

## RATES OF MOLECULAR DESORPTION FROM SOLID SURFACES: ADSORPTION SITE DEPENDENCE FOR CO ON Ni(100)

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The role of different adsorption sites on the rate of desorption of CO from Ni(100) surfaces has been studied using the classical stochastic diffusion theory (CSDT) formulation. The microscopic parameters of the system (force constants and bond energies) have been obtained from ab initio cluster calculations (Ni<sub>14</sub> and Ni<sub>20</sub> clusters) with generalized valence bond wavefunctions. In good agreement with experiment, our calculations show that desorption occurs in two temperature ranges: 400–600 K and 150–250 K. In the higher-temperature range, the one-fold and two-fold sites are primarily responsible for the desorption rate, while for the lower-temperature range, the four-fold (weakest binding site) is dominant (experimentally achieved by poisoning the surface with S).

Recently we have proposed [1,2] a new theoretical approach using classical stochastic diffusion theory (CSDT) to predict desorption rates from solid surfaces. In this paper we consider a system with several non-equivalent surface sites and examine the rates of desorption from these various sites. This is a problem of considerable experimental importance since, in many metals, several competing sites for adsorption may simultaneously play a role. In addition, a knowledge of the rates of desorption from different sites on a surface can serve as a useful tool in the interpretation of experiments where some of the sites are blocked (poisoned) by other coadsorbed species. For example, recent experiments by Madix and co-workers [3], using temperature-programmed desorption (TPD), show that CO desorption from a sulfur-poisoned Ni(100) surface occurs from the weakly bonded four-fold site. In contrast, on a clean Ni(100) surface, CO is known to adsorb preferentially on the one-fold and two-fold sites [3]. In addition, Goodman et al. [4] and Koel et al. [5], using TPD to study coadsorbed hydrogen and CO on Ni(100), have found evidence for a weakly

bound CO state that desorbs at  $\approx 200$  K, while CO adsorbed on the clean surface desorbs in the range 500–600 K.

We will present here the rates of desorption of CO from the one-fold, two-fold, and four-fold sites of a Ni(100) surface. The rates of desorption were evaluated using the CSDT recently developed to treat desorption of atoms and molecules from solid surfaces [1,2]. This theory relates the desorption rates to a simple expression involving the microscopic parameters of the system (vibrational frequencies, and bond energies). These parameters were obtained using ab initio generalized valence bond (GVB) calculations on finite clusters to model a CO molecule adsorbed at various sites of the metal surface.

To calculate the interaction potentials we have used two different nickel clusters, Ni<sub>14</sub> and Ni<sub>20</sub> (see fig. 1) previously used to model adsorption sites on Ni(100) surfaces. The Ni<sub>14</sub> cluster was employed in the calculation of CO adsorbed to the one-fold (on-top) site, which is shown as site A in fig. 1a. The Ni<sub>20</sub> cluster was used in the study of CO adsorbed on the two-fold and four-fold sites of the Ni(100) surface (sites B and C, respectively, in fig. 1b). These clusters were chosen so as to minimize edge effects on the chemisorptive bond. Details of these clusters, including work functions, elec-

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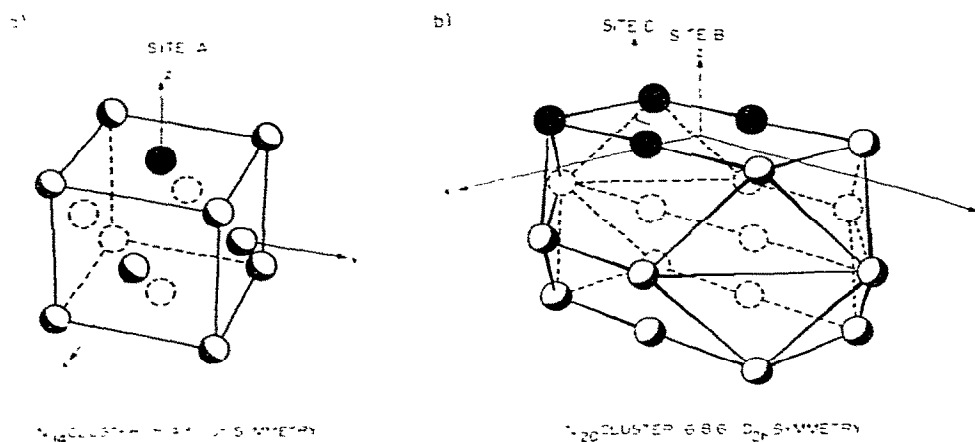


Fig. 1. Clusters used for the ab initio calculations. (a) Ni<sub>14</sub> cluster. Site A denotes the one-fold (on-top) bonding site. (b) Ni<sub>20</sub> cluster. Sites B and C denote the two-fold (bridging) and four-fold (hollow) bonding sites, respectively.

tron affinities, spectrum of states, and complete calculational details, have been presented elsewhere (for Ni<sub>14</sub>, see ref. [6]; for Ni<sub>20</sub>, see ref. [7]). All the calculations have been performed using the GVB method with a double-zeta (DZ) basis set [6], and including correlation in the two  $\pi$  bonds of CO [GVB(2/4)]. A more complete description of the calculational details can be found in refs. [6,7].

