaces: these are Cu-like sites with low desorption energy, Ni-like sites with high desorption energy, and two mixed (Cu–Ni) sites with intermediate desorption energy. Figure 1 shows the desorption from the Ni sites of a (110) Cu–Ni surface with 25% Cu content, taken with 1 K/s heating rate after saturating the surface at 10^{-6} Pa CO and 120 K surface temperature.

The solid line indicates the pressure development during desorption after subtraction of the background due to the mixed-

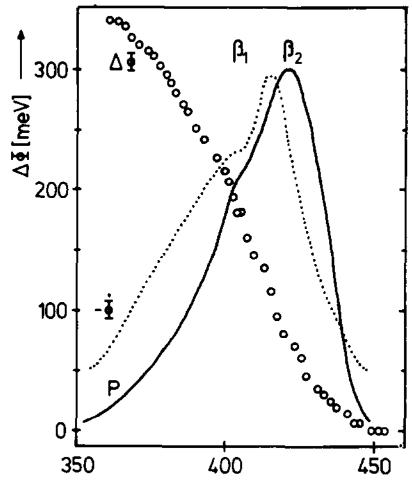

Fig. 1. Thermal desorption spectrum of CO desorbing from Ni sites on a Ni-rich (110) Cu–Ni surface. (Solid line: pressure p, in arbitrary units, as a function of sample temperature T; open circles: work-function change $\Delta\Phi$ during desorption; dotted line: $-\dot{\Phi} = -d(\Delta\Phi)/dt$ in arbitrary units.)

site desorption which appears just below 350 K. In accordance with earlier results on pure Ni (*8*, *12–14*), two desorption maxima (β_1 and β_2) can be distinguished.

The points in Fig. 1 showing the work-function change $\Delta\Phi$ during desorption were obtained by digitizing the continuous $\Delta\Phi(t)$ record with a 5-mV resolution. Here $\Delta\Phi = 0$ was taken for the clean surface. For further evaluation we will assume that $\Delta\Phi$ is proportional to the amount of CO adsorbed on the Ni sites of the surface.

Because of the danger of adsorption-induced Ni surface enrichment, this assumption may not be proved in the usual manner by determining $\Delta\Phi$ for several adsorption–desorption cycles with different values of Θ calculated as the time integral of the pressure curve during desorption. We have therefore obtained the $\Delta\Phi$-Θ relation from the $\Delta\Phi$- and the pressure curve of a single TDS, and found that $\Delta\Phi$ versus Θ is linear up to $\Theta = 0.8$ with an experimental stray less than 10% (*8*).

The dotted line in Fig. 1 shows the negative of the time derivative of the work-function change during desorption ($-\dot{\Phi} = -d(\Delta\Phi)/dt$), derived from $\Delta\Phi(t)$ by numerical differentiation and additional smoothing. The maxima of $-\dot{\Phi}(T)$ appear at slightly lower temperatures (about 10 K lower) than those of $p(T)$. This may be due to a not quite exact background subtraction in $p(T)$, or to the fact that the time constant of the vacuum system is too high.

Since the CO desorption from Ni sites is a first-order reaction (*8*, *9*, *11*), G_D can be calculated according to Eqs. (1) and (2) without knowledge of the constant c. Before applying this relation, the $\Delta\Phi$ data as given in Fig. 1 were smoothed using a five-point Savitsky–Goulay smoothing (least-squares fit to a parabola). The derivative $\dot{\Phi}(t)$ was determined by numerical differentiation of the smoothed $\Phi(t)$ curve. Additional smoothing was applied to $\dot{\Phi}(t)$ before calculating the G_D values. The points in Fig. 2 show G_D obtained through this procedure, as a function of the relative coverage Θ of the Ni sites, which was determined according to Eq. (3). We have also evaluated G_D without any smoothing, directly from the $\Delta\Phi$ data of Fig. 1, and could conclude that, aside from a reduction of the fluctuation of the values, the G_D curve is not influenced by the applied smoothing procedure. It should be noted, however, that the G_D values for small coverages ($\Theta < 0.1$) may not be considered very reliable since $\Delta\Phi$ is already small in this region.

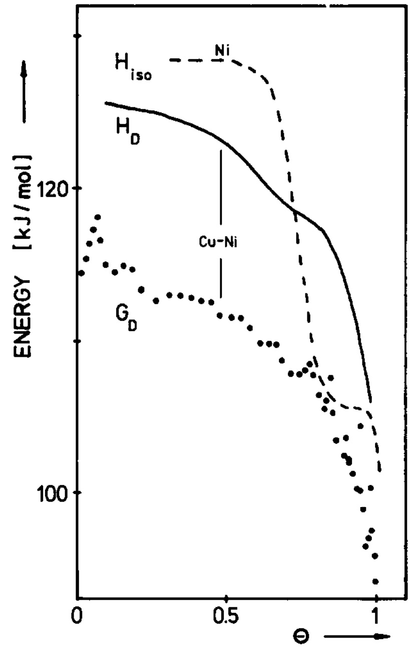

FIG. 2. Gibbs free energy G_D (points) and enthalpy H_D (solid line) of activation for CO desorption from Ni sites on a Ni-rich (110) Cu–Ni surface as a function of the relative coverage (Θ) of these sites, and isosteric heat of adsorption H_{iso} (dashed line) for (110) Ni/CO taken from (*14*).

