

SURFACE SCIENCE LETTERS

THE INTERACTION OF COADSORBED HYDROGEN AND CARBON MONOXIDE ON Ni(100) *

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One of the more important problems of the surface science of heterogeneous catalysis is the understanding of how coadsorbed species interact. This problem is central to an understanding of the chemical reactions that occur during the dissociation and reassembly of reactants on a surface to form products. Recently, Goodman et al. [1] have reported a very interesting temperature programmed desorption (TPD) study of hydrogen coadsorbed with carbon monoxide on Ni(100) in which they postulate that a surface complex is formed by adsorbed CO interacting with preadsorbed H at 99 K. They showed that this complex was formed in significant quantities and caused both CO and H₂ desorption around 200 K. Since nickel is a good methanation catalyst [2], it is tempting to suppose that this surface species may be important at high pressures and high temperatures where methanation occurs readily.

We report here experimental measurements which confirm the TPD data of Goodman et al. [1] and extend it with very interesting ultraviolet photoelectron spectroscopy (UPS) data.

A Ni(100) single crystal sample was prepared by standard methods and was mounted inside an ultra high vacuum system using a manipulator which could be cooled to 95 K and heated to 1400 K. The sample was cleaned by chemical methods using O₂ and H₂ [1,3]. Oxygen, carbon, and sulfur were detected initially, but prior to each experiment Auger spectroscopy showed no impurities at a level greater than 1%. High purity CO and H₂ were handled on an auxiliary gas handling system and were admitted through a gas doser [3] or by backfilling the chamber. The experiments reported here were done by adsorbing the gases at 98 K. This temperature was achieved by passing liquid nitrogen through an internal reservoir to which the sample was coupled by conducting rods. Temperatures were measured with a chromel–alumel thermocouple spot-welded to the rear of the crystal. The crystal was heated resistively by passing current through 20 mil Ta wires spot-

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welded to the crystal. For TPD experiments, the heating rate was nearly linear at 11 K s^{-1} .

UPS measurements were made using He II radiation ($\hbar\omega = 40.8 \text{ eV}$) from a standard high voltage discharge source. Photoelectrons were detected using a double pass cylindrical mirror analyzer operated in the retarding mode at a pass energy of 25 eV . This gives a minimum resolution of 0.4 eV . Pulse counting techniques were used to record the spectra and the data were stored temporarily on a multichannel analyzer typically with 0.08 eV/channel resolution.

Fig. 1 shows four TPD spectra observed by line-of-sight mass spectrometry for the species of interest here. Curve (a) shows the spectrum for H_2 desorption from Ni(100) following a 17 langmuir (L) saturation exposure to hydrogen at 98 K . This spectrum shows a single peak which is quite symmetric with the temperature of the peak maximum at 330 K . Curve (c) is for CO desorption following a 17 L saturation CO exposure at 98 K . This spectrum shows a distribution of several states with a major desorption maximum occurring at 421 K . Curves (b) and (d) show corresponding desorption spectra for H_2 and CO occurring subsequent to a 17 L H_2 exposure followed by a 17 L CO exposure at 98 K . These spectra for the coadsorbed species are remarkably different from those observed for the pure compo-

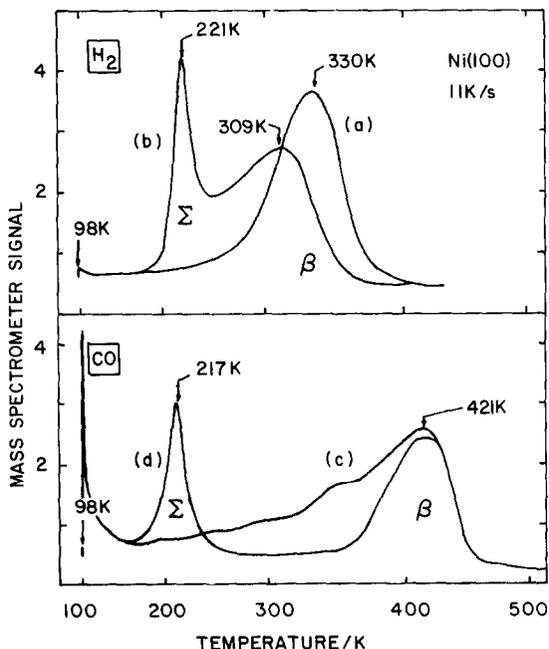


Fig. 1. TPD spectra for H_2 and CO on Ni(100), the adsorption temperature was 98 K and the heating rate was 11 K s^{-1} : (a) $m/e = 2$, 17 L H_2 ; (b) $m/e = 2$, 17 L H_2 followed by 17 L CO; (c) $m/e = 28$, 17 L CO; (d) $m/e = 28$, 17 L H_2 followed by 17 L CO.

nents and are in very nice agreement with those obtained by Goodman et al. [1]. Our resolution is somewhat better, particularly in the case of CO, because we have been able to remove most of the interference due to desorption from the leads. Following these authors we have labeled the low temperature states as Σ and the high temperatures as β . When the order of adsorption was reversed, 17 L of CO followed by 17 L of H₂, subsequent TPD showed negligible H₂ desorption and a CO desorption very much like spectrum (c). This result confirms earlier work [1] which shows that adsorbed CO poisons the surface for subsequent hydrogen adsorption.

