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Coverage and site distribution effects in the desorption of carbon monoxide from sulfur-covered Ni(100)

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Abstract

Static and time resolved Fourier transform infrared spectroscopic studies were combined with threshold temperature programmed desorption studies to examine the effects of adsorbed sulfur on the kinetics of CO desorption from Ni(100). The appearance of new desorption states upon the addition of sulfur to Ni(100) can be attributed to the occupation of four-fold hollow and modified bridge-bonded species produced by the presence of sulfur. The observed kinetics of desorption from these surfaces is very sensitive to the initial binding site distribution of the adsorbed CO. Adsorbing at 100 K without anneal leads to a reduction in the measured desorption energy, except at the highest sulfur coverages studied. Apparently, relaxation of the adsorbed phase from a nonequilibrium distribution among sites on the surface during temperature programmed desorption is incomplete, leading to stronger repulsive interactions on the average and reduced desorption energies following adsorption at low temperature.

Keywords: Adatoms; Auger electron spectroscopy; Carbon monoxide; Catalysis; Low index single crystal surfaces; Models of surface kinetics; Nickel; Thermal desorption; Vibrations of adsorbed molecules

1. Introduction

The adsorption of carbon monoxide on Ni(100) and sulfided Ni(100) surfaces has been characterized using temperature programmed desorption and vibrational spectroscopies [1–7]. In thermal desorption studies on sulfided Ni(100), Johnson and Madix [1] and Goodman and Kiskinova [5] observed a decrease in the CO saturation coverage in the high temperature state and the emergence of new binding states with lower desorption activation energies in the presence of adsorbed sulfur. Gland et al. suggested [2], based on the electron energy loss vibrational spec-

trum of CO adsorbed on S/Ni(100), that the modification of CO adsorption is caused by local interactions between CO and adsorbed sulfur. Hardegree, Ho and White [3] also showed that adsorbed S redistributes CO into several lower temperature desorption states. Their results indicated that site-blocking is the dominant mechanism by which CO coverage is affected, while short-range electronic interactions influenced the desorption energies. Benzinger, Schoofs, and Myers, who studied the effects of the $p(2 \times 2)$ adlayer on CO adsorption [4], concluded that sulfur atoms block CO adsorption at nearest-neighbor on-top sites when CO is adsorbed at 170 K, but when the mixed adlayer is heated to 325 K, it appears to undergo rearrangement to accommodate adsorption of CO onto atop sites.

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The objective of the work reported here was to determine the binding site distributions of CO on Ni(100) at different sulfur coverages, to associate the binding sites with the desorption states introduced by the coadsorption of sulfur and to investigate the possible effects of differences in the initial site distribution on the kinetics of desorption using Fourier transform infrared spectroscopy. Understanding the dependence of the Arrhenius rate parameters on the surface coverage is necessary in order to account for possible variations in reaction rates over wide ranges of temperature and pressure. These values may depend on the exact conditions used for their determination. In particular, rate parameters determined by temperature programmed desorption using the threshold method following adsorption at low temperature may not necessarily be suitable for extrapolation to conditions of steady state at a higher, constant temperature for estimates of desorption rates in heterogeneously catalyzed reactions, for example.

Sulfur adsorption on Ni(100) has been well characterized by several groups [8–10]. Sulfur adsorbs into the four-fold hollows of the Ni(100), forming a $p(2 \times 2)$ structure at 0.25 ML and a $c(2 \times 2)$ structure at 0.50 ML.

Carbon monoxide adsorbs molecularly [2] and desorbs by first order kinetics on the clean Ni(100) and sulfided Ni(100) surfaces [1]. On clean Ni(100) carbon monoxide adsorbs into atop and bridge sites [2]. As sulfur is adsorbed, new sites for CO adsorption develop. Carbon monoxide adsorbs into atop and bridge sites in clean surface patches, but in addition four-fold and bridge sites defined by $p(2 \times 2)$ S cells or sites associated with the $c(2 \times 2)$ S structure are occupied [1,2,11–14].

In this work the relationship between the desorption kinetics of CO and its site distribution on the Ni(100) and S/Ni(100) was studied using threshold temperature programmed desorption (TTPD) and reflection absorption infrared spectroscopy (RAIRS). The RAIRS spectrometer was used to probe adlayers, varying in coverage, prepared by dosing at 100 K. In addition, surfaces initially saturated with CO were ramped slowly while IR spectra were collected simultaneously. It is clear from both TTPD and RAIRS that the initial preparation of the CO adlayer on the clean and sulfur-covered surfaces has a significant effect on the kinetics of desorption, and the

desorption kinetics parameters depend sensitively on the initial distribution of adsorbed CO. Also sulfur affects the site distribution and appears to interfere with redistribution by hindering CO diffusion.

2. Experimental

The experiments were conducted in an ultra-high vacuum chamber containing a quadrupole mass spectrometer, an argon bombardment gun, and a retarding field analyzer for both low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). A chromel–alumel thermocouple spot welded at the edge of the crystal was used to monitor temperature. The crystal was cooled by conduction through tantalum wires in thermal contact with a liquid nitrogen cooled copper block. These same wire supports were used to heat the crystal resistively.

The surface was cleaned through a series of Ar^+ ion bombardments at room temperature followed by annealings to 1200 K. Oxygen treatments at 600 K were performed as necessary to remove the excess carbon. Cleanliness was monitored by AES, and the surface was considered clean when no contaminants were observable, indicating a carbon coverage of less than 0.01 ML¹. The Ni(100) surface was verified to be well ordered using LEED.

