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IRAS Observations of Phase Transitions at Ni/Mo(110) and Co/Mo(110) Interfaces

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Abstract: Ultra-thin, annealed films of Ni and Co on a Mo(110) surface show structural phase transitions ((8×2) to (7×2) for Ni and pseudomorphic to (8×2) for Co) at Ni and Co coverages of ~0.95 and ~1.0 ML (1 ML = 1.428×10^{15} atoms cm^{-2}), respectively. These phase transitions are clearly reflected in the CO IR spectra. In addition, the disorder–order transitions of Ni/Mo(110) and Co/Mo(110) that occur upon annealing are also indicated in the corresponding CO IR spectra. The transitions of these ordered and disordered two-dimensional phases appear to occur via an island growth mechanism with expansion at the island edges.

1. Introduction

Phase transitions at gas–metal interfaces have been extensively studied.[1] Like phases in 3-dimensions, different 2-dimensional phases on a surface often exhibit quite different chemical and physical properties. For example, the (5×20) surface of Pt(100), which is reconstructed from the (1×1) surface, shows a sticking coefficient for dissociative oxygen adsorption that is two orders of magnitude smaller than that for the (1×1) surface.[2–4] Likewise, phase transitions on surfaces are frequently associated with other interesting surface phenomena such as kinetic oscillation[1,2] and zero-order thermal desorption.[5,6]

Recently, a number of phase transitions have been reported for metal overlayers on single-crystal metal substrates. These include the (7×2) to (8×2) transitions for Ni/Mo(110)[7,8] and a pseudomorphic to (8×2) transition for Co/Mo(110)[7,9] and Co/W(110).[10] Previous investigations of surface phase transitions have been performed mainly using low-energy electron diffraction (LEED) which requires long-range order in the phases.

In our recent studies on ultra-thin metal overlayers on single-crystal metal surfaces, CO IRAS spectra have shown a remarkable sensitivity to the phase transitions on Ni/Mo(110) and Co/Mo(110). In addition, due to the intrinsic high resolution of IR spectroscopy, interesting properties of the phases and phase transitions have been observed. The results of these studies are presented in this paper. Although phase transitions have been studied at gas/metal interfaces by IRAS,[11,12] the study of the structural phase transitions of ultra-thin metal films on single-crystal metal substrates is, to our knowledge, reported for the first time using IRAS with CO as a probe molecule.

2. Experimental Section

The experiments were carried out in an ultra-high vacuum chamber equipped with infrared reflection absorption spectroscopy (IRAS), Auger electron spectroscopy (AES), and low-energy electron diffraction (LEED). The sample was spot-welded to two Ta wires on the back face of the crystal which allowed resistive heating of the sample to 1500 K and cooling to 80 K. In addition, the sample could be heated to 2300 K via e$^-$-beam heating. The Mo(110) sample was cleaned as follows: heated in 10^{-7} Torr of oxygen at 1800 K and then annealed under vacuum at 2000 K. AES indicated a clean surface with no detectable impurities, and LEED showed a sharp pattern. The infrared spectra were obtained with a Mattson Fourier transform infrared spectrometer (Cygnus 100) in a single-reflection mode at an incident angle of 85°. The resolution was 4 cm^{-1} and the number of scans collected per spectrum was 320. The spectra shown are raw data, corrected only for the base line.

The Ni and Co were deposited via evaporation from a Ni wire and a Co rod wrapped with a W filament. Prior to each deposition, the source was outgassed extensively. AES showed that no impurities accumulated on the surface during the metal deposition. The Ni or Co coverage was determined by using the metal TPD method,[8,9] which defines 1 ML as 1.428×10^{15} atoms cm^{-2}, the atomic density of a Mo(110) surface.

