Pd, Cu, and Au particles on Al$_2$O$_3$ thin films: An infrared reflection absorption spectroscopy study of monometallic and bimetallic planar model supported catalysts

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The chemisorptive behavior of CO on several planar model monometallic and bimetallic Pd, Cu, and Au catalysts supported on thin film Al$_2$O$_3$ has been investigated using infrared reflection absorption spectroscopy (IRAS). For Pd and Cu monometallic catalysts, CO adsorption spectra indicate a high representation of low index planes, while the morphologies of smaller particles are characterized more by high densities of low coordinated step/edge defect sites. For Au particles, CO was observed to be present on the surface at conditions where low index Au single crystals have been observed to be inactive for CO adsorption, indicating the modified chemisorptive properties at step/edge sites. For the IRAS studies of supported Pd–Au and Pd–Cu catalysts, no conclusive indications of ligand effects were apparent in the CO stretching frequencies. The spectra for the bimetals resemble combinations of both analogous monometallic catalysts, even though a significant degree of metal mixing is apparent from thermally induced changes in the IRAS, and from previous ion scattering spectroscopy studies. A peak possibly attributable to Pd diluted in the surface by the presence of a dissimilar metal is apparent for each of these bimetallic supported catalysts. © 1997 American Vacuum Society. [S0734-2101(97)58803-8]

I. INTRODUCTION

The employment of planar model supported catalysts, obtained by the vapor deposition of catalytic metals onto oxide thin film supports in ultrahigh vacuum (UHV), has recently emerged as a promising avenue of research into the physical and catalytic properties of supported metal systems. These types of model catalysts feature many of the advantages of metal single crystals (i.e., tractability for fundamental, atomic level investigation using modern surface science methods) while still addressing important issues such as the effect of particle size and the metal-support interaction.\(^1\)-\(^4\) The utility of these models is attested to by the numerous studies appearing in the literature examining the effect of particle size on such properties as electronic structure, chemisorptive properties, and kinetic activity for a particular reaction.\(^1\)-\(^15\) Of particular interest for the work presented here is the application of in situ infrared reflection adsorption spectroscopy (IRAS) using CO as a probe molecule to study the morphologies of the supported metal particles as a function of their size. Comparisons of the vibrational spectra acquired for the models with analogous results for well defined single crystals reveals particle size dependent structural information regarding specific binding site and, to a more limited degree, facet distribution.\(^16\)-\(^18\) The relatively narrow particle size distributions that are obtained for these model catalysts\(^12\),\(^19\)-\(^21\) make them ideal subjects of this kind of particle size resolved experiments.

Bimetallic systems have long commanded considerable interest in the study of heterogeneous catalysis. The addition of a second dissimilar metal often modifies the catalytic behavior of the first, in many cases enhancing the stability, activity, and/or selectivity beyond that of either catalyst alone. These catalytic modifications due to metal mixing are generally categorized in one of two broad classes: ensemble effects, referring to the situation where a prescribed number of atoms in a particulate geometric orientation to one another is required for some catalytic process, or ligand effects, referring to the electronic modifications that occur upon the addition of a second metal and the formation of heteronuclear metal–metal bonds.\(^22\),\(^23\) A difficult problem associated with identifying and separating these effects for supported bimetallic catalysts is the ambiguity surrounding the composition of the small metal particles. IRAS using bimetallic planar supported model catalysts offers some intriguing possibilities for addressing this issue.

This study employs IRAS to investigate the surface morphology of several monometallic and bimetallic Al$_2$O$_3$ supported metal systems. The mixed metal results are discussed with reference to previous ion scattering spectroscopy (ISS) work on analogous alloy systems, as well as with the results from the monometallic supported counterparts.

II. EXPERIMENT

These experiments were performed in a conventional UHV chamber coupled to an in situ elevated pressure IR cell, previously described in the literature,\(^24\) with a base operating pressure of \(\sim 5 \times 10^{-10}\) Torr. The IR cell is equipped with KBr windows and can accommodate pressures ranging from UHV up to several Torr. Pressures in the cell are monitored using an ionization gauge or a 10 Torr baratron gauge. The single crystal metal substrate was mounted on a transferable probe, which could be cooled by liquid N$_2$ or heated either resistively or by an electron beam filament, allowing surface
temperatures ranging from 90 to 2000 K to be achieved. The sample temperature was monitored using a type "C" thermocouple spot welded to the edge of the crystal.

