The chemical nature of the surface species formed either by the interaction of H₂ and CO on transition metal surfaces or by the decomposition of molecules composed of hydrogen and CO is vital to the understanding of many current catalytic problems [1–5]. In a systematic attempt to identify a catalytic interaction between adsorbed-CO and adsorbed-H on a Ni(100) surface, we have discovered the irreversible formation of a new adsorbate molecular entity. Temperature programmed desorption (TPD) data indicate that H(ads) interacts with CO(ads) to form a significant concentration of interacting species which exhibit new bonding states of CO and H₂ desorbing simultaneously near 200 K.

Ancillary experiments examining the decomposition of methanol were carried out in an attempt to generate, by means of decomposition, a species similar to that observed in the catalytic H₂/CO interaction. The methanol results do suggest the formation of a surface complex; however, no link between the two surface species can be established. TPD evidence is presented for the presence of an adsorbed alcoholic “CO-H” species which decomposes at 500 K into CO and H₂. We have used hydrogen isotopic labeling in methanol to follow upon desorption the chemical behavior of the inequivalent hydrogen in the molecule, viz., CH hydrogen compared to CO-H hydrogen.

A Ni(100) single crystal disk, ground and polished on both faces, was mounted inside a stainless steel ultrahigh vacuum system [3]. It was repeatedly chemically cleaned in O₂ at 1400 K and 1 × 10⁻⁷ Torr and was then reduced on both faces at 1400 K in high pressure molecular beams of H₂ at 2 × 10⁻⁴ Torr. Auger spectroscopy (fig. 1) indicated that this method of cleaning leads to a crystal containing only small quantities of surface carbon and sulfur. High purity H₂ and CO were used without further purification. CH₃OH and CH₃OD were prepared by vacuum distillation into glass ampules. The isotopic purity of the distilled CH₃OD was checked by NMR and found to be 99%. Deposition of these adsorbates onto the Ni(100) crystal was carried out by means of two symmetrical molecular beam effusers [3]. Dosing through the effusers was controlled by adjusting the methanol.
vapor pressure behind a calibrated conductance capillary by varying the temperature of the liquid. The use of molecular beam dosing of the crystal effectively reduces the gas load into the vacuum system and assures gas purity at the crystal face. The gas flux at the crystal is 40 times the random flux using this arrangement [3].

Following cleaning, the crystal was cooled to 77 K and exposed to H₂ using various exposures; a sequence of H₂ desorption spectra were observed as shown in fig. 2A. The majority of the H₂ was desorbed via second order kinetics as a state

Fig. 1. Auger spectrum of clean Ni(100) produced by chemical treatment using O₂ and H₂.

Fig. 2. Temperature programmed desorption from Ni(100). Pure adsorbates: (A) H₂ exposures range from <1 L to 17 L; (C) CO exposures range from 0.2 L to 7 L. Mixed adsorbates: (B) 17 L H₂ exposure + 1 L CO, 2 L CO, 3 L CO, 8 L CO, and 17 L CO; (D) 17 L H₂ exposure + 1.2 L CO, 1.8 L CO, 2.4 L CO, 3 L CO, 8 L CO, and 17 L CO.
designated $\beta$-H$_2$ which is identical to the state studied in detail by Christmann et al. [6]. Similar studies with CO adsorption yielded a complex set of overlapping desorption states shown in fig. 2C.

Following these preliminary measurements, a saturated layer of adsorbed H at 77 K was exposed to CO for various exposures, and H$_2$ desorption spectra shown in fig. 2B were then obtained. During this exposure, no H$_2$ was observed to desorb. It can be seen that a new H$_2$ desorption state was produced above $\sim 1 \times 10^{-6}$ Torr · s exposure to CO, and it is designated $\Sigma$-(H$_2$). Repeating the experiment and observing CO desorption (fig. 2D) revealed that a new CO state, designated $\Sigma$-(CO), was also observed to desorb from the interacting layer. These two $\Sigma$-states desorb in the same temperature region during temperature programming. The constancy of the peak temperature for both $\Sigma$-states at various coverages indicates that first order desorption kinetics govern the desorption of both species. $\Sigma$-desorption peaks corrected for background contributions are shown in fig. 3, and it should be noted that the kinetic behavior of the two desorption processes are not identical, based on the curve shapes and position. Reversing the order of addition of adsorbates by first

Fig. 3. Comparison of temperature programmed desorption from fully-populated $\Sigma$-(CO) and $\Sigma$-(H$_2$) states on Ni(100). The experimental desorption traces have been corrected by subtraction of background contributions.