3. Results

3.1. The (8×2) to (7×2) Transition of Ni/Mo(110). Figure 1 shows the IR spectra of CO on Ni/Mo(110) at the indicated Ni coverages (θ_{Ni}). The Ni was deposited onto Mo(110) at 100 K and annealed to 900 K. The CO exposure (saturation) and IR spectral acquisition were carried out at 90 K. CO adsorbed on Mo(110) (θ_{Ni} = 0 ML) shows a single peak with a stretching frequency of 2035 cm^{-1}. As the Mo surface is covered with Ni, this peak is greatly attenuated and disappears by θ_{Ni} = 0.54 ML. At θ_{Ni} = 0.26 ML, two peaks arise at 2100 and 2083 cm^{-1}. As θ_{Ni} increases from 0.42 to 0.95 ML, the spectra exhibit a peak at 2087 cm^{-1} and its intensity increases with the peak frequency remaining essentially unchanged. At θ_{Ni} = 0.95 ML, another peak appears at 2065 cm^{-1}. By θ_{Ni} = 1.08 ML, the 2065 cm^{-1} peak has become predominant, and the 2087 cm^{-1} peak is markedly attenuated. The 2087 and 2065 cm^{-1} peaks are labeled β_1 and β_2, respectively. The frequencies of these two peaks are higher than that of linear CO adsorbed on a Ni(111) surface (2054 cm^{-1}),[14,15] and therefore they are assigned to CO bound linearly to the Ni overlayers. Figure 2 shows the peak frequencies and normalized integrated intensities as a function of Ni coverage for the two peaks. It is evident from Figure 2 that at θ_{Ni} = 0.95–1.08 ML, the intensity of the β_1 peak decreases with a concomitant intensity increase in the β_2 peak, while the peak frequencies of β_1 and β_2 remain essentially unchanged. It is also noteworthy that both peaks are sharp and symmetric with a full width at half maximum (fwhm) of 10 cm^{-1}, indicating excellent order in the adsorbed CO molecules and consequently implying well-ordered Ni atoms.

LEED observations show that the abrupt spectral change at θ_{Ni} = 0.95–1.08 ML correlates with a surface phase transition from an (8×2) to (7×2) Ni overlayer structure. A schematic drawing of the (8×2) LEED pattern is shown in Figure 3. The large and small points represent the LEED spots of the Mo

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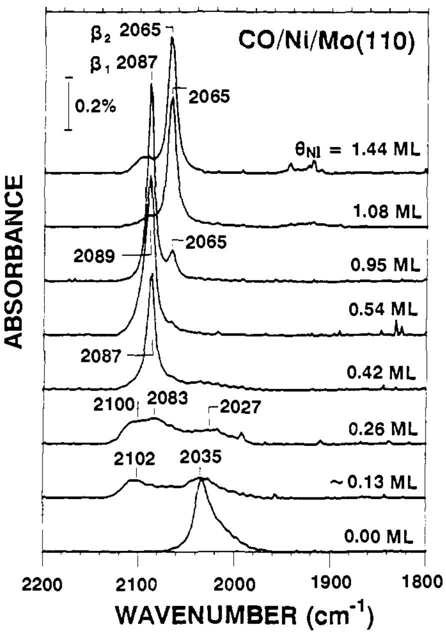

Figure 1. IR spectra of CO on Ni/Mo(110) at the Ni coverages indicated. Ni was deposited onto the Mo(110) surface at 100 K, flashed to 900 K, and then dosed with 10 L of CO at 90 K. The IR spectra were collected at 90 K.

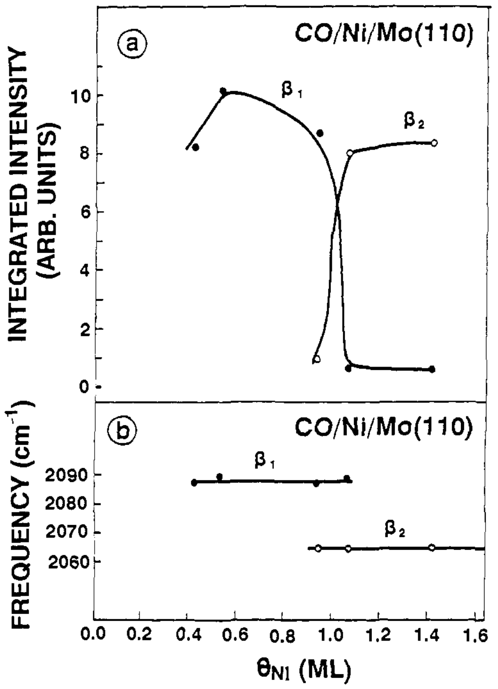

Figure 2. Integrated intensities and the peak frequencies of the β_1 and β_2 peaks in Figure 1 as a function of Ni coverage. The data are taken from Figure 1.