The areas beneath the curves (a) and (b) in fig. 1 are almost identical when plotted as a function of time. Preadsorbed hydrogen is not displaced upon exposure to CO. A similar analysis of curves (c) and (d) shows that preadsorbed hydrogen lowers the saturation amount of CO_(a) in subsequent CO adsorption. When (c) and (d) are plotted as a function of time the ratio of the areas is 0.76.

The near coincidence of the peak temperatures and the narrow widths (~ 20 K) of the Σ states for H₂ and CO desorption suggests the dissociation of a complex containing H, C and O. From TPD spectra for CO, it appears that this complex might be formed from adsorbed CO which would occupy, in the absence of adsorbed H, states other than the highest binding energy state (β). It is apparent that the presence of coadsorbed CO shifts the entire H₂ desorption spectrum to lower temperatures. For curve (b) in fig. 1, the β (H₂) state peak maximum is shifted lower by about 20 K.

Another interesting feature of the low temperature Σ states is revealed by an analysis of their leading edges. The desorption rates rise very sharply over the range 190–215 K and for different, but sufficiently high coverages in this state, the edges are superimposable. In addition the peak temperatures move to higher values as the areas increase. All of this suggests zero order desorption kinetics which may be due to the decomposition (explosion) of a surface complex. A plot of $\log R$ versus $1/T$ gives an activation energy of 7.2 ± 0.8 kcal mole⁻¹. Some of the uncertainty in this energy is a reflection of the fact that the CO and H₂ desorption spectra are not exactly superimposable. This suggests that decomposition of the surface complex does not always lead to desorption of products. Further evidence that this is the case has been found in separate experiments to be reported elsewhere [3] which show that the relative amounts of Σ (CO) and Σ (H₂) are dependent upon the temperature of exposure and the relative exposures of CO and H₂. We conclude that the interacting species formed by coadsorption of H₂ and CO at 98 K on Ni(100) dominates the surface more fully than would be indicated by the areas under the Σ states shown in fig. 1. During TPD, decomposition of this species leads to partial desorption of CO and H₂ in the temperature region around 220 K, but much of the CO and H is retained by the surface.

Fig. 2 shows a set of three H II UPS difference spectra taken of CO_(a) and coadsorbed mixtures of H and CO on the Ni(100) surface. The difference spectra were obtained by subtracting (without scaling the intensities) the $N(E)$ spectra for