The model catalysts were prepared by the vapor deposition of the catalytic metal(s) (Pd, Cu, and Au) onto an Al₂O₃ thin film supported on the metal single crystal [Mo(110) or Mo(100)]. The alumina films were obtained by the vapor deposition of Al onto the refractory metal substrate in a 1 × 10⁻⁶ Torr O₂ background, followed by annealing to 1200 K in O₂. The Al dosing was carried out by resistively heating a ceramic tube 1 mm × 7 mm packed with 99.999% purity Al wire and wound with a Ta heating filament. Film thicknesses were calibrated using Auger electron spectroscopy (AES), and were typically in the 20–30 Å range. The Al₂O₃ growth mode has been shown to differ on each of these single crystal substrates but for Al₂O₃ films of the thickness employed here, IRAS and CO temperature programmed desorption (TPD) results have indicated that these differences exert very little if any influence on the deposited metal particle size distribution or morphology.

Vapor deposition of the catalytic metals was accomplished using resistively heated dosing sources consisting of high purity Pd, Cu, or Au wire wrapped tightly around a Ta heating filament. Metal coverages are reported in terms of equivalent monolayers, calibrated using either TPD peak area or AES.

The IRAS spectra were obtained on a Mattson Cygnus 100 spectrometer at a resolution of 4 cm⁻¹ and an incidence angle of 85°. Backgrounds were collected at elevated substrate temperatures sufficient to insure negligible concentrations of adsorbed CO. The CO (99.995% purity, Matheson) was stored in a glass bulb immersed in liquid N₂ in order to condense undesirable hydrocarbons and/or carbonyls.

III. RESULTS AND DISCUSSION

A. Pd/Al₂O₃/Mo(100)

An IRAS annealing series for a Pd(5.0 ML)/Al₂O₃/Mo(100) catalytic in a 2 × 10⁻⁶ CO Torr background pressure is presented in Fig. 1. TEM images of analogous carbon supported Pd/Al₂O₃ model catalysts have indicated an average particle size of ~70 Å for this Pd coverage. Virtually identical IRAS results have previously been obtained for Pd (5.0 ML)/Al₂O₃/Ta (110) model catalysts. At 500 K, peaks attributed to CO bound in bridging and threefold hollow sites appear at 1894 and 1835 cm⁻¹, respectively. As the sample is cooled and the CO equilibrium coverage increases, these peaks are shifted to higher frequencies due to lateral CO–CO interactions, and the threefold hollow feature disappears as the intensity in the bridging region increases. At ~350 K, a peak at 2074 cm⁻¹ appears that has been attributed to CO bound in the linear atop position, and the bridging feature is observed to resolve itself into two peaks. It has been suggested that the shift that occurs in the linear atop peak between 250 and 150 K in Fig. 1, represents the transition from a compressed to an uncompressed CO overlayer; the implications of this for interpreting the mixed results are important, as is shown below. Between 200 and 150 K, a phase transition occurs in which the bridge-bound feature at ~1950 cm⁻¹ is dramatically attenuated, with an accompanying increase in linear atop and threefold hollow intensity at 2108 and 1887 cm⁻¹, respectively. This very specific phase transition has been observed on the Pd(111) single crystal and has led to the conclusion that the morphology of ~70 Å Pd particles in the thin film Al₂O₃ model catalysts is primarily characterized by relatively well-defined low index faceting. Similarly, the peak at 1996 cm⁻¹ is consistent with bridge-bound CO on the (100) face; single crystal studies indicate that CO binds exclusively in this position on the Pd(100) surface.

Previous Pd particle size dependent IRAS studies have demonstrated that significant changes appear in the vibrational spectra that indicate higher proportions of low coordinated step/edge defect sites and less well defined faceting with decreasing particle size. Peak widths are observed to broaden, suggestive of greater surface heterogeneity and/or disorder in the CO overlayer, and contributions from CO bound in the threefold hollow site at 100 K are entirely absent for particles <30 Å in diameter. These results for monometallic Pd model supported catalysts are important in interpreting the spectra for the bimetallic systems discussed below and will be referred to again in the appropriate sections.
B. Cu/Al₂O₃/Mo(100)

Transmission infrared spectroscopy studies of high surface area supported Cu catalysts have consistently yielded a single adsorption band between ~2100 and 2110 cm⁻¹ for fully reduced catalysts, with some notable exceptions on supports that promote epitaxial growth of low index planes.