substrate and those induced by the Ni overlayer, respectively. The unit cell for Mo(110) is indicated by the solid line. This LEED pattern is assigned as (8×2) with respect to the ⟨110⟩ and ⟨001⟩ Mo lattice parameters, following a previous assignment for the same structure of Ni/Mo(110).[7] The (7×2) phase has a similar structure but with six satellite spots (instead of seven) between two integral spots along the ⟨001⟩ direction. From $\theta_{Ni} = 0.42$ to 0.95 ML, the Ni/Mo(110) surface exhibited the (8×2) pattern. The (7×2) pattern was observed at $\theta_{Ni} \geq 1.08$ ML. The Ni coverages for the (8×2) and (7×2) structures are 1.250 and 1.286 ML, respectively.[7,8] The surface density of a Ni(111) surface would correspond to 1.303 ML. Therefore, the (8×2) and (7×2) Ni phases are more densely packed than the Mo(110) surface (25% and 29%, respectively) but less dense than a Ni(111) surface (4% and 1%, respectively). In a recent study, the (8×2)-to-(7×2) transition also was found at $\theta_{Ni} = \sim 0.74-1.29$ ML for Ni deposition on Mo(110) at room temperature.[7] The (8×2) phase, however, was reported to be metastable, and unobserved by LEED for Ni deposition at $T > 600$ K.[7] The appearance of these structures at submonolayer Ni coverages suggests island formation on the Mo(110) surface.

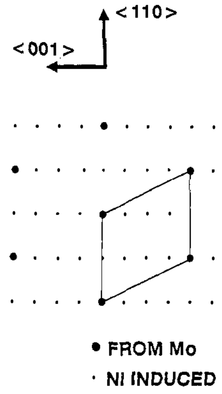

Figure 3. A schematic drawing of the (8×2) LEED pattern of Ni on Mo(110). The solid lines represent the unit cell of the Mo substrate lattice.

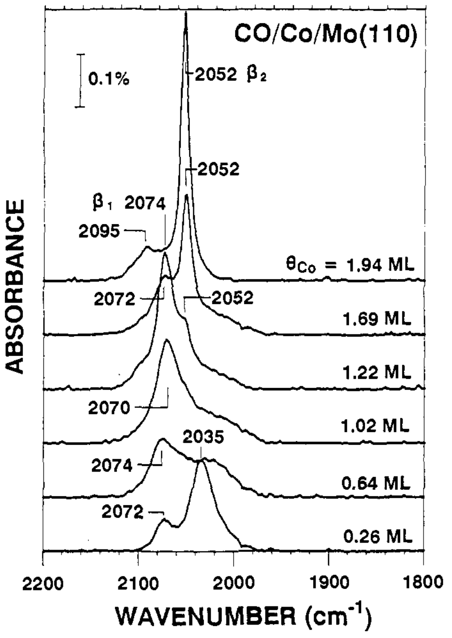

Figure 4. IR spectra of CO on Co/Mo(110) at the Co coverages indicated. Co was deposited onto the Mo(110) surface at 100 K, flashed to 900 K, and then dosed with 10 L of CO at 90 K. The IR spectra were collected at 90 K.

3.2. The Pseudomorphic to (8×2) Transition of Co/Mo(110). Co forms a pseudomorphic structure on Mo(110) for Co coverages less than 1 ML, i.e., the Co atoms assume the Mo(110) substrate lattice.[7,9] At $\theta_{Co} \geq 1$ ML, an ordered structure appears and is assigned as (8×2) (shown in Figure 3). The Co coverage of the (8×2) structure is 1.250 ML[9] and is, therefore, 25% more densely packed than the pseudomorphic structure and 2% less densely packed than the Co(0001) plane. A similar transition (pseudomorphic to (8×2)) was also observed for the Co/W(110) system.[10] Figure 4 presents the IR spectra of CO on Co/Mo(110) at the indicated Co coverages (θ_{Co}). The Co was deposited onto the Mo(110) surface at 100 K, heated to 900 K, and then dosed with 10 L of CO at 90 K; the IR spectra were then acquired. The pseudomorphic to (8×2) phase transition is clearly reflected in the spectra as θ_{Co} increases from 1.02 to 1.69 ML. CO adsorbed on the pseudomorphic and (8×2) phases shows peaks at 2074 (β_1) and 2052 (β_2) cm^{-1}, respectively. As the intensities of the two peaks change, the peak frequencies remain essentially unchanged.

