the C–O bond strength and increase the bonding of the molecule to the Rh(111) surface. This occurs through increased back donation from the rhodium metal into the 2π* orbitals of chemisorbed CO. The overlap and charge transfer is increased for the bridged site, and so this site becomes increasingly preferred at higher potassium coverages. The donation of electron density from potassium to the rhodium substrate affects more than just the nearest-neighbor CO molecules, giving rise to a nonlocal effect. At high potassium coverages, the C–O bond is weakened enough by coadsorbed potassium to induce CO dissociation, in contrast to that seen on Pt(111).

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Summary Abstract: Correlation of surface electronic properties and poison/promoter effects on the reactivity of Ni(100)

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The adsorption of small amounts of species such as S on Ni surfaces is known to dramatically effect the adsorption properties of CO. Because of its electronegative nature, coadsorbed S is believed to withdraw electron density from the surface and from other adsorbed species. For this removal of electron density shows up as a strengthening of the CO molecular bond and a weakening of the CO–metal bond. We can probe this site specific charge transfer effect of coadsorbed species by using line shape comparisons in AES.

AES is an ideal tool for this type of study since the Auger transition involves an element specific, spatially localized core-hole state. The locality of this state means that core–valence–valence transitions are sensitive to valence electron density in the very near vicinity of the atom producing the Auger electrons. We have used AES to probe the valence electronic properties at the site of C atoms adsorbed on a Ni(100) surface in the presence and absence of the prototypical poison/promoter species S and K. Line shapes resulting from 0.5 monolayer (ML) of C on Ni(100) compared with those from this surface with 0.25 ML of coadsorbed S show a decrease in the intensity of the Auger line shape near the high kinetic energy threshold, which involves states expected to be important in subsequent C chemistry. In contrast, comparing the line shapes for 0.1 ML C with that obtained 0.33 ML C in the presence of 0.1 ML K (a typical donor species) on Ni(111) we find that the near-threshold intensity increases. Thus the Auger results support the donor/acceptor model for the electronic role of coadsorbate species.

Another site-specific technique is LEELS or surface vibrational spectroscopy. In studies of CO on Ni surfaces, one can directly probe the changes in the bonding properties of the molecule that result from metal adsorption or from coadsorption with other species. We have followed variations in the C–O stretching energy with CO coverage on Ni(100) and find a continuous increase in the stretching energy starting at about 1880 cm⁻¹ for 0.02 ML CO coverage and ranging to a value of about 1960 cm⁻¹ at approximately 0.5 ML. This means that the C–O bond is becoming more molecular as the coverage increases. The effect manifests itself in both thermal desorption and isosteric heat of adsorption measurements as a decrease in the CO–metal bond strength with increasing CO coverage, i.e., the CO adsorption is self-poisoning. Our preliminary results show that the CO stretching energy for 0.11 ML coverage of CO on Ni(100) increases by 30 cm⁻¹ in the presence of only 0.015 ML S and that the stretching energy for 0.2 ML CO increases by 60 cm⁻¹ in the presence of 0.11 ML S. These results are consistent with the effects that are found for coadsorbed S on the thermal desorption behavior and for the buildup of C on Ni surfaces as a result of CO exposures at high-pressures, i.e., the CO-metal binding energy is decreased and the dissociation probability inhibited by the presence of coadsorbed S.

Another experiment that may prove useful in determining the spatial extent over which adsorbed poison/promoter species act is following the behavior of the surface state intensity as a function of adsorbate coverage in angular resolved photoemission. Ni(100) has a very narrow, intense, surface-state contribution to its valence-band photoemission at certain emission angles and its intensity has been found to be sensitive to the presence of surface impurities such as...
Work on a similar surface state on Cu(100) suggests that this state exists in a d-band symmetry gap in the surface-projected density of states having been displaced to this position as a result of the different potential of the surface layer with respect to that of the bulk. Presumably the role of various adsorbates in "poisoning" the surface state is that of reducing the surface potential perturbation sufficiently to remove these states from the symmetry gap. Thus, the sensitivity of the surface-state poisoning with adsorbate coverage is a useful measure of the spatial range of the surface potential perturbation.

Our measurements using He I radiation are in basic agreement with earlier work. Our results indicate, however, that it is very difficult to get the Ni(100) surface clean. Using a chemical cleaning procedure prescribed in earlier work, we produce a surface with impurity levels below our detection capabilities and a large surface-state intensity. However, even at system pressures of $1.0 \times 10^{-10}$ Torr (principally CO and H$_2$), it only takes a few minutes to build up 0.05 ML CO coverage on the surface and this reduces the surface-state intensity by about 20%. Ordinarily one can rid the surface of this CO simply by heating to $\sim 200 \, ^\circ C$. We find that at this level of cleanliness, however, the 200 $^\circ$ C flash produced some degree of CO dissociation. Thus, one must be extremely careful to minimize the time between chemical cleaning and data acquisition in order to produce the most intense surface-state contribution. After a sharp initial drop, we observe a linear decrease in surface-state intensity to about 20% of the "cleanest" value for saturation 5 adsorption at 0.5 ML. A similar behavior is seen as a function of CO coverage. II adsorption, however, has little effect on the surface-state intensity.

We conclude from our overall results that: (1) the electronic properties of sites such as (those which can be occupied by) CO molecules and C atoms are affected by the presence of coadsorbed species; and (2) the spatial range of influence of typical poison/promoter species such as S and K is considerably in excess of their covalent radii and, thus, these species can be considered to produce a "long range" electronic or ligand effect.