Fig. 4. Method for determining relative coverages in $\Sigma$-(H$_2$) state on Ni(100) at various CO coverages.
saturating Ni(100) with CO followed by exposure to H₂ at 77 K produced no hydrogen adsorption. Of particular interest regarding these data is the fact that the Ni(100) surface can accommodate the equivalent of a monolayer of H₂ in the presence of a monolayer of CO. This coexistence very likely reflects the surface environment at higher temperatures and higher pressures — those conditions required for H₂/CO catalytic reactions.

It was of interest to compare the desorption yields of Σ-(H₂) and Σ-(CO) at various stages of CO exposure on the hydrogen monolayer. This was done in the case of H₂ desorption by integration of the leading edge of the Σ-(H₂) peak as shown in fig. 4, and on this basis estimating the total number of H₂ molecules evolved within the Σ-(H₂) state. A similar estimate for Σ-(CO) was made by integration of the entire Σ-peak. Knowing the relative sensitivity of the mass spectrometer to CO and H₂ (H₂/CO = 0.4) and using the relative pumping speeds of the two gases in the vacuum system permits an estimate to be made of the ratio of absolute coverages in the two states and this ratio is shown in the top of fig. 5. At low CO exposure (≤ 1 × 10⁻⁶ Torr · s) on a hydrogen monolayer, it appears that more than ~120 adsorbed H atoms are influenced by one CO molecule — an interaction ratio clearly too high to be reasonable, as discussed below. As CO coverage increases the ratio drops to ~6H/CO. This may be viewed in another way by plotting the fractional coverage, θ₆, of the Σ-states (fraction computed on basis of Σ-state full coverage) as shown in the lower portion of fig. 5. It is seen here that there is a monotonic increase in Σ-(H₂) with CO exposures above 1 × 10⁻⁶ Torr · s. However, the yield of Σ-(CO) as observed by temperature programmed desorption is initially retarded in its development.

Recently a related study of the interaction of H(ads) + CO(ads) on Ni(100) has been reported by Andersson [7,8], using electron energy loss vibrational spectroscopy (EELS). At an adsorption temperature of 175 K it was found that pre-adsorption of hydrogen caused CO to adsorb predominantly into bridged sites in which
CO was multiply coordinated to two or more surface Ni atoms. In the absence of pre-adsorbed hydrogen, CO adsorbed predominantly at lower coverages as a linear species attached to a single Ni atom [8]. Unfortunately, the CO exposures on top of a hydrogen layer were not carried above $1 \times 10^{-6}$ Torr $\cdot$ s. From fig. 5 it may be seen that this is below the CO-exposure level at which appreciable amounts of $\Sigma$(H$_2$) and $\Sigma$(CO) are formed at an adsorption temperature of 77 K; it is unlikely that bridged-CO would desorb at lower temperatures than linear-CO and the state changes induced by EELS may not be related to the $\Sigma$-state effect. It should be noted that Andersson's adsorption temperature was ~100 K higher than ours and that this difference in adsorption temperature could lead to differences in CO effects on a preadsorbed hydrogen layer.

The desorption of $\Sigma$(H$_2$) and $\Sigma$(CO) suggest that both species originate from a surface complex. The limiting ratio of $\sim$6H/CO suggests that the interaction effect is a local phenomenon centered around a CO molecule immersed in a region containing adsorbed H atoms. A definitive picture of the surface complex awaits spectroscopic study of the interaction.

In fig. 5 it is seen that thermal desorption measurements do not detect $\Sigma$(CO) formation until after extensive production of $\Sigma$(H$_2$) is observed, i.e., until after extensive adsorption of CO on the monolayer of H(ads). We believe this may be due to the fact that at low CO coverages, pathways for conversion of $\Sigma$(CO) to other states ($\alpha$-CO, $\beta$-CO) may exist and that these thermal conversion processes occur more readily in the mixed adsorbate layer than does thermal desorption. Only at higher CO coverages (produced by exposures $\geq 2 \times 10^{-6}$ Torr $\cdot$ s CO exposure) do we detect $\Sigma$(CO) by desorption. This rationale is appropriate to explain the results shown in fig. 5.