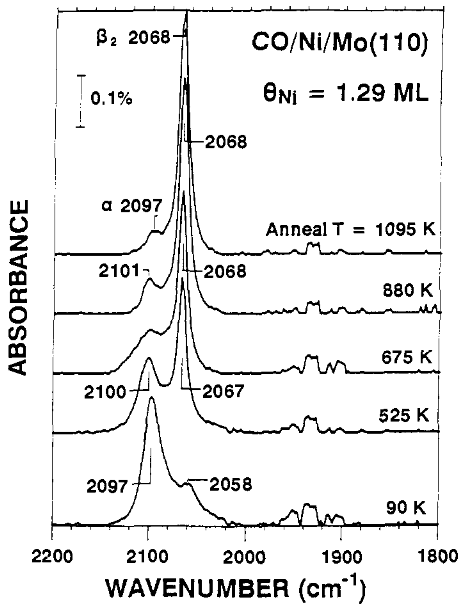

Figure 5. IR spectra of CO on 1.29 ML of Ni on Mo(110). The Mo(110) was deposited with Ni at 100 K, flashed to the temperatures indicated, and then dosed with 10 L of CO at 90 K after each flash. The IR spectra were collected at 90 K.

The peak at 2035 cm^{-1} corresponds to CO adsorbed on the Mo surface. The small peak at 2095 cm^{-1} is associated with trace surface C from dissociated CO on the Co overlayers.[9] The fwhm for the β_2 peak at θ_{Co} = 1.94 ML is 10 cm^{-1}.

3.3. Disorder-to-Order Transitions of Ni/Mo(110) and Co/Mo(110). In our previous IRAS study of CO adsorption on Cu/Rh(100), annealing a 1-ML film of Cu on the Rh(100) surface was found to induce a sharp peak in the CO IR spectra.[13] This sharp peak has been interpreted to correspond to the formation of a well-ordered pseudomorphic Cu overlayer on the Rh(100) surface.[13] In Figures 5 and 6, the disorder-order transitions of Ni and Co films on Mo(110) are also indicated by their CO IR spectra. For these spectra, the Mo(110) surface was covered with 1.29 ML of Ni or Co at 90 K and then flashed to the indicated temperatures. Each annealed surface was exposed to 10 L of CO at 90 K followed by IR spectral acquisition.

The spectrum from the unannealed Ni/Mo(110) surface shows peaks at 2097 and 2058 cm^{-1}. Annealing to higher temperatures increases the intensity of the 2058 cm^{-1} peak with its frequency shifted to 2068 cm^{-1}. This intensity increase is at the expense of the intensity of the 2097 cm^{-1} peak. At annealing temperatures higher than 675 K, the spectra are essentially identical with the spectrum at 1.44 ML in Figure 1. LEED observations showed that the deposition of Ni at 90 K attenuated the substrate spots and increased the background intensity significantly, indicating a disordered Ni overlayer. Annealing above 500 K decreased the background intensity considerably and yielded the (7×2) pattern. The IR spectral changes in Figure 5 correlate well with the LEED results and reflect the formation of the ordered (7×2) structure from a relatively disordered Ni overlayer. During this surface ordering, the peak frequencies for the ordered and disordered phases are essentially unchanged. The broad peak at ~1932 cm^{-1} is interpreted as bridge-bound CO on the Ni overlayer.[14,15]

IR spectra showing the disorder to (8×2) transition for Co on Mo(110) are presented in Figure 6. As the surface is annealed above 535 K, a peak at 2050 cm^{-1} appears and becomes dominant at the expense of the intensity of the 2073 cm^{-1} peak. LEED observation demonstrated that annealing above 500 K decreased the background intensity and yielded an (8×2) pattern. Similar to the Ni/Mo(110) system, as discussed above, the correlation of the IR spectral changes in Figure 6 with the LEED results indicates the formation of an ordered (8×2) structure from a relatively disordered Co overlayer. The high-frequency peaks at ~2100 cm^{-1} are associated with dissociated CO. CO has been shown to dissociate on ultra-thin Co films on a Mo(110) substrate, with subsequent recombination and desorption at ~950 K.[9]