Subsaturation sulfur overlayers were formed by background dosing H_2S (Matheson, 99.5%) at 300 K [15–17]. The surface was then annealed to 800 K for five minutes to assure decomposition of the H_2S and uniformity of the overlayer structure. For saturation coverages the procedure was repeated until further amounts of sulfur could not be deposited. In order to deposit further sulfur to saturate the $c(2 \times 2)$ S structure the sample temperature was increased to 700 K while dosing. This was followed by further annealing to 800 K for five minutes. In order to establish the completion of the $c(2 \times 2)$ overlayer structure a saturation dose of CO followed by a temperature programmed desorption experiment was performed. The absence of CO desorption above 200 K in the TPD

¹ A monolayer (ML) is defined as one adsorbate molecule per surface nickel atom.

spectrum indicates that the sulfur $c(2 \times 2)$ overlayer is complete [12].

The IR spectra were obtained with a Nicolet model 740 Fourier transform infrared spectrometer with a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector. Sample and background spectra, with the crystal at constant temperature, were collected by averaging 1200 scans at 8 cm^{-1} resolution over an acquisition time of 8 min. The sample was prepared by background dosing carbon monoxide (Matheson, research purity, 99.99%) at 100 K to obtain the desired coverage. Immediately thereafter the IR spectrum was recorded, TPD was performed to determine the coverage, and a background IR spectrum was recorded for normalization. To produce the time-resolved IR spectra, sample and background spectra were collected by averaging 120 scans at 8 cm^{-1} resolution over an acquisition time of 16 s. The sample was prepared by saturating the surface with CO at 100 K. IR spectra were then recorded as the temperature was ramped at 0.3 K/s. The surface was then cooled and background IR spectra were obtained, as the surface was heated at 0.3 K/s, for normalization. The surface was then resaturated with CO, and a TPD at the same heating rate was collected.

3. Results

Temperature programmed desorption (TPD) and infrared (IR) spectra for saturation coverages of CO adsorbed on Ni(100) at 100 K with varying sulfur coverages (0.00–0.50 ML) are shown in Fig. 1. These spectra are in agreement with previous studies [1–7]. Generally, there is a decrease in the amount of CO that can be adsorbed and an increase in the desorption rate with increasing sulfur coverage, indicated by a shift of the desorption peaks to lower temperature. Initially for $\theta_s = 0.00 \text{ ML}$, there is a dominant desorption peak at 456 K (β_2) and a broad feature composed of states near 305 K (α) and 227 K (γ), which are a consequence of CO–CO lateral interactions [18–20]. As the sulfur coverage is increased to 0.27 ML, where the $p(2 \times 2)\text{S}$ overlayer structure is dominant, four desorption features are evident; σ (141 K), α' (286 K), β_1 (367 K), and β_2 (407 K). The α' state is broad and may actually consist of two desorption features, since a distinct shoulder near 310 K is evident. Further increase of θ_s to 0.50 ML leads to the complete development of the $c(2 \times 2)\text{S}$ structure causing a disappearance of the α' , β_1 , and β_2 states. The only desorption feature present at $\theta_s = 0.50 \text{ ML}$ is the σ state.

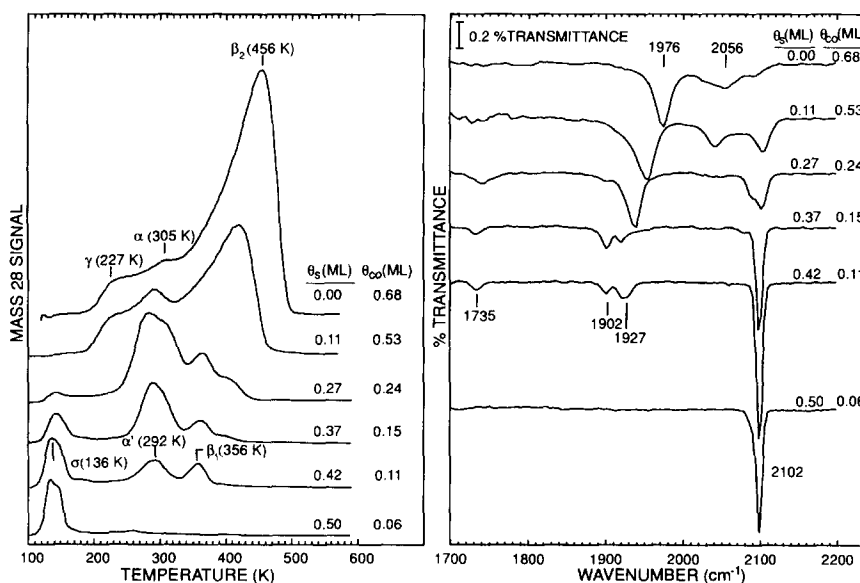


Fig. 1. TPD and FTIR spectra of saturation coverages of CO on Ni(100) with varying sulfur overlayer coverages (0.00 to 0.50 ML). Heating rates for the TPD spectra were 10 K/s.

The infrared spectra give further insight into the evolution of the desorption states as the coverage of sulfur increases. For $\theta_s = 0.00$ ML a broad feature appears at 2056 cm^{-1} along with another peak at 1976 cm^{-1} which are assigned to adsorption onto atop and bridge sites, respectively [11,21]. The presence of 0.11 ML of sulfur produces three distinct vibrational features for adsorbed CO. These features are associated with bridge and atop sites (1956 and 2042 cm^{-1}) and a new site populated at 2104 cm^{-1} . The frequencies for the bridge bonded and atop CO are redshifted from their values on the clean surface just as expected for decreased CO–CO lateral interactions at the lower coverage, indicating that sulfur does not appear to have any *additional* effect on the atop and bridge bonded CO frequencies. At a fractional coverage of sulfur of 0.27 ML, there is a substantial decrease in the population of the atop site and increase in population of the state at 2103 cm^{-1} , which is associated with the $c(2 \times 2)$ S overlayer structures (see below). The feature assigned to adsorption on bridge sites is further redshifted to 1942 cm^{-1} , since the CO coverage and therefore the CO–CO interactions are reduced. For θ_s between 0.27 and 0.42 ML a feature which is assigned to adsorption in four-fold hollows in the sulfur over-

layer appears at 1743 cm^{-1} [2]. The splitting in the peaks near 1900 cm^{-1} (1902 and 1927 cm^{-1}) indicates local nonuniformities in the structure of adsorbed sulfur in the vicinity of the bridging sites. As the coverage of sulfur is increased to 0.50 ML the peak at $\sim 2100\text{ cm}^{-1}$ narrows and increases in height. Also, the peaks associated with adsorption on bridge and four-fold hollow sites vanish at $\theta_s = 0.50$ ML.

