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Coadsorption of Hydrogen and Carbon Monoxide on Nickel and Platinum[1]

Recently we have studied the coadsorption of hydrogen and carbon monoxide on Ni(100) (*1*), Rh(100) (*2*), and Ru(001) (*3*). When CO was adsorbed on H-presaturated surfaces at 100 K, new low-temperature thermal desorption peaks for both H_2 and CO were observed for Ni(100). For Rh(100), a new low-temperature state was observed only for H_2. These, as well as other surface spectroscopic data (*4*, *5*), indicate that CO and H interact attractively on these two metals and that local mixing of the CO(a) and H(a) is very important. For Ru(001) there are no new desorption states; there is a repulsive interaction between the CO(a) and H(a) which indicates, in conjunction with work function data, that the two adspecies are segregated into separate islands.

In this note we report thermal desorption spectroscopy (TDS) results for two additional close-packed crystal faces, Pt(111) and Ni(111), and compare the latter with data for Ni(100). Like the close-packed Ru(001) surface, neither Ni(111) nor Pt(111) shows any evidence for new desorption states when CO is adsorbed on a H-saturated surface. In addition, recent work on Rh(111) (*6*) shows evidence for segregation. From these results we generalize that close-packed surfaces of transition metals, which do not readily dissociate CO, tend to form segregated islands while the more open faces, at least (100) Ni and Rh, tend to form mixed and attractively interacting overlayers when CO is adsorbed on H-precovered surfaces. While these differences are readily detected only at low temperatures, where entropy effects are relatively small and high concentrations of surface species accumulate at low pressures, it is important to recognize that the same forces do participate at catalytically interesting temperatures and should, therefore, be considered.

The data for Ni(111) and Pt(111) are shown in Figs. 1 and 2, respectively. In

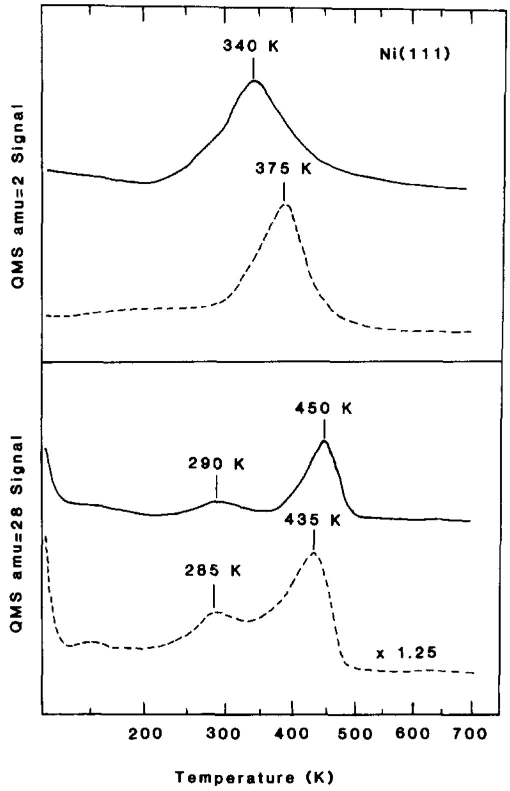

FIG. 1. Thermal desorption spectra for CO and H on Ni(111). Adsorption was at 100 K and the heating rate was 10 K/s. The upper and lower panels are for H_2 and CO desorption, respectively. The broken curves are for CO and H adsorbed alone on Ni(111). The solid curves are for CO and H coadsorbed (H adsorbed first) on Ni(111).

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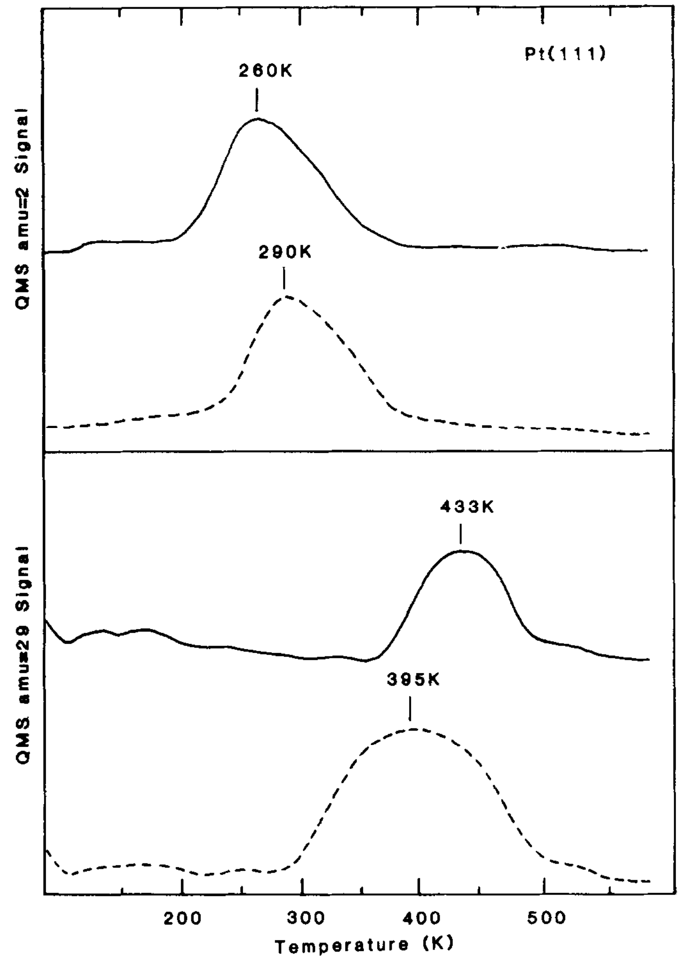