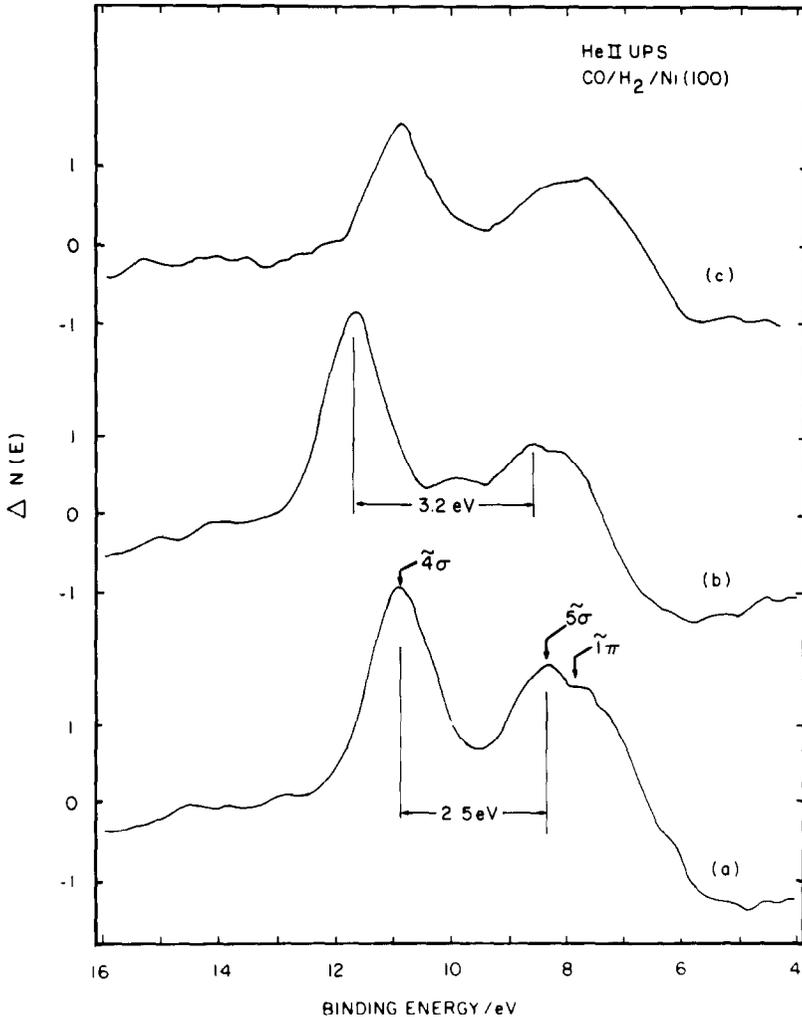


Fig. 2. He II UPS difference spectra at 98 K: (a) 17 L CO, arrows mark position of denoted orbitals (see text); (b) 17 L H₂ followed by 17 L CO; (c) same dose as (b) but warmed to 260 K and recooled to 98 K. In each case the UPS spectrum for clean Ni(100) has been subtracted.

the clean surface from the $N(E)$ spectra after chemisorption. Curve (a) shows the $\Delta N(E)$ spectra for a surface exposed to 17 L of CO at 98 K. The binding energy scale is referenced to the Fermi level of the Ni(100) substrate so that $E_F = 0.0$ eV BE. We find CO-derived emissions in the regions around 8 and 11 eV. The arrows along this panel show the peak positions for CO_(a) on Ni(100) which have been reported in the literature [4] on the basis of angle-resolved spectra. The agreement

between our results and this work is excellent and gives values of 10.9, 8.4, and 7.9 eV for the binding energies of the $\tilde{4}\sigma$, $\tilde{5}\sigma$, and $\tilde{1}\pi$ levels, respectively. Curve (b) shows the $\Delta N(E)$ spectra of a surface saturated with hydrogen by a 17 L H_2 exposure and followed by 17 L of CO. The $\tilde{4}\sigma$ peak is shifted by 0.78 eV towards higher binding energy and has about the same FWHM and intensity as the $\tilde{4}\sigma$ peak in curve (a). An interesting difference between these two curves is the change in the relative intensity of the peaks for (a) and (b). Interestingly, there is no evidence in (b) for two distinct kinds of CO. This result confirms that the coadsorbed interacting species is present in very large concentrations under the conditions of these experiments and is consistent with the notion that during subsequent TPD some of this species decomposes to give gas phase products while the remainder is retained by the surface and desorbs at higher temperatures.

Curve (c) in fig. 2 shows the $\Delta N(E)$ spectrum taken after the species present in (b) were heated to 260 K and recooled to 98 K. It is clear from fig. 1 that this procedure should remove all of the Σ states provided they are not repopulated upon cooling. Subsequent TPD spectra show that no repopulation occurs [3]. Comparing curves (c) and (a) in fig. 2 indicates that the binding energy of the $\tilde{4}\sigma$ peak has shifted back to its original value and the $\tilde{5}\sigma/\tilde{1}\pi$ regions are more comparable. The intensity distributions in these two regions are not identical however and this suggests that the $H_{(a)}$ present in (c) does induce some change in the electronic structure of $CO_{(a)}$.

One interpretation of the results presented here is that heavy doses of CO onto a surface presaturated with H at 98 K results in the formation of a single interacting species with its own characteristic UPS and TPD spectra. This species retains an electronic structure that is readily derivable from that of $CO_{(a)}$. However, the UPS intensity distribution is significantly different from that of chemisorbed CO on Ni(100). Preadsorbed H does cause changes in the valence band spectra of Ni [5] and, when CO is coadsorbed, a longer CO/M bond may be formed than would be present in the absence of adsorbed H. If the interaction between $H_{(a)}$ and $CO_{(a)}$ occurs largely through the metal, we would expect the final state screening of the $CO_{(a)}$ orbitals to be less in the presence of $H_{(a)}$ than for a clean surface. Thus, the 0.78 eV shift of the $\tilde{4}\sigma$ feature would be due mostly to a final state effect.