It should be noted that adsorbate-adsorbate interactions leading to a decrease in surface binding energy are commonly observed for the mutual interaction of single adsorbates [9], and have often been observed for mixed adsorbates [10]. The unique feature of this phenomenon for CO and H$_2$ on Ni(100) is that the interacting species both desorb in the same temperature region indicating that a cooperative phenomenon may be controlling the rate of desorption of the species. The surface concentrations of the fully covered $\Sigma$-states of H and CO are of sufficient magnitude to warrant spectroscopic studies of this interesting interaction.

Shown in fig. 6a is the observed Mass 31 thermal desorption spectrum between 157 to 182 K from a CH$_3$OH multilayer on Ni(100), designated $\alpha$-CH$_3$OH. The shape of the desorption curve is indicative of zero order desorption from the multilayer. Multilayer desorption should proceed via zero order kinetics, as in the case of free sublimation. Thus, the leading edge of fig. 6a should increase exponentially with $T$. Fig. 6b is a plot of the relative desorption rate as a function of the temperature as extracted from the leading edge of fig. 6a. For multilayer desorption, the slope of this plot should give a value approximately the heat of vaporization of CH$_3$OH at 173 K. This experimentally found value of 11.3 kcal/mole may be com-
pared with the heat of vaporization of the liquid of 8.96 kcal/mole at 298 K [11]. Thus, a kinetic method-TPD-yields a value of the CH₃OH sublimation energy in good agreement with equilibrium thermochemical methods. Similar conclusions have recently been reported for multilayer desorption of H₂O and hydrocarbon from Ru(001) [12].

In addition to the low temperature α state, a second CH₃OD state, designated β, is observed to desorb at higher crystal temperatures as shown in fig. 7a. This state, with a maximum at 360 K, corresponds to molecular desorption from chemisorbed CH₃OD. A fragmentation assay of the desorbing species showed complete correspondence with the CH₃OD cracking pattern, except for additional H₂ evolution in the β-CH₃OD region, which is shown as a solid line in fig. 7c. This additional H₂

Fig. 6. (a) Thermal desorption spectrum from α-CH₃OH multilayer on Ni(100); adsorption at 77 K. (b) Plot of the relative desorption rate of α-CH₃OH multilayer as a function of temperature taken from the leading edge of (a).
evolved in the $\beta$-CH$_3$OD region arises from CH$_3$OD dehydrogenation, with the resulting hydrogen deficient species remaining on the surface.

At a temperature in excess of that required to desorb chemisorbed CH$_3$OD, a significant amount of CO (Mass 28) is evolved (fig. 7b). Coincident in temperature with the CO evolution, D$_2$ (Mass 4) and HD (Mass 3) are observed to desorb as shown in figs. 7c and 7d, respectively. The desorption temperature of the D$_2$ and HD is well past that at which H(ads) could be retained on the surface, as judged from separate studies of hydrogen chemisorption (fig. 7g). This D$_2$ and HD then must arise from the thermal decomposition of a COH$_x$ surface complex. Thermal desorption monitoring Mass 2 following CH$_3$OH adsorption is shown in fig. 7f. At the same temperature at which D$_2$ is observed to desorb following the evolution of chemisorbed CH$_3$OD, H$_2$(g) is desorbed as would be expected from CH$_3$OH. No corresponding peak is present in the thermal desorption spectrum measured following adsorption of pure H$_2$ (fig. 7g). A comparison of the deconvolved 500 K H$_2$ desorption peak area with the CO desorption peak area, correcting for pumping speed and QMS sensitivity differences, gives an estimate of the CO/H ratio in the surface complex of 1/1.1. This data then suggests that the surface species-COD is retained on the surface following the desorption of chemisorbed CH$_3$OD. The presence of significant amounts of H–D isotopic exchange in this state is not surprising since during the thermal desorption and the concurrent decomposition of chemisorbed CH$_3$OD, mobile hydrogens are available for exchange with the hydroxyl deuteriums.
The interaction of H₂, CO, and CH₃OH with a clean Ni(100) surface has been studied using temperature programmed desorption methods. These studies have shown:

(1) An irreversible formation of a new surface entity upon interacting CO with pre-adsorbed H(ads). This species, designated as the Σ-state, is formed in significant quantities and exhibits new bonding states of CO and H₂ desorbing in the same temperature region near 200 K.

(2) Upon adsorption of CH₃OH at 77 K and subsequent desorption, an adsorbed alcoholic "COH" species is formed and decomposes at 500 K into CO and H₂.

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References