# Determination of the Active Site for CO Adsorption on Ni (111)

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The effect of Au on CO adsorbtion on the (111) surface of Ni has been investigated in a nickel–gold alloy. The principle effect of Au is to reduce the amount of CO adsorbed by reducing the concentration of active sites. The active site for CO adsorption is identified as a three nickel atom site.

The composition of an alloy surface can differ greatly from its bulk composition (*1–3*). This effect can have a profound influence on the catalytic activity of an alloy (*4*). We have previously shown that the activity of copper–nickel alloys for ethane hydrogenolysis can be explained quantitatively in terms of segregation of copper to the nickel surface (*5*). The presence of copper on the nickel surface sharply reduces the concentration of nickel-atom pairs in the surface plane; we showed that nickel-atom pairs are the active site for ethane hydrogenolysis on copper–nickel alloys. Similarly, van Schaik *et al.* (*6*) have examined isomerization of alkanes on extremely dilute alloys of Pt in Au. Their data indicate that the catalytic reaction proceeds on a one Pt-atom site. These results support the concept that the active sites for the individual fundamental reaction steps of a complex catalytic reaction may have highly specific atomic compositions (*7–9*). This idea is closely related to the well-known concept of active sites possessing specific geometrical configurations such as surface steps or kinks (*10, 11*).

The study reported in this paper, on CO adsorption on the (111) surface of a gold–nickel alloy, examines the effects of alloying on a fundamental reaction step. In this work, unlike that of previous investigators on the effects of alloying on catalysis (*5, 6*), we are looking at a fundamental reaction step rather than an overall catalytic reaction. Also, unlike previous investigators, we have actually measured the surface composition of the alloy. Our results suggest that the effect of Au on CO adsorption on Ni (111) is due almost entirely to its reduction of the concentration of active three nickel-atom sites.

## EFFECT OF ALLOYING ON ACTIVE SITES

Alloying a catalytically inactive metal with a catalytically active metal can produce two conceptually distinct effects on the chemically active sites: (i) a ligand or electronic effect (*12*) in which the inactive alloying element perturbs the chemical properties of the active site of the host metal; and (ii) a multiplet (*7, 8*) or ensemble (*12*) effect in which the inactive metal reduces the surface concentration of active sites of multiplets of host atoms.

Flash desorption of gases adsorbed on clean surfaces at low pressures provides a convenient way to look for these alloying effects. In the flash desorption experiment, the sample is rapidly heated after suitable

dosing with gas, and the gas desorption from the sample is monitored with a mass spectrometer. The desorption spectrum seen is characteristic of the adsorbed gas and adsorbing surface. It is sometimes possible to detect the alloying effects mentioned above by looking at how the flash desorption spectrum changes with surface composition. A ligand effect (i) could express itself as a shift in the location of the desorption peak or as a subtle change in its shape. A multiplet effect (ii) will lead to a change in the number of molecules adsorbed. As we will see, if a multiplet effect occurs, analysis of the surface composition dependence of amount of gas adsorbed can give the number of atoms in the active site.

## METHODS

The adsorption of CO on 99% Ni–1% Au was chosen for this investigation of alloying effects on fundamental reaction steps for several reasons. Williams and Boudart (1) have previously established that gold does segregate to the nickel surface; therefore, it is possible to vary the surface composition of the alloy through suitable heat treatment while keeping the bulk composition fixed (13). CO adsorption was chosen as one of the simplest gas surface reactions; CO does not adsorb on Au at room temperature, while it does adsorb on Ni. Finally, Helms et al. (14) have previously shown that segregation of Cu (which does not adsorb CO at room temperature) to the Ni surface significantly alters the adsorption of CO.

We have examined in considerable detail the thermodynamics of gold segregation to the (111) surface of nickel (13), as well as the structure of the surface segregated layer (15). The crucial result of this work, for the purposes of this paper, is that, starting with a freshly sputtered (111) surface of a Ni sample containing 1% Au, it is possible, by suitable heat treatment, to produce gold surface concentrations (as

measured by Auger spectroscopy) between 2 and 100% of a monolayer (13).

The surfaces, partially covered with gold, were exposed to $5 \times 10^{-8}$ Torr (1 Torr $= 133.3$ N m$^{-2}$) of CO for 1 min (3-Langmuir exposure) at 50°C. This treatment is sufficient to saturate the high-energy binding site of the Ni(111) surface and puts about one-third to one-half of a monolayer of CO onto a pure Ni surface (16). After exposure to the CO, the chamber was pumped down to $5 \times 10^{-10}$ to remove the background CO, and then the sample was heated to 350°C at a rate of 60°/sec. The CO flash desorption pressure burst in the chamber was monitored with a mass spectrometer. The flash desorption spectra obtained are shown in Fig. 1. The surface compositions indicated in the figure were obtained from the Auger spectra (13) using pure Ni and pure Au for calibrations and assuming that the escape depth of the 61- and 69-eV electrons employed is about 3A (17). The surface compositions were measured before and after each experiment; the surface composition did not change during the CO adsorption experiment. We also
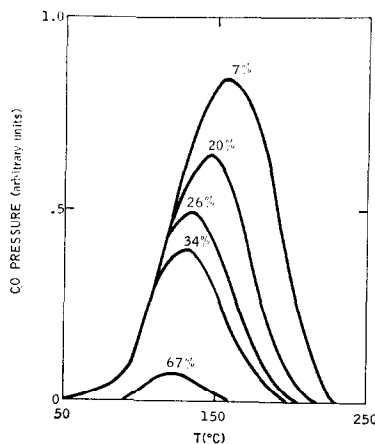


FIG. 1. CO flash desorption spectra from a partially gold-covered Ni (111) surface after exposure to 3 Langmuirs of CO at 50°C. The percentage of Au in the surface plane is indicated in the figure. Note that Au greatly suppresses the amount of CO adsorbed, but only slightly shifts the shape and location of the desorption peak.

found that the desorption spectra were highly reproducible and did not depend on the CO exposure for exposures between 2 and 50 Langmuir.