To gain further insight into the changes in the kinetics of desorption of CO as the amount of sulfur is increased, a series of coverage variation TPD and FTIR experiments were conducted over the entire range of sulfur coverage. TPD and IR spectra obtained for decreasing coverages of CO on clean Ni(100) collected by dosing at 100 K or by dosing at 100 K and annealing to progressively higher temperatures have been published previously [14]. The previous results showed that the kinetics of desorption of CO from the clean surface was significantly affected by the initial state of the adlayer. Heating at a rate of 10 K s^{-1} was sufficiently rapid to prevent relaxation of the adsorbed layer into its lowest energy configuration. In order to illustrate the effects of adsorbed sulfur the TPD and time-resolved FTIR are shown for CO desorption from clean Ni(100) for a

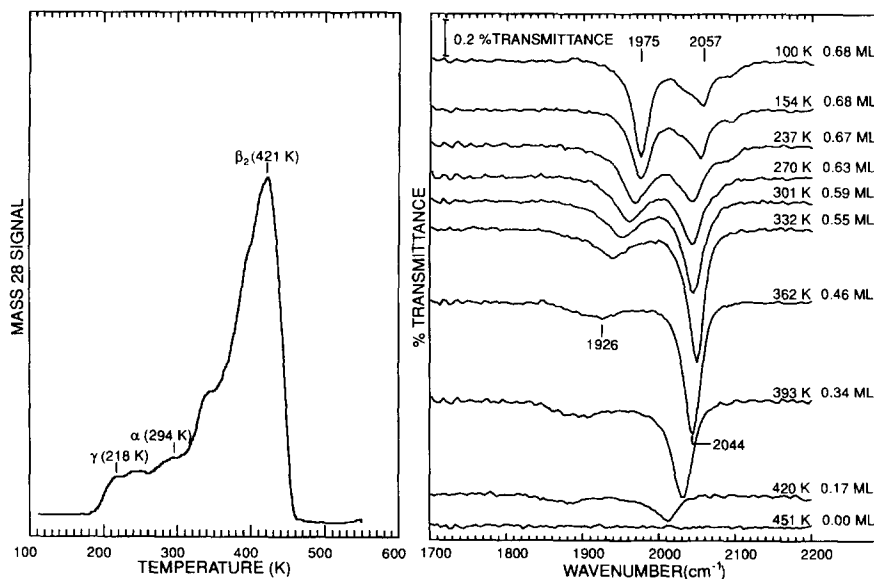


Fig. 2. TPD and FTIR spectra of a saturated Ni(100) surface obtained by ramping the temperature at 0.3 K/s.

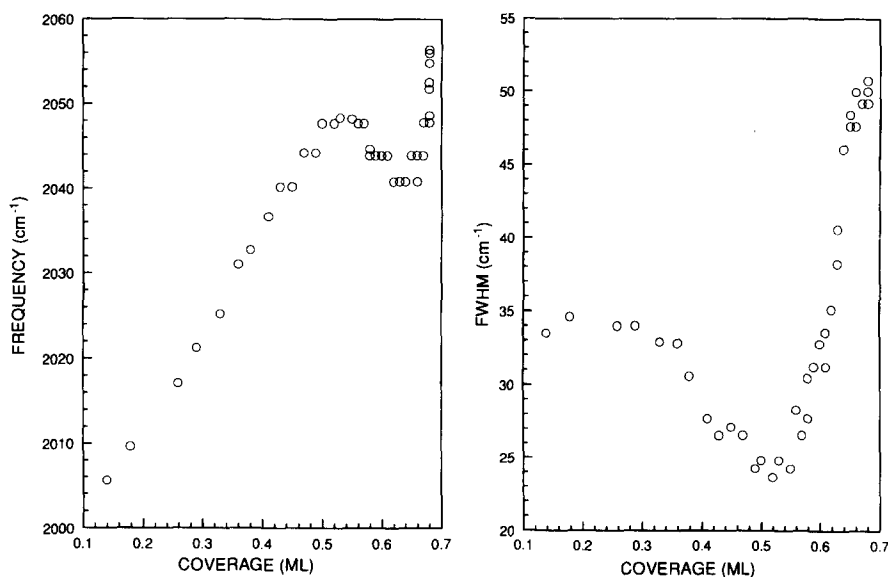


Fig. 3. Frequency and FWHM of the atop mode on Ni(100) as a function of coverage during the anneal.

heating rate of 0.3 K s^{-1} in Fig. 2. At this heating rate an equilibrium population of sites appears to be maintained throughout the temperature ramp.