FIG. 2. Thermal desorption spectra for CO and H on Pt(111). The adsorption was at 100 K and the heating rate was 10 K/s. The upper and lower panels are for H_2 and CO, respectively. The broken curves are for CO and H adsorbed alone. The solid curves are for CO and H coadsorbed (H adsorbed first).

both, the adsorption temperatures was 100 K and, for the coadsorption experiments, saturation exposure to H_2 preceded saturation CO exposure. The surfaces were cut, polished, and cleaned using standard methods. Cleanliness was verified using Auger electron spectroscopy. As indicated in the upper panels of both figures, H_2 desorption from a coadsorbed layer (solid curves) is shifted by about 30–35 K to lower temperatures in the presence of CO(a) as compared to H(a) on CO-free Ni and Pt (broken curves). This is typical of a repulsive interaction between the adspecies. For the coadsorbed layer, CO desorption peaks at the temperature expected for CO alone since the surface is free of H(a) when it desorbs. The shift of the CO peak temperatures in Figs. 1 and 2 is the result of the lower CO coverage for the coadsorbed case and the sharp decline at low temperature in Figs. 1 and 2 is attributed to desorption from the heater leads. The area under the H_2 curves is independent of the presence or absence of CO(a) indicating that exposure to CO does not induce any H_2 desorption.

The areas under the CO desorption curves are smaller when there is H(a) present indicating that presaturation with H(a) partially inhibits CO adsorption. For the Ni(111) case, the CO coverage drops from 0.60 monolayer (ML) on the H-free surface to 0.28 ML when saturation H(a) is present. For the Pt(111), the drop is from 0.67 to 0.23 ML. These coverages are given in terms of the number of surface metal atoms and were calibrated as described previously using LEED and thermal desorption (*1*, *4*). When the order of adsorption is reversed, CO(a) is found to block the chemisorption of H(a). No products other than H_2 and CO were detected in these coadsorption experiments for either order of adsorption.

It is important to note that there is some disagreement in earlier coadsorption work on annealed polycrystalline Pt foils. In some cases (*7*, *8*) but not others (*9*), new high-temperature states for H_2 desorption were observed. In one study, residual surface carbon gave rise to a high-temperature (560 K) H_2 desorption peak from a coadsorbed system. We are presently investigating coadsorption on polycrystalline Pt under a variety of conditions of surface damage and impurity levels to examine the role of these surface properties in controlling the character of the desorbing species (*10*). Our coadsorption results for Ni(111) are in good agreement with earlier work (*11*) on this surface with the exception that in some cases (*11a*) the high-temperature side of the H_2 desorption curve is unshifted from that observed in the absence of CO. We plan to study the coadsorption of CO and H on both Ni(100) and Ni(111) as a function of adsorption temperature in an effort to understand these differences. We already have data on Ni(100) which show that exposure of H(a)/Ni(100) at 200 K to CO slowly desorbs H_2 and that the shapes of the desorption spectra depend on the adsorption temperature in this region (*12*).

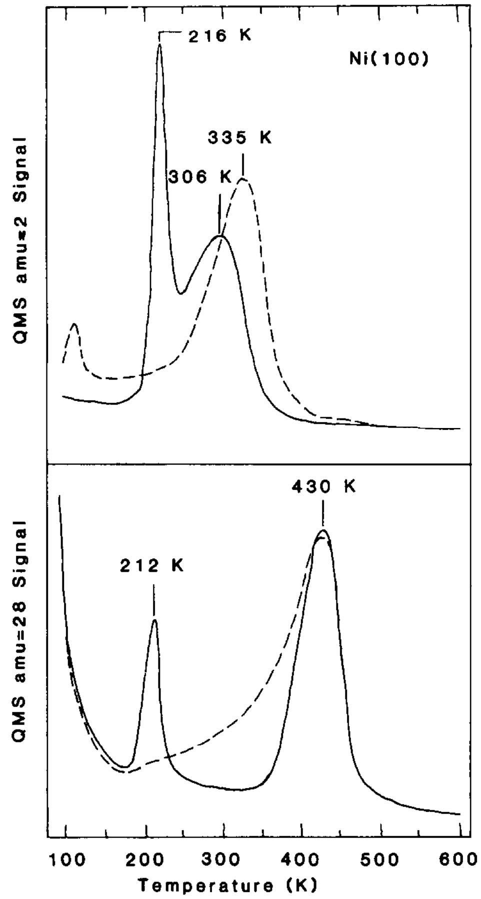

FIG. 3. Thermal desorption spectra for CO and H on Ni(100). The conditions and curve labels are the same as those for Figs. 1 and 2.

In contrast to Ni(111), coadsorption on Ni(100) (*1*) gives rise to sharp CO and H_2 desorption peaks at 212–216 K, indicated in Fig. 3, which are not present in the spectra for adsorption of either species alone. UPS, XPS, work function, and vibrational spectra (*4*, *5*, *13*) are all consistent with a strong attractive local interaction between CO and H on Ni(100) but with no evidence for either C–H or O–H bonds, while the data presented here are consistent with a repulsive interaction and segregation between CO and H on Ni(111).

Regardless of the interpretation, the clearly different thermal desorption for CO and H coadsorbed on these two surfaces points to a significant surface structural effect. It is interesting to consider how such differences might influence catalytic reactions. While the high-temperature conditions characteristic of catalytic reactions will destroy the local order found in the cases discussed here, so that the concepts of mixing and segregation will not be applicable, the local interatomic forces which give rise to the low-temperature distinctions will still operate. In other words, the repulsive and attractive local interactions between CO an H on Ni(111) and Ni(100) will still operate and will influence the activity and selectivity in those catalytic reactions where an elementary H + CO reaction controls the rate of a given pathway.

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