## DISCUSSION

The data in Fig. 1 indicate a ligand effect (i) of alloying in that the desorption spectrum shifts to a slightly lower temperature with increasing Au; however, this effect is small. As the amount of CO adsorbed, as indicated by the area under the curves in Fig. 1, decreases rapidly with increasing Au, there is also, apparently, a multiplet effect (ii). The size of the active site or multiplet of Ni atoms can be deduced by analyzing this decline in the amount of CO adsorbed.

We assume, as in our earlier analysis of the effect of adding Cu on ethane hydrogenolysis on Ni (5), that the Au reduces CO adsorption by reducing the concentration of active nickel multiplet sites. If the multiplet contains $n$ Ni atoms and the surface concentration of Ni is $X_{Ni}{}^s$, then, from the law of mass action,[1] we would expect that the concentration of these active multiplets should vary as $(X_{Ni}{}^s)^n$. If these assumptions are valid, then a log–log plot of the amount of CO adsorbed against the surface composition $X_{Ni}{}^s$, as determined by Auger spectroscopy, should give a straight line with slope $n$. This plot is shown in Fig. 2. The data are well-represented by a straight line with $n = 3$.[2]

It is interesting to speculate on the nature of the three Ni sites involved in bonding CO to the (111) surface of Ni. The obvious site for CO adsorption on the triangular mesh (111) surface is the site lying between three Ni atoms. This site, like the adsorption site, is consistent with Tracy's work on CO adsorption of Ni (100) in which he showed that the molecule adsorbed on this square mesh surface is the site lying between four Ni atoms (19). However, Christman obtained a $[(3)^{\frac{1}{2}} \times (3)^{\frac{1}{2}}]$ R30° LEED pattern for CO adsorbed on Ni (111), which he interpreted as indicating that CO has two Ni neighbors (16). The interpretation of this LEED pattern is not unambiguous; Comrie interpreted the same $[(3)^{\frac{1}{2}} \times (3)^{\frac{1}{2}}]$ R30° LEED pattern as indicating that the CO was adsorbed on the site lying between three neighbors (20). This interpretation of the LEED results seems consistent with our conclusion that the active multiple for CO adsorption on Ni (111) contains three atoms.

[1] Here we are implicitly assuming that the Au atoms are disordered and not clustered on the surfaces. This assumption, which is unproven, seems warranted from LEED studies (15), theoretical calculations (18), and the very strong (nonlinear) effect of Au on the total amount of CO adsorbed.

[2] The log–log plot employed in Fig. 2 is strictly correct only in the case of dilute solutions. However, the answer we have obtained, $n = 3$, is correct despite our use of data for $X_{Ni}{}^s$ near 1. When $X_{Au}{}^s$ is small, each Au atom actually poisons three adsorption sites on the (111) surface, and so the active site concentration in this regime varies like $(1-3X_{Au}{}^s)$. Fortunately, for our analysis, when $X_{Au}{}^s$ is near 0, $(X_{Ni}{}^s)^3 = (1-X_{Au}{}^s)^3 \approx (1-3X_{Au}{}^s)$.
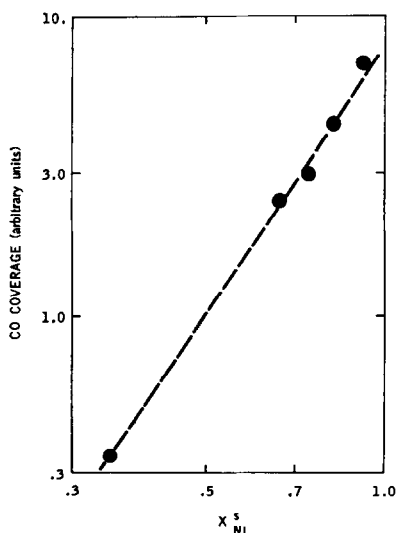


FIG. 2. Log–log plot of total CO coverage (in arbitrary units) of a partially gold-covered Ni (111) surface after exposure to 3 Langmuirs of CO at 50°C as a function of the Ni concentration in the surface layer, $X_{Ni}{}^s$. The data show that a site with three Ni atoms is the active site for CO adsorption.

## CONCLUSIONS

Our results strongly suggest that the active site for CO adsorption of the Ni (111) surface involves three nickel atoms. The ligand effect of Au on the properties of these three Ni-atom sites are apparently small. Thus, the effect of alloying Au with Ni on CO adsorption on the (111) surface is due almost entirely to its effect on the concentration of active sites.

The work reported in this paper supports the idea that the fundamental reaction steps of complex catalytic reactions may occur on sites with highly specific atomic composition. It raises the hope that it may some day be possible to tailor-make a complex alloy catalyst so as to have the right concentrations of active sites to produce the desired reactions. The study of simple reaction steps on carefully prepared and characterized alloy surfaces is a first and necessary step toward achieving this goal.

## ACKNOWLEDGMENT

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