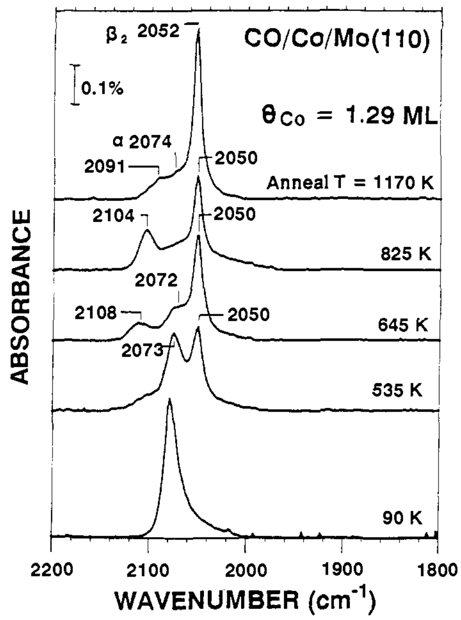

Figure 6. IR spectra of CO on 1.29 ML of Co on Mo(110). The Mo(110) was deposited with Co at 100 K, flashed to the temperatures indicated, and then dosed with 10 L of CO at 90 K after each flash. The IR spectra were collected at 90 K.

4. Discussion

The present work has demonstrated that CO IRAS spectra show a remarkable sensitivity to the structural phase transitions of Ni and Co overlayers on a Mo(110) surface. As mentioned above, the (8×2) and (7×2) phases of Ni/Mo(110) both have a distorted Ni(111) lattice with surface coverages of 1.250 and 1.286 ML (1 ML is defined as 1 overlayer atom per substrate atom), respectively. Thus, the density difference in the two surfaces is only 3%. The two structures, however, are unambiguously identified by their CO peaks at 2087 and 2065 cm^{-1}. Similarly, the CO IR spectra clearly characterize the pseudomorphic and the (8×2) overlayer structures of Co/Mo(110) with surface coverages of 1.0 and 1.250 ML, respectively.

The ability to use CO as a molecular probe for phase transitions obviously results from a different CO bonding strength and/or configuration to the different metal overlayer structures, as well as the intrinsic high resolution of IRAS. During the structural phase transitions, the changes in electronic and structural properties of the metal overlayers induce a frequency shift in the adsorbed CO. The phase change may result in an alteration of the CO–CO intermolecular spacing and consequently change molecule–molecule interactions, such as dipole–dipole coupling.[12] In addition, changes in the electronic properties of the overlayer could alter substrate–CO interactions, such as charge backdonation from the metal overlayers to the adsorbed CO. However, any effect due to the overlayer geometric change is expected to be negligible on the basis of the following: (a) As mentioned above, the density difference between the Ni (8×2) and (7×2) phases is only 3%, while the difference between the Co pseudomorphic and (8×2) phases is 25%. This corresponds to a change of only 1.5% and 12% in the respective lattice constants. These small variations (0.05 and 0.38 Å) are expected to have little effect on the molecular interactions. (b) The spectra in Figure 1 show that the integrated intensity and the full width at half maximum for the spectra at 0.95 and 1.08 ML are invariant during the phase transition. This further discounts the possibility that CO adsorbed on the two phases has significantly different molecule–molecule interaction. It is well-known that as CO coverage increases, the increase in molecular interactions usually results in a decrease in IR intensity (due to depolarization) and an up-shift in frequency (due to dipole–dipole coupling).[12]

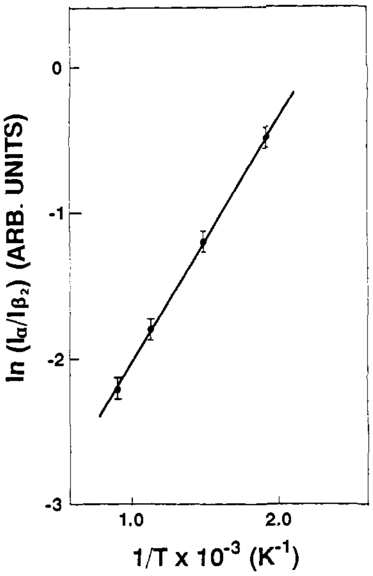

Figure 7. A Van't Hoff plot of ln (I_α/I_{β_2}) vs $1/T$ for the spectra in Figure 5. The enthalpy difference ΔH between the disordered and ordered phases is deduced to be 3.5 ± 0.4 cal/mol.