The IR spectrum in Fig. 2 indicates that as the temperature is increased CO converts from the bridge to atop position, and there are slight shifts in frequency. As the temperature was increased to 362 K ($\theta_{\text{CO}} = 0.46 \text{ ML}$), there was a dramatic narrowing of the IR peak associated with the atop site and an

increase in its intensity. The narrowing of the atop peak is further illustrated by Fig. 3 which shows the full width at half maximum (FWHM) as a function of coverage. The feature associated with bridge sites broadened and decreased in peak magnitude; the frequencies also shifted to 2044 and 1926 cm^{-1} . Further, increasing the temperature to 420 K ($\theta_{\text{CO}} = 0.17 \text{ ML}$) lead to a continuous decrease in the population of atop and bridge sites. The frequency of CO

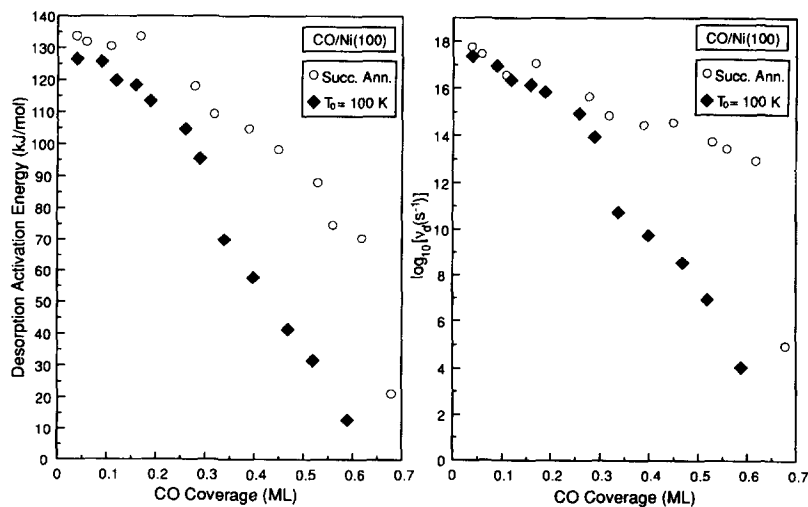


Fig. 4. Desorption activation energy and pre-exponential factor for CO adsorbed on Ni(100).

on the atop site decreased to 2022 cm^{-1} , while the bridge site feature broadened into a feature centered at 1879 cm^{-1} [11,21]. Note that the frequency associated with the atop-bound CO exhibits under went a complex dependence on coverage (Fig. 4), while the frequency in the bridge position decreased continuously with decreasing coverage. The continuous decrease in frequency with decreasing coverage below 0.5 ML is indicative of decreasing lateral interactions due to both dipolar and through-surface interactions. The dramatic narrowing of the linewidth at 0.5 ML has been attributed to increased homogeneity of the adlayer with CO residing in atop positions at this coverage forming a $c(2 \times 2)$ structure [11,21,22]. The effects of the nonequilibrium distribution on the desorption kinetics from the clean surface are reproduced here for comparison (Fig. 4).

The TPD obtained at a heating rate of 10 K s^{-1} and the IR spectra obtained by dosing at 100 K on a Ni(100) surface covered with 0.27 ML sulfur for various coverages of CO are shown in Fig. 5; the four desorption states observed in Fig. 1 are reproduced. As the CO coverage was decreased from 0.24 to 0.18 and 0.14 ML, desorption from the σ , α' , β_1 ,

and β_2 states diminished simultaneously. The shift of the peak temperature of the α' state with CO coverage indicates the presence of lateral interactions among the adsorbed CO and a coverage-dependent desorption energy. Below $\theta_{\text{CO}} = 0.14\text{ ML}$ the σ state became undiscernible, and the only desorption states populated were the α' , β_1 , and β_2 . The population of all three peaks decreased with coverage ($\theta_{\text{CO}} = 0.06\text{--}0.03\text{ ML}$), accompanied by a slight shift to higher temperatures.

The IR spectra reveal several features at saturation (Fig. 5). A small peak centered at 1743 cm^{-1} is present which is assigned to adsorption into four-fold hollows of $p(2 \times 2)\text{S}$ structures. The strong feature which appears at 1942 cm^{-1} and its small shoulder at 1903 cm^{-1} are assigned to adsorption onto two distinct bridge sites. At 2049 cm^{-1} a small broad feature appears which is associated with adsorption on atop sites essentially unaffected by adsorbed sulfur. Finally a peak at 2103 cm^{-1} with a shoulder at 2093 cm^{-1} is present. The peak at 2103 cm^{-1} is associated with the $c(2 \times 2)\text{S}$ structure (Fig. 1). As the CO coverage was decreased from saturation to 0.18 ML there was a decrease in the peak height of

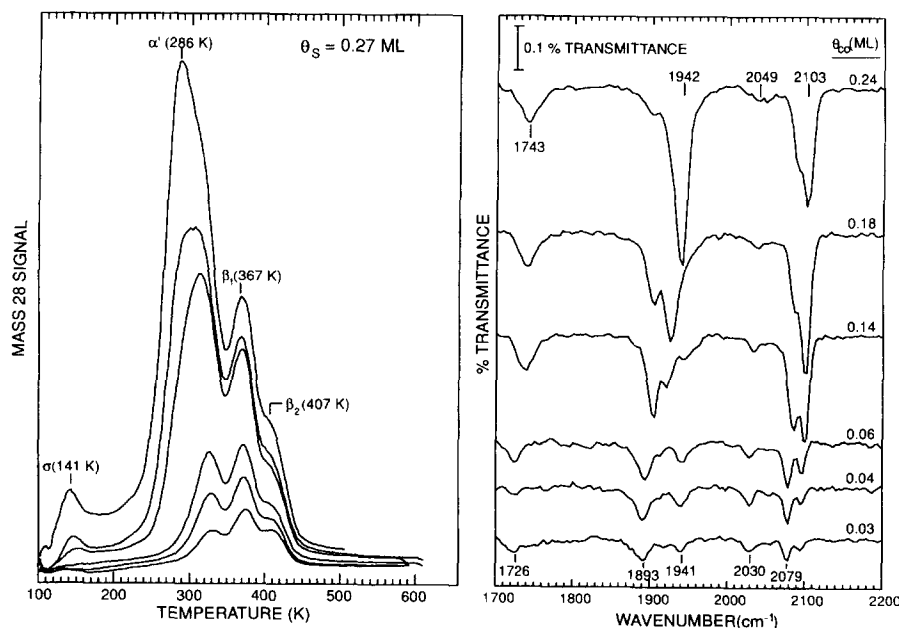


Fig. 5. TPD and FTIR spectra of various coverages of CO adsorbed on $\text{S}(\theta = 0.27\text{ ML})/\text{Ni}(100)$ obtained by dosing at 100 K. Heating rates for the TPD spectra were 10 K/s .