IRAS studies on various low index Cu single crystal surfaces have exhibited bands at significantly lower frequencies than those observed on the supported catalysts. For the (111) and (100) faces, a single band around 2080 cm⁻¹ appears. The more open (110) surface exhibits a slightly higher band at ~2090 cm⁻¹, but still significantly lower than the band consistently observed on the supported catalysts. IRAS studies conducted on highly stepped single crystal and polycrystalline surfaces, on the other hand, do indeed display the same higher frequency bands associated with the supported catalysts. Isotopic dilution studies have shown that the IR spectra for CO adsorbed on Cu are dominated by intensity transfer from CO bound on the terraces to CO bound on the steps. In fact, even for a Cu(16,15,0) surface [110] terraces 16 atoms wide separated by monatomic steps] studied by Hollins et al., at CO saturation coverage the feature above 2100 cm⁻¹ assigned to CO bound on the step site is larger than the peak representing the much more abundant CO on the terraces. The effect is quite dramatic and must be considered in interpreting the data presented here.

Figure 2(a) shows IRAS spectra for CO adsorbed on a 1.0 ML Cu coverage deposited at 140 K and unannealed. The catalyst was cooled to 110 K and introduced into a 2 × 10⁻⁶ Torr background pressure of CO. At this temperature, three features are evident in the spectrum. A large peak occurs at 2090 cm⁻¹ with a lower frequency shoulder centered around 2057 cm⁻¹. Based on the previous discussion, these features would seem to represent CO bound on low index terraces; specifically, the largest peak at 2090 cm⁻¹ is suggestive of CO bound on a (110)-like surface, and the shoulder at 2057 cm⁻¹ implies the presence of (111) and (100) facets. A smaller peak appears at 2107 cm⁻¹, consistent with CO bound on a low-coordinated step/edge or defect site. These results seem to indicate that two-dimensional island growth is dominating under these growth conditions, resulting in low index Cu islands, as has been observed in previous studies for Cu/SiO₂. In fact, the large majority of CO must be adsorbed on these low index planes. Otherwise, the intensity sharing that dominates the IR spectra of CO on supported Cu particles would result in a much larger peak at 2107 cm⁻¹ at the expense of the peak at 2090 cm⁻¹.

As the temperature increases, several changes in the spectrum are observed. As expected, the combined integrated IR
absorbance intensity decreases as the CO coverages decrease. The peak at 2191 cm\(^{-1}\), tentatively assigned to CO bond on CuO (Ref. 30) or isolated Cu\(^{2+}\) incorporated in the alumina film,\(^{31}\) has disappeared entirely at 165 K. The peak and shoulder below 2100 cm\(^{-1}\), attributed to CO bound on the low index terraces, decrease more rapidly than does the defect CO, shifting to higher frequency with decreasing coverage until they merge and disappear into the remaining high frequency peak. This defect peak increases slightly in frequency to 2111 cm\(^{-1}\) before being fully attenuated at 350 K. It is noteworthy that the CO bound on the defect sites appears to be the most strongly bound species. This is the opposite behavior to that displayed upon Pd (see above), where CO adsorbed in the bridge bond and threefold hollow sites are preferred at the lowest coverages, reflecting the differing natures of the CO-metal bonds for these two substrates.

Figure 2(b) compares the IRAS spectra at 110 K for the annealed and unannealed samples. The average particle di-

meter on the annealed sample is estimated to be \(\sim 70 \, \text{Å}\), whereas the particles for the unannealed sample are presumably much smaller.\(^{12}\) Annealing to 400 K results in an attenuation in the total absorbance intensity and an almost complete intensity shift to the defect feature. This is wholly consistent with thermally induced particle sintering, resulting in a net decrease of Cu surface area and a higher incidence of step/edge defect sites upon the formation of small particles.

This interpretation is supported by IRAS spectra obtained for an equivalent monolayer Cu coverage deposited at a substrate temperature of 500 K to promote three-dimensional growth, and subsequently annealed to 600 K (Ref. 32) (not shown here) that are consistent with CO bound on small Cu particles with a high concentration of step/edge defect sites (2104 cm\(^{-1}\)) and low-index faces (2068 cm\(^{-1}\)). Compared to the Cu monolayer deposited at 140 K, a higher fraction of the (111) and (100) facets is represented, with no obvious contribution from the (110) facet. The increased contribution from these lowest index facets implies the formation of particles of greater thermodynamic stability linked to the elevated deposition temperature for this model catalyst. Even after annealing to 400 K, the Cu (1 ML) deposited at 140 K [Fig. 2(b)] displays only a small shoulder at 2071 cm\(^{-1}\) associated with the (111) and (100) facets, representing a smaller proportion of low-index planes compared to the Cu deposited at 500 K and annealed to 600 K. This suggests that there is a kinetic limitation to the thermally induced formation of the most thermodynamically stable particles for the Cu initially deposited at low temperatures.