For the on-top site of the Ni<sub>14</sub> cluster we find an optimum Ni-C distance of 1.94 Å, and a perpendicular geometry (table 1). For the two-fold and four-fold sites (Ni<sub>20</sub> cluster), we also obtain a perpendicular geometry with surface-to-carbon distances of 1.67 and 1.46 Å, respectively (table 1). For all three sites the total energy increases sharply as we bend the CO molecule away from the perpendicular configuration. The C-O bond lengths remained practically unchanged (see table 1). In agreement with experiment

[3-5,8] we find that CO binds strongly to the one-fold and two-fold sites (1.34 and 1.19 eV, respectively), while binding weakly to the four-fold site (0.47 eV). The existence of this weaker bond at four-fold sites has been previously suggested by Goodman et al. [4] and Koel et al. [5] for CO coadsorbed with hydrogen on Ni(100) surfaces. The adsorption of CO on the four-fold site has also been observed by Madix et al. [3] on sulfur-poisoned Ni(100) surfaces. The frequencies and force constants for CO-surface and C-O stretch vibrations, as well as the frustrated rotation (bending of the CO away from the linear geometry in a plane bisecting two adjacent surface Ni atoms), are shown in table 2. As expected, the *surface-adsorbate stretch* frequency decreases for systems with longer equilibrium Ni-C distances (401, 331, 236 cm<sup>-1</sup> for one-fold, two-fold and four-fold, respectively). The *bending* frequencies for the on-top and bridging

Table 1  
Calculated equilibrium distances, angles, and bond energies for CO on Ni(100) (all distances in Å, angles in deg and energies in eV)

Site	$R^a$ )	$R_c^b$ )	$R_{C-O}$	$\angle$ surface-C-O	CO-surface bond energy
one-fold	1.943	1.943	1.146	180	1.34
two-fold	1.666	2.079	1.147	180	1.19
four-fold	1.460	2.286	1.159	180	0.47

a) Optimum perpendicular distance between the carbon atom and the Ni(100) surface.

b) Distance from carbon to nearest neighbor nickel atom(s).

Table 2  
Calculated frequencies for CO chemisorbed on Ni(100) surfaces  
(all frequencies are given in  $\text{cm}^{-1}$ )

Site	$\Omega_0$ a)	$\Omega_\tau$ b)	$\Omega_{\text{CO}}$
one-fold	401	327	2129
two-fold	331	338(361)	2209
four-fold	236	484	1933

a) Surface-CO stretching frequency. These frequencies were not modified in calculating desorption rates.

b) Surface-C-O bending frequency (for the two-fold site the quantity in parentheses represents bending of the C-O towards a surface Ni atom).

(two-fold) sites are nearly the same (327 and 338  $\text{cm}^{-1}$ ), while the four-fold site exhibits a much larger value (484  $\text{cm}^{-1}$ ). The calculated C-O *stretch* frequencies are shown in table 2 (2129, 2209, and 1933  $\text{cm}^{-1}$ , for one-fold, two-fold, and four-fold, respectively). These values are  $\approx 10\%$  larger than the corresponding experimentally observed results [9]. This discrepancy may be a consequence of our not including Ni-Ni vibrations in the normal-mode analysis as well as the lack of coverage effects in the theoretical calculations.

The CSDT approach to calculate molecular desorption rates [1,2] is based on a classical formulation the desorption process whereby the motion of the adsorbed particle is described by the classical newtonian equation. The motion of those surface atoms, which are strongly interacting with the adsorbed particle, is described using the generalized Langevin approach developed by Adelman and Doll [10] and Tully and co-workers [11]. In the present formulation [1,2], the equations describing the motion of the surface atoms are solved formally (by the Laplace transform method) and substituted into the equation of motion for the adparticle. This leads to a generalized Langevin equation of motion for the adsorbate, including the interaction with the crystal. This equation describes the motion of the adsorbed molecule interacting directly with a heat bath (consisting of all remaining crystal atoms). Since the characteristic desorption times are much longer than the typical molecular vibration periods we apply the markovian approximation to transform the generalized Langevin equation for the adparticle into a Langevin equation (brownian oscillator). This equation is further transformed to the corresponding generalized Liouville equation [12] for

the probability distribution function. Following Kramers' procedure [12], we solve the generalized Liouville equation under steady-state conditions and obtain the desorption flux. The final expression [1,2] for the rate of desorption can be directly obtained from the flux and is given by

$$R = (kT/2\pi m)^{1/2} \left( \int_{-\infty}^{\infty} \exp[-V(z)/kT] dz \right)^{-1} \times f(T) \exp(-D_e/kT), \quad (1)$$

where  $m$  is the mass of the adparticle,  $k$  is Boltzmann's constant,  $T$  is the absolute temperature,  $V(z)$  the surface-adparticle interaction potential, and  $D_e$  is the corresponding dissociation energy. The function  $f(T)$  will be discussed below. For the temperatures relevant for desorption ( $kT \ll D_e$ ), the expression for the rate, eq. (1) simplifies to

$$R = (\Omega_0/2\pi) f(T) \exp(-D_e/kT), \quad (2)$$

where  $\Omega_0$  is the (surface-adsorbate stretch) frequency associated with the minimum in  $V(z)$ .