the mode at 1942 cm^{-1} , a slight increase of the peak height of the lower frequency bridge site, and a shift in the frequency of each state to 1926 and 1917 cm^{-1} , respectively. There was also a redshift in the modes at 1743 and 2049 cm^{-1} to 1741 and 2039 cm^{-1} , respectively. As the coverage was further decreased to 0.14 ML there was a continuous decrease in peak height of the modes near 1926 and 2103 cm^{-1} . Also, two sets of overlapping peaks became further resolved; the three peaks at 1907 , 1924 and 1943 cm^{-1} and the two peaks at 2089 and 2101 cm^{-1} emerged. The features at 1741 and 2039 cm^{-1} shifted to 1740 and 2036 cm^{-1} , respectively. At $\theta_{\text{CO}} = 0.06\text{ ML}$ the peak heights of all the modes decreased to similar values. As the coverage was decreased to 0.03 ML the number of discernible peaks remained the same, as each further decreased in peak height. Generally, the redshifts observed are indicative of the persistence of CO–CO interactions at this sulfur coverage.

The saturation TPD spectra obtained for a $\text{S}(0.28\text{ ML})/\text{Ni}(100)$ surface saturated at 100 K and the corresponding time-resolved IR spectra collected are shown in Fig. 6. At saturation ($\theta_{\text{CO}} = 0.22\text{ ML}$) the four desorption states (121 K (σ), 253 K (α'), 321 K (β_1) and 356 K (β_2)) are similar to those popu-

lated in the coverage variation experiments, as expected. The saturation IR spectrum is similar to the spectrum collected in the coverage variation experiment with only slight shifts in some of the peaks. A small peak is centered at 1736 cm^{-1} and assigned to adsorption into $p(2 \times 2)\text{S}$ four-fold hollows. The prominent feature at 1931 cm^{-1} and the small peak at 1903 cm^{-1} are assigned to adsorption onto bridge sites. Finally a peak at 2103 cm^{-1} with a shoulder near 2083 cm^{-1} is present. The peak at 2103 cm^{-1} is associated with the local patches of $c(2 \times 2)\text{S}$ structures, since it is the sole feature observed in the IR of CO adsorbed on the fully saturated $c(2 \times 2)\text{S}$ surface. As the temperature is increased above 132 K ($\theta_{\text{CO}} = 0.20\text{ ML}$), there is a dramatic decrease in the 2103 cm^{-1} peak height, while the shoulder at 2083 cm^{-1} increases slightly. The other features remain approximately the same. Further increase in temperature to 147 K ($\theta_{\text{CO}} = 0.20\text{ ML}$) leads to resolution of the peak near 2083 at 2088 cm^{-1} . The feature at 1736 cm^{-1} is nearly gone at this temperature also. Other discernible modes appear at 1905 , 1933 , and 2058 cm^{-1} . Increasing the temperature to 179 K ($\theta_{\text{CO}} = 0.20\text{ ML}$) did not cause any significant change. Further increase to 272 K ($\theta_{\text{CO}} = 0.09\text{ ML}$) led to a simultaneous decrease of the features at

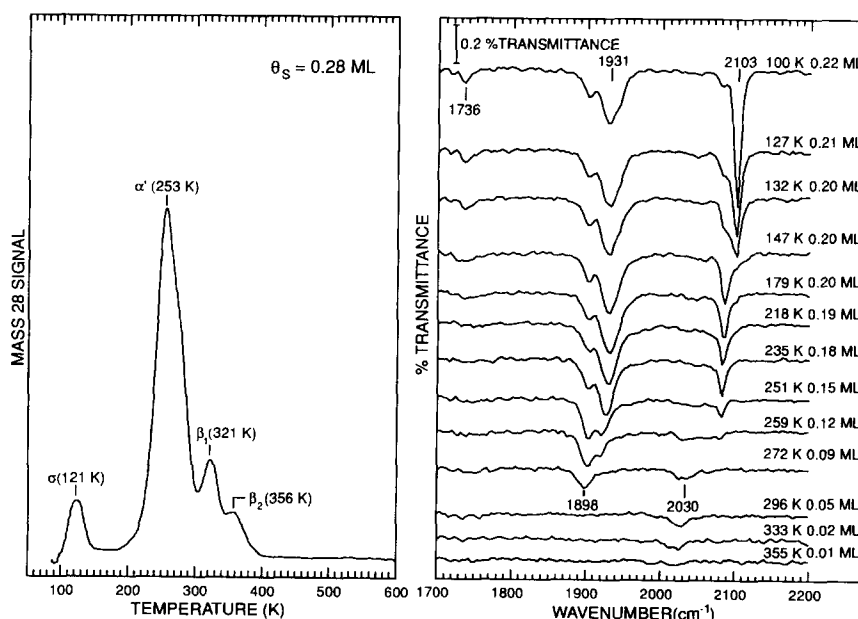


Fig. 6. TPD and FTIR spectra of a saturated $\text{S}(\theta = 0.28\text{ ML})/\text{Ni}(100)$ surface obtained by ramping the temperature at 0.3 K/s .

2083, and 1932 cm^{-1} , leaving a peak at 1893 cm^{-1} and a broad feature centered at 2032 cm^{-1} . At 296 K ($\theta_{\text{CO}} = 0.05\text{ ML}$) the peak at 2028 cm^{-1} was the only observed feature; this peak vanished above 355 K . It is noteworthy that the frequencies of all states remain constant up to 251 K and that the redshifts that occur above 250 K amount only to a few wavenumbers. For this slow heating rate it appears that desorption of CO between 0.22 and 0.18 ML does not change the average CO–CO lateral interaction. Only when the coverage falls below 0.18 ML is there evidence for decreased lateral interactions.