For a determination of the activation entropy the isosteric heat of adsorption is required in addition to G_D. Unfortunately, reliable measurements of adsorption heats at Cu–Ni surfaces are, at least for the entire coverage range, hampered by the danger of Ni surface enrichment during adsorption at elevated pressure and temperature. We therefore tried to get an estimation of S_D by comparing G_D, as determined at our Cu–Ni surface, with the isosteric heat of adsorption H_{iso}, as determined by Madden *et al.* (*14*) at a (110) surface of pure Ni (dashed line in Fig. 2). For this comparison we had to take into account that H_{iso} and G_D depend on the coverage, and that G_D decreases with increasing Cu content of the alloy surface (*8, 9, 11*). Therefore, by means of Eq. (4) we first calculated the low coverage value of the activation enthalpy H_D for the pure Ni surface from the corresponding value of H_{iso}, using the well-known fact that the CO adsorption on Ni is nonactivated ($E_a = 0$). Then we determined the value of G_D in the limit of zero coverage and zero Cu content, using a series of desorption spectra obtained with surfaces of different composition (*8*). From these two values the activation entropy of desorption—again, for zero coverage and zero Cu content—could be obtained as $S_D = 27$ J/K mole, giving $k_0 = 2.4 \times 10^{14}$ s^{-1} as preexponential.

Because of the poor reliability of $H_{iso}(\Theta)$ and $G_D(\Theta)$, and because of the ambiguity caused by the applied extrapolation it was not possible to determine S_D as a function of Θ. Therefore, for comparison purposes, we have only calculated $H_D(\Theta)$ consistent with a constant S_D (solid line in Fig. 2).

DISCUSSION

The function $H_D(\Theta)$ for the alloy shows an overall form similar to that of $H_{iso}(\Theta)$ for pure Ni. The fact that for low coverage H_D is smaller than H_{iso} reflects the composition dependence of the desorption energy at the alloy surfaces. As $\Delta\Phi$ is no longer proportional to Θ for higher coverages, a comparison of H_D and H_{iso} is not very meaningful, and we have to restrict our discussion to the low coverage range.

Considering the somewhat indirect way in which the low coverage and low Cu content values of S_D (27 J/K mole) and k_0 (2.4×10^{14} s^{-1}) have been determined, they are in satisfactory agreement with the values $k_0 = 8.5 \times 10^{15}$ s^{-1} and $S_D = 57$ J/K mole obtained by Falconer and Madix (*3*) for the system (110) Ni/CO. The difference between these results and ours, on the other hand, indicates that a final test of our method would require for G_D and H_{iso} data to be measured at the same surface of a pure metal. Our result is yet another example of the experience (*7, 15*) that the preexponential for CO desorption is considerably greater than the 10^{13} s^{-1} usually assumed for TDS analyses. As a consequence, the desorption energies derived by means of the usual value of the preexponential are too high by an amount between 10 and 30 kJ/mole.

Recently Ibach *et al.* (*15*) published a new approach to the determination of desorption kinetic data. Taking into account that the properties of a desorption reaction are mainly determined by the properties of the adsorbed state, and not the transition state, they determined the coverage dependence of k_0 from equilibrium (pressure–temperature) data, equating equilibrium adsorption and desorption rates. For (111) Ni/CO they found an adsorption energy of 150 kJ/mole, from which they derived $k_0 = 10^{17}$ s^{-1} for the low coverage limit of the preexponential, which is equivalent to $S_D = 77$ J/K mole. If we had taken this adsorption energy, instead of about 130 kJ/mole taken from Madden *et al.* (*14*), for a comparison with our $G_D(\Theta)$ data, we would have arrived at nearly the same values for k_0 and S_D. We make this point because Christman *et al.* (*10*) in contradiction to Ibach *et al.* (*15*) found an isosteric heat of 130 kJ/mole for the Ni (111) surface, too. This discrepancy, already discussed in Ref. (*15*), shows that it would be interesting to compare the method of Ibach *et al.* and ours using data obtained for the same surface.

Generally, it can be said that the method of Ibach *et al.* provides more detailed information about desorption reactions than does ours. However, because it is based on detailed model considerations, its application is restricted to adsorption systems with well-characterized structural and vibrational properties (*15*). Moreover, it needs equilibrium data and therefore requires very time consuming measurements. Our method, on the other hand, allows one to extract the coverage dependence of the Gibbs free activation energy of desorption from a single desorption spectrum. Although it might be argued that the transition-state theory, on which our method is based, cannot unambiguously be applied to desorption reactions, our method should be preferred to the conventional TDS maxima evaluation, in that is extracts more information from a desorption spectrum.

Finally it should be mentioned that the application of our method is not restricted to adsorption systems which exhibit a proportionality between work-function change and coverage. A great variety of physical quantities may be used as a coverage monitor during desorption, such as, for instance, Auger electron or photoelectron intensities. Norton *et al.* (*16*) recently used UPS to monitor thermal desorption. Using a simple, new experimental setup proposed by Feulner and Menzel (*17*), even by pressure monitoring it should be possible to obtain TDS results sufficiently reliable for our method to yield useful results.

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