The function  $f(T)$  in eqs. (1) and (2) takes into account the fact that energy stored in adsorbate modes (other than surface-adsorbate stretching motion) can aid the desorption process. In particular, for CO desorbing from Ni surfaces, the surface-C-O bending motion (frustrated rotation) has an important influence upon the desorption rate due to its direct coupling to the surface. The inclusion of this mode (in the harmonic approximation) in the formalism [1,2] leads to an expression for  $f(T)$  of the form

$$f(T) = 2\mu^2 \Omega_\tau^2 \vartheta_0^2 / \pi kT, \quad (3)$$

where  $\mu^2 \Omega_\tau^2$  is the force constant for the frustrated rotational mode and  $\vartheta_0$  is the maximum angle of rotation (which we take to be  $\pi/2$ ). For the one-coordinate and four-coordinate sites, the four-fold symmetry axis implies that in the harmonic approximation the potential energy for the azimuthal rotation (of a bent surface-C-O unit) about the surface-carbon axis will be uniform (since both bending modes have equal force constants). For the two-coordinate site, the two bending modes have nearly the same frequencies (338 and 361  $\text{cm}^{-1}$ ) so that the azimuthal potential curve is nearly flat. As a consequence, the force coupling this azimuthal rotational mode with the surface will be negligible and

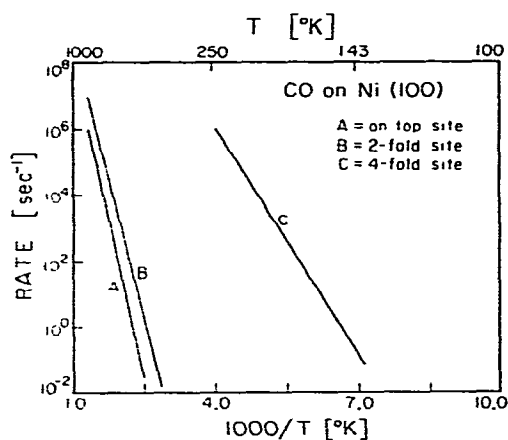


Fig. 2. Rates of desorption versus temperature. Curves A, B and C represent the desorption rates from sites A, B and C in fig. 1.

the energy stored in this mode cannot be easily transferred to the translational motion of the desorbing molecule.

Using eq. (1), including the frustrated rotation as in eq. (3), we obtain the calculated rates of desorption (fig. 2) of CO adsorbed on the three different sites of the Ni(100) surface. Curves A and B correspond to rates of desorption from the one-fold and two-fold sites, respectively. As one would expect from the smaller bond energy, the two-fold site leads to a faster desorption rate (about two orders of magnitude). However, the one-fold site shows a similar pre-exponential factor ( $2.0 \times 10^{15} \text{ s}^{-1}$  at 400 K) to that of the two-fold site ( $1.9 \times 10^{15} \text{ s}^{-1}$  at 400 K). Desorption from these two sites occurs in a temperature range between 400 and 600 K. From the present calculations one should expect coverage-dependence effects in the desorption rates. In particular, at low coverages the CO molecules should chemisorb on the on-top sites, leading to a desorption rate given by curve A in fig. 2. At higher coverages, repulsive CO-CO interactions [13] can lead to population of the two-fold sites resulting in a total rate of desorption that will be a combination of curves A and B (fig. 2).

Curve C in fig. 2 corresponds to the rate of desorption from a four-fold site. In excellent agreement with experiment [3-5], the desorption from this site occurs in a temperature range between 150 and 250 K. The pre-exponential factor in this case ( $2.1 \times 10^{15} \text{ s}^{-1}$  at 400 K) is similar to that of the one-fold and

two-fold sites. Although the surface-carbon stretch frequency for the four-fold site is about half of that of the other two sites, the frustrated rotational frequency is larger, compensating for the decrease in  $\Omega_0$ . This effect can be easily seen by comparing the pre-exponential factors for the same value of the desorption rate (at different temperatures). For example, the pre-exponential factors corresponding to a desorption rate of  $\approx 1 \text{ s}^{-1}$  are  $1.7 \times 10^{15}$  and  $1.8 \times 10^{15} \text{ s}^{-1}$  (at 500 K) for the one-fold and two-fold sites, respectively. The corresponding value for the four-fold site is  $5.5 \times 10^{15} \text{ s}^{-1}$  (at 200 K).

Summarizing, we have compared the rates of desorption of CO from three different sites of the Ni(100) surface. We find that our theoretical calculations for the four-fold site are consistent with this being the weakly bonded adsorption site for which desorption is observed at  $\approx 200 \text{ K}$ . Moreover, we predict a substantial difference in the desorption rates from the one-fold and two-fold sites that may be observed in experimental studies of coverage dependence. At present we are in the process of calculating the CO-CO and CO-sulfur interaction potentials in order to study both coverage dependence of the desorption rates and the effects of sulfur poisoning.

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