The relationships inferred from the TPD and IR between the desorption states, the mode frequencies and the site populations are listed in Table 1; overall there is agreement with previous results [2]. Moreover, the resolution of IR indicates that desorption from the α' state is a composite, comprised of desorption from two distinct bridging sites and a four-fold hollow. Kinetic parameters calculated for the CO adlayers prepared by dosing at 110 K or annealing surfaces saturated at 200 K prior to TPD are shown in Fig. 7 for 0.28 ML adsorbed sulfur. To determine the coverage dependence of the desorption activation energy, E_d , and pre-exponential factor, ν_d , for desorption, the threshold temperature programmed desorption (TTPD) analysis method was employed [23]. Note that near saturation at 110 K the

Table 1

Correlations between desorption states, the mode frequencies and site populations for CO on S(0.27 ML)/Ni(100)

σ	$2104\text{--}2100\text{ cm}^{-1}$	associated with local $c(2\times 2)\text{S}$ patches
α'	$2093\text{--}2078\text{ cm}^{-1}$	
	$1942\text{--}1920\text{ cm}^{-1}$	bridge "clean"
	$1907\text{--}1893\text{ cm}^{-1}$	bridge $p(2\times 2)\text{S}$
	$1743\text{--}1724\text{ cm}^{-1}$	four-fold $p(2\times 2)\text{S}$
β_1	–	–
β_2	$2053\text{--}2025\text{ cm}^{-1}$	atop "clean"

σ state is not used in the kinetic analysis. Varying the CO coverage by dosing at 100 K gave $E_d = 40 \pm 10\text{ kJ/mol}$ and $\nu_d = 10^{6 \pm 2}\text{ s}^{-1}$, independent of coverage. However, desorption from surfaces on which the saturated coverages of CO were preannealed led to a desorption activation energy ($E_d = 90 \pm 5\text{ kJ/mol}$) independent of coverage up to $\theta_{\text{CO}} = 0.15\text{ ML}$, whereafter E_d decreased gradually to 70 kJ/mol . The pre-exponential factor of $10^{14 \pm 1}\text{ s}^{-1}$ was approximately constant throughout the coverage range [12]. These differences in kinetic parameters appear to result from the very different initial site distributions and the different manner with which the site distribution and lateral interactions change during desorption.

The overlayer structure at a sulfur coverage of 0.42 ML is predominately $c(2\times 2)$. TPD and IR

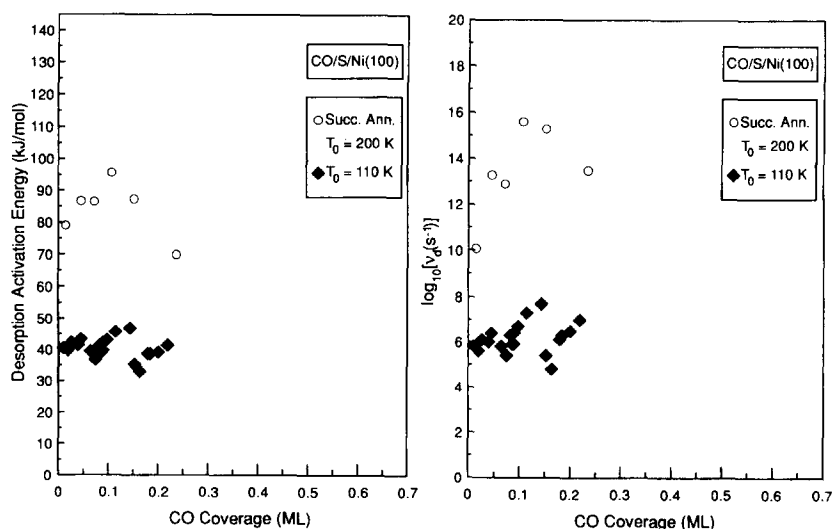


Fig. 7. Desorption activation energy and pre-exponential factor for CO adsorbed on S($\theta = 0.28\text{ ML}$)/Ni(100).

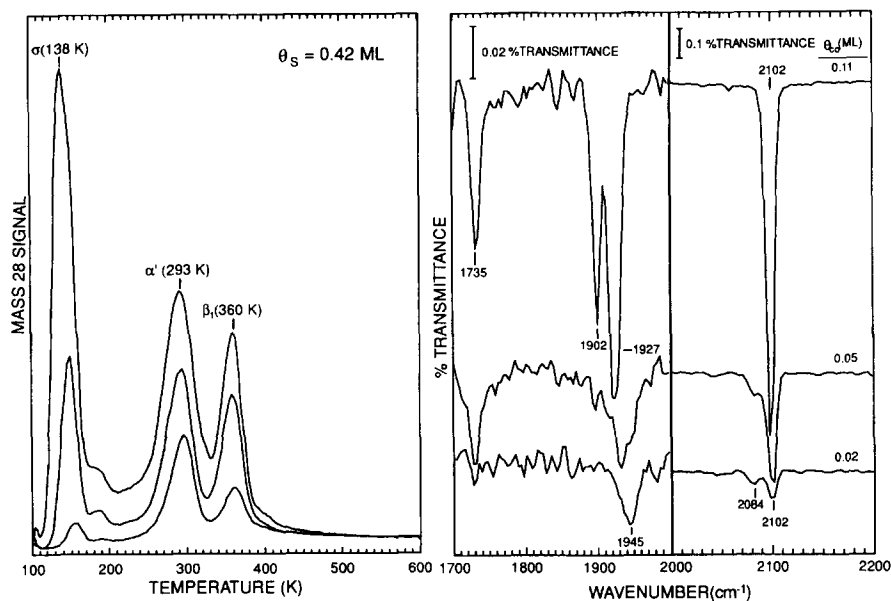


Fig. 8. TPD and FTIR spectra of various coverages of CO adsorbed on S($\theta = 0.42$ ML)/Ni(100) obtained by dosing at 100 K. Heating rates for the TPD spectra were 10 K/s.