Fig. 3 shows an interesting comparison of spectra (a) and (b) of fig. 2. In the lower panel, we have assumed a uniform relaxation/polarization shift and shifted curve (b) to lower binding energies by 0.78 eV to align the $\tilde{4}\sigma$ peaks. The solid line shows the UPS features for $CO_{(a)}$ on a clean surface and the dashed line shows that for $CO_{(a)}$ on a surface presaturated with hydrogen. The amplitudes of the two $\tilde{4}\sigma$ peaks match almost exactly with no scaling of intensities. Clearly the spectra align very well with the exception of the region between 7 and 10 eV. In the upper panel we have subtracted the dashed curve from the solid curve. The major feature is at 8.4 eV which is the position of the $\tilde{5}\sigma$ feature for $CO_{(a)}$ on clean Ni(100) [4]. Since this orbital is characterizable as predominately a lone pair on C in the gas phase and is heavily involved in bonding to the metal, any changes which occur in

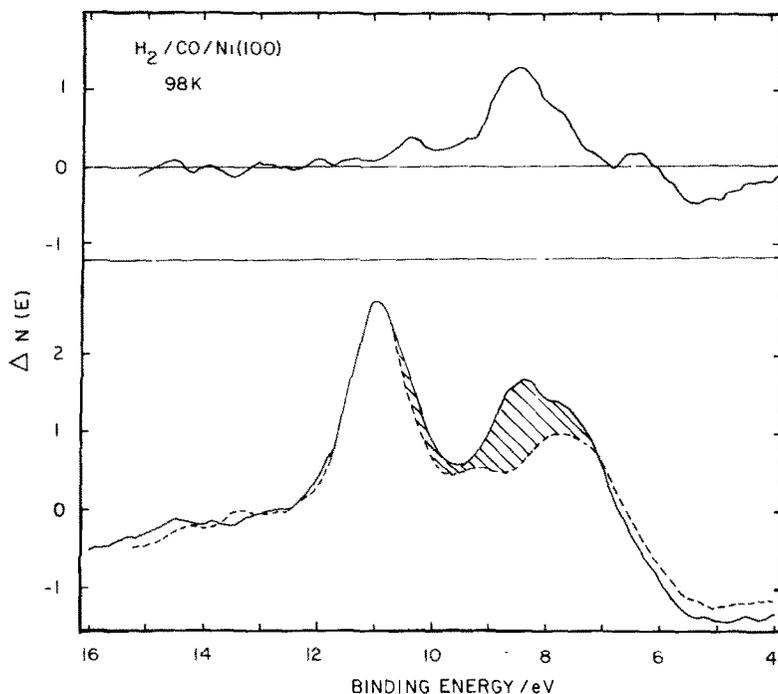


Fig. 3. Lower panel: solid line is spectrum (a) of fig. 2; dashed line is spectrum (b) of fig. 2 after shifting by 0.78 eV to align the peaks at 10.9 eV. Upper panel: difference between the two spectra in the lower panel.

the binding of CO to the surface would be expected to change its relative intensity and/or position.

TPD spectra indicate that only about 80% as much $\text{CO}_{(a)}$ is on the surface for the dashed curve. Comparing the intensity distribution of the two curves and accounting for this CO coverage difference indicates that with $\text{H}_{(a)}$ present the $\tilde{4}\sigma$ emission is enhanced while the $\tilde{1}\pi$ is not. The $\tilde{5}\sigma$ emission is depressed in the presence of $\text{H}_{(a)}$ and may show a differential chemical shift.

An electron energy loss vibrational spectroscopic study of this system has been reported by Andersson [6]. Preadsorption of 3 L H_2 at 175 K caused subsequent CO chemisorption (1 L CO) to occur into bridged sites, while on the clean surface CO occupied predominantly atop sites. Although the conditions of these experiments were not identical to those reported here, we have shown in separate experiments [3] that CO and H_2 Σ state desorption can be observed under the conditions of Andersson's experiment. Andersson found no evidence for the formation of either C-H or O-H bonds suggesting that a "COH" surface molecule is not formed. This is consistent with our interpretation of the UPS spectra, but the desorption kinetics of the Σ states must be rationalized without invoking the decomposition

of a "COH" molecular fragment. One possibility involves a surface phase change with cooperative effects between many CO, H and Ni atoms leading from a surface with weakly held CO adsorbed on top of a Ni-H substrate to a surface with CO bound strongly to Ni with some coadsorbed hydrogen. The initial stages of this change of state would involve strong dynamical coupling of CO and H which leads to some desorption and the simultaneous formation of new CO and H adsorption states.

Changes in CO-derived UPS features in the presence of adsorbed H have also been found in the W(100) system [7]. The comparison with Ni(100) is complicated by the fact that some of the adsorbed CO is dissociated on W(100). However, emission from molecularly adsorbed CO was observed. As for Ni(100), they found enhancement of the $\tilde{4}\sigma$ peak and broadening of the $\tilde{5}\sigma/\tilde{1}\pi$ region but no significant shifts were noted.

In summary, our results confirm that in the CO/H/Ni(100) system, coadsorbed CO and H form a surface complex which gives rise to low temperature CO and H₂ TPD features [1]. Our UPS results indicate that there is a single type of weakly held CO on a surface presaturated with hydrogen. We propose that strong dynamical couplings between adsorbed H and CO are important for the observed low temperature desorption peaks.

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