The abrupt frequency shifts observed during the phase transitions are, therefore, attributed mainly to changes in the electronic properties of the metal overlayers. During the phase transitions, the overlayer density increases to approach that of the corresponding bulk metal surface. The work function of and the CO desorption temperature from the metal overlayers also increase to approach those for a Ni(111) or Co(0001) surface.[7,9] As the Ni or Co overlayers change from strained structures to relatively relaxed ones ((8×2) to (7×2) for Ni and (1×1) to (8×2) for Co), the strain-induced electronic perturbations of the overlayer atoms are reduced. Thus, the backdonation from the metal overlayer to the CO $2\pi^*$ orbital increases, and the C–O stretch frequency is consequently red-shifted. This work shows a red-shift of 20–30 cm^{-1} as the surfaces change from relatively open to relatively close-packed structures ((8×2) to (7×2) for Ni and (1×1) to (8×2) for Co).

It is noteworthy that the formation of ordered phases ((7×2) for Ni/Mo(110) and (8×2) for Co/Mo(110)) from disordered Ni or Co overlayers is also clearly indicated in the corresponding CO IR spectra as shown in Figures 5 and 6. It has been observed that annealing an ultra-thin film usually induces a red-shift in the stretching frequency of adsorbed CO. Assuming that the integrated intensities of the peaks in Figure 5 represent the coverage of the ordered and the disordered phases, a Van't Hoff plot is constructed (Figure 7). The slope of the plot yields an enthalpy difference of 3.5 ± 0.4 kcal/mol between the disordered and the (7×2) phase with the (7×2) phase being more stable. To make this plot, it has been further assumed that CO has the same effective dipole moment on the disordered and (7×2) phases (this assumption is supported by the fact that the total integrated intensity in Figure 5 remains unchanged in the anneal temperature range 525–1095 K) and that annealing leads to an irreversible change in the surface phases which are in equilibrium at the annealing temperature.

During the phase transitions on Ni/Mo(110) and Co/Mo(110), the stretching frequency of CO adsorbed on each phase remains virtually unchanged (see Figures 1–4). This strongly implies a 2-D island growth mechanism of the phases, with two-dimensional phase expansion at the island edges. The configuration and bond strength of CO at the island interiors would thus be preserved during the phase transition. This mechanism has also been observed in the disorder-pseudomorphic transition of Cu/Rh(100)[13] and appears to be general for all the phase transitions at metal–metal interfaces that we have addressed to date. In an early study of CO adsorption on a Ru(0001) surface, the CO within the ordered CO islands of the $\sqrt{3} \times \sqrt{3}$ R 30° structure showed a different frequency from the CO at the island edges.[16] In the present work, each ordered phase is represented by a single, highly symmetric peak. Therefore, the contribution of CO at the island edges is negligible. However, the IR peaks at 2100 and 2083 cm^{-1} at θ_{Ni} = 0.26 ML in Figure 1 may correspond to CO adsorbed on small islands and island edges. As Ni coverage is further increased to 0.42 ML, the spectrum shows only a single peak for the (7×2) structure, indicating that the islands have grown in size and the fraction of the CO adsorbed at the edges has become small. The present work does not yield quantitative information on island size.

Finally, it is noteworthy that in both the order–order and the disorder–order phase transitions, a small percentage of the initial phase remains in co-existence with the final phase. In other words, the phase transitions observed in this work never yield a totally uniform, single phase on the surface. This demonstrates further the utility and sensitivity of IRAS to monitor surface phases.

5. Conclusions

The present work has shown that CO IRAS is a sensitive probe for studying phase transitions at Ni/Mo(110) and Co/Mo(110) interfaces. This capability is based on the fact that CO adsorbed on different phases has distinct stretching frequencies. Whether both phases are ordered or one ordered and the other disordered, CO IRAS can be used to characterize the surface phases present. The present study has also shown that the phase transitions on Ni/Mo(110) and Co/Mo(110) occur via a mechanism of two-dimensional island growth with expansion at island edges and that CO adsorbed on less strained structures has a stronger CO–metal interaction.

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Registry No. Ni, 7440-02-0; Co, 7440-48-4; Mo, 7439-98-7; CO, 630-08-0.

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