spectra for various coverages of CO on S(0.42 ML)/Ni(100) surfaces obtained by dosing at 100 K are shown in Fig. 8. At saturation ($\theta_{\text{CO}} = 0.11$ ML) three major desorption states are present. The σ

state which increases with sulfur coverage, is centered at 138 K. The α' and β_1 states, which decrease with further sulfur coverage, are shifted to 293 and 360 K, respectively. As the CO coverage is

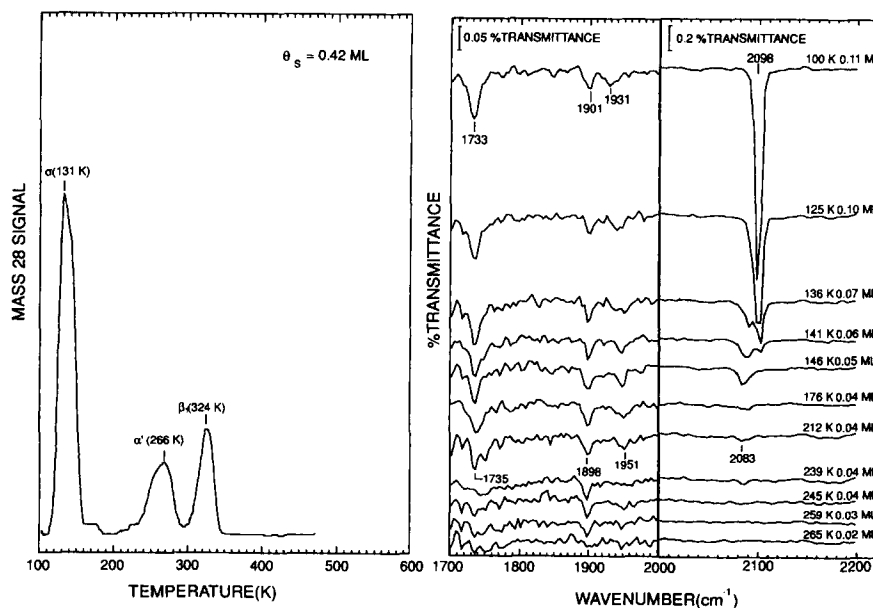


Fig. 9. TPD and FTIR spectra of a saturated S($\theta = 0.42$ ML)/Ni(100) surface obtained by ramping the temperature at 0.3 K/s.

decreased from saturation to 0.05 ML, desorption from the σ , α' and β_1 states decreases simultaneously. Desorption from the σ state decreased preferentially. Decreasing the initial CO coverage to 0.02 ML led to a further decrease of the σ , α' and β_1 states; the σ (153 K) state was less populated than the α' (299 K) and β_1 (362 K) at low total coverage. The constancy of the desorption temperatures of the three states with CO coverage indicates that the desorption energy is independent of CO coverage and that CO–CO interactions are minimal.

At saturation four peaks are distinguishable on this surface in the IR spectrum. These states appear to be the same as those observed at $\theta_s = 0.28$ ML. The dominant feature is a narrow peak centered at 2102 cm^{-1} ; the minor features appear at 1927 , 1902 , and 1735 cm^{-1} . The line widths for the features at 1902 and 1927 cm^{-1} are notably narrower than the corresponding bridge bonded features at a sulfur coverage of 0.28 ML. This difference in the linewidths also suggests that CO–CO interactions are weaker at a sulfur coverage of 0.42 ML. As the CO coverage decreases to 0.05 ML the discernible IR features decrease in peak height, and a shoulder is resolved at 2083 cm^{-1} . Further decrease in CO coverage (0.02 ML) leads to a continuing decrease in peak heights. A blueshift of the bridge bonded CO from 1927 to 1945 cm^{-1} occurred over the CO coverage range. No shift in the frequency of the binding state associated with the $c(2 \times 2)$ S structure was observed.

A TPD and time resolved IR spectra obtained with a heating rate of 0.3 K/s for a $S(0.42\text{ ML})/\text{Ni}(100)$ surface saturated at 100 K are shown in Fig. 9. At saturation three desorption states are present in the TPD spectrum – the σ state at 131 K , the α' state at 266 K and the β_1 state at 324 K . At saturation the IR spectrum consists of a dominant narrow feature centered at 2098 cm^{-1} , while minor features appear at 1931 , 1901 and 1733 cm^{-1} . Increasing the temperature to 136 K ($\theta_{\text{CO}} = 0.07\text{ ML}$) causes a dramatic decrease in the intensity of the peak at 2098 cm^{-1} . Also, a new feature is resolved at 2090 cm^{-1} , while the others remain approximately the same. Further increase to 146 K ($\theta_{\text{CO}} = 0.05\text{ ML}$) leads to the disappearance of the peak at $\sim 2100\text{ cm}^{-1}$. Increasing the temperature to 245 K ($\theta_{\text{CO}} = 0.04\text{ ML}$) leads to a simultaneous decrease of

the peaks at 1735 , 1949 , and 2083 cm^{-1} leaving the peak at 1898 cm^{-1} the only discernible feature. At 265 K ($\theta_{\text{CO}} = 0.02\text{ ML}$) there are no distinguishable features in the spectra. Kinetic parameters for desorption of the α' state of CO on $S(0.41\text{ ML})/\text{Ni}(100)$ were equal to $E_d = 40 \pm 5\text{ kJ/mol}$ and $\nu_d = 10^{7 \pm 1}\text{ s}^{-1}$ independent of both the CO coverage (up to 0.09 ML) or the adsorption temperature (100 – 200 K) [12].

4. Discussion

As evident from this study, sulfur changes the adsorption of CO on $\text{Ni}(100)$ in many ways. As discussed earlier, sulfur adsorbs into the four-fold hollows of $\text{Ni}(100)$ forming strong bonds with the surface. This leads to local effects whereby the sulfur physically blocks sites for CO adsorption. Furthermore, binding states for CO near the sulfur are expected to be altered. A smooth replacement of clean surface states by states characteristic of the sulfur-modified surface would be expected as the sulfur is increased, as is evident in Fig. 1 [1,7,24,25].

As the amount of sulfur is increased (0.00 – 0.50 ML) the amount of CO that can adsorb at saturation decreases (0.68 – 0.05 ML). Also, there is a continuous decrease in the magnitude of the desorption features associated with the clean surface (γ , α , β_2) and a growth in the states associated with sulfur (σ , α' , β_1) (Fig. 1). The infrared spectra show conversion of CO in the atop and bridge sites on the clean surface to CO adsorbed in four-fold hollows and bridge sites in the $p(2 \times 2)$ S structure and ultimately to sites associated with the $c(2 \times 2)$ S structure. The sulfur-covered surfaces affect dramatically the desorption kinetics of CO. The dominant desorption peak occurs at 286 K at $\theta_s = 0.27\text{ ML}$, compared to 456 K on the clean surface, producing a difference in desorption energies of approximately 45 kJ/mol . Also, it is clear from this study that the initial distribution of CO in the adlayer on the clean and sulfur-covered surfaces has a significant effect on the desorption kinetics.

The effect of site distribution on the desorption kinetics is pronounced on the $S(0.28\text{ ML})/\text{Ni}(100)$ surface. The sulfur overlayer, which is predominately a $p(2 \times 2)$ structure, yields additional sites for

adsorption. Adsorbing CO at 100 K (Fig. 5) leads to a similar distribution of site population throughout the entire range of coverage up to saturation. This distribution is reflected in the desorption profiles, which show population of the three major features at all CO coverages. This parallel occupation of sites of differing binding energy occurs apparently because sulfur interferes with the redistribution of CO by hindering CO diffusion. During TPD (Figs. 6 and 9) there is a sequential desorption from specific sites with limited diffusion of CO to other sites. Examination of the TRFTIR data of Figs. 6 and 9 shows that the σ desorption state arises from CO associated with the $c(2 \times 2)$ S structure (2103 cm^{-1}) and that the β_2 state arises from CO in atop sites relatively unaffected by coadsorbed sulfur (2030 cm^{-1}). The α' state, however, is a composite, arising initially from desorption from bridge (1950 cm^{-1}) and four-fold hollow sites (1735 cm^{-1}) at $\theta_s = 0.42 \text{ ML}$ and from bridge (1930 cm^{-1}) and four-fold hollow sites (1736 cm^{-1}) at $\theta_s = 0.28 \text{ ML}$. The high temperature shoulder on the α' TPD state is due to desorption from a second bridge site (1900 cm^{-1}). Either the binding state giving rise to the β_1 state was not observed in the TRFTIR or it must originate from the mode at 2030 cm^{-1} also. Even though the site distribution appears similar in Figs. 5 and 6, these different adlayers clearly produce slightly different CO–CO interactions. These differences manifest themselves in significantly different initial desorption kinetics.

The development of the $p(2 \times 2)$ S structure affects the coverage dependence of the kinetic parameters for desorption of CO in both the annealed and unannealed layers. At $\theta_s = 0.28 \text{ ML}$ the kinetic parameters are independent of CO coverage – certainly for the annealed adlayer. It appears that the adsorbed sulfur mitigates the CO–CO interactions so that they do not contribute significantly to the desorption kinetics. Indeed, the TRFTIR of Fig. 6 show smaller shifts in frequency of any of the states as desorption proceeds compared to the clean surface (Fig. 3). We do note, however, that redshifts are observed with decreasing CO coverage for the mixed CO/S adlayer when CO is adsorbed at 100 K (Fig. 5). We infer from this that the mixed adlayer can relax during heating to relieve these lateral interactions during desorption, if the heating rate is sufficiently

low. It is possible that the relaxation of these interactions give rise to the increase in desorption energy observed for the annealed layers compared to those obtained following adsorption at 100 K without anneal.

As the amount of sulfur was increased to 0.42 ML the patches of $c(2 \times 2)$ structures further developed throughout the surface. The desorption kinetics obtained for CO adlayers prepared by dosing at 100 and 200 K were determined using the leading edge of the α' state. The parameters calculated were $E_d = 40 \pm 5 \text{ kJ/mol}$ and $\nu_d = 10^{7 \pm 1} \text{ s}^{-1}$ both independent of coverage and temperature (Fig. 7). This indicates that the CO–CO interactions are minimal and that desorption is dictated by CO/Ni/S interactions. This behavior is expected since the Ni(100) is almost saturated with sulfur. The reason the desorption kinetics are similar for both adlayer preparations is that the site distributions are similar as a function of CO coverage. As seen in Figs. 8 and 9 as the coverage is increased there is a continuous population of the desorption states (σ , α' , β_1) and adsorption sites up to saturation.

5. Conclusions

The desorption kinetics of CO as determined by temperature programmed desorption are markedly affected by the initial state of the adlayer on both clean and sulfur-covered surfaces. For low to moderate sulfur coverages heating rates of 10 K/s lead to inhomogeneous distributions that reduce the apparent desorption energy. At higher sulfur coverages, inhomogeneities are reduced due to isolation of the adsorbed CO within the sulfur overlayer and the desorption kinetics depend less on the method of preparation.

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