A 5.0 ML Cu\(_{12}\)O\(_2\)/Mo(100) sample was also prepared, the Cu deposited at 500 K and subsequently annealed to 600 K. The resulting IRAS annealing series is qualitatively identical to that of the 1.0 ML Cu model catalyst, with the notable difference of an increased ratio of the low frequency peak to the high frequency peak at 110 K for this 5.0 ML Cu catalyst compared to the analogous spectrum for the 1.0 ML Cu deposition.\(^{32}\) Again, this is consistent with an increasing ratio of the low index (111) and (100) planes to step/edge sites on the larger Cu particles, which was the same trend observed for the Pd.

C. Au/Al\(_2\)O\(_3\)/Mo(110)

Supported Au particles provide an excellent example of the effect surface morphology can have on chemisorptive properties. For single crystal Au(100) surfaces, previous studies under comparable conditions have indicated that CO will not adsorb at temperatures down to 125 K.\(^{33,34}\)

IRAS spectra for CO adsorbed on a Au(0.5 ML)/Al\(_2\)O\(_3\)/Mo(110) model catalyst at a CO background pressure of \(1 \times 10^{-5}\) Torr are presented in Fig. 3(a). The Au was deposited at 300 K. At 100 K, a single peak at 2100 cm\(^{-1}\) (atop bound CO) appears. At 200 K, the peak undergoes a frequency shift to 2111 cm\(^{-1}\) and the integrated absorbance intensity has decreased. This blueshift with decreasing coverage is opposite to the trend observed on Pd, and is consistent with previous work on Au/SiO\(_2\) powder catalysts\(^{35}\) that shows a large negative shift which offsets the positive dipolar shift as CO coverage increases. At 300 K, the spectrum indicates no CO on the surface. A similar annealing series of CO pumped away after initial exposure at 100 K (not shown), displays peak positions and shifts consistent with the previous set, and exhibits a desorption temperature for CO at \(-200\) K or lower.

CO adsorption as a function of Au loading was also investigated. Figure 3(b) shows the IRAS spectra at 100 K for several different coverages of Au in the supported model catalyst. As the Au coverage (average particle size) increases, a modest blueshift (\(-7\, \text{cm}^{-1}\)) is observed in the C=O stretching frequency. This may be related to a CO coverage effect. The lack of CO adsorption activity for Au(110) at 125 K (Ref. 33) suggests that CO bonds only on undercoordinated step/edge defect sites. As the particle size increases, the concentration of these sites is expected to decrease, as has been demonstrated for Pd and Cu. This results in a decrease of the surface coverage of CO at 100 K. This particle size dependent shift may also reflect changes in the electronic structure of Au as the average coordination number increases.

D. Cu–Pd/Al\(_2\)O\(_3\)/Mo(100)

Figure 4(a) shows an annealing series for a Cu (1.0 ML)/Pd (7.0 ML)/Al\(_2\)O\(_3\)/Mo(100) model catalyst in a \(2 \times 10^{-6}\) Torr CO background. The Pd was deposited at 500 K and subsequently annealed to 800 K, followed by a 1.0 ML deposition of Cu at 120 K. At 105 K, two features appear in the spectrum. The spectrum is dominated by a peak at 2108 cm\(^{-1}\) that corresponds to CO bound in the atop position on Cu and/or Pd. Additionally, a very small peak appears at 1989 cm\(^{-1}\), in the region normally associated with CO adsorbed on Pd in a bridge-bound position. The extreme attenuation of this peak in relation to a pure Pd catalyst (Fig. 1) is consistent with Cu wetting the surface of the Pd very effectively. It implies that very few Pd atoms exist side by side on the surface. Similarly, there is no feature for CO bound in the threefold hollow site.
As the sample is annealed in CO, several changes are apparent in the spectrum. At 225 K, the peak in the Pd bridge-bound region is starting to intensify slightly. Also, a new peak appears at \( \sim 2060 \text{ cm}^{-1} \), being fully attenuated by \( \sim 450 \text{ K} \). The origin of this peak is not immediately obvious. It seems unlikely that this feature can be attributed to CO bound on Cu, because the temperature range over which it is observed is too high.

For the pure Cu/AI\(_2\)O\(_3\) catalysts discussed earlier, the atop CO feature was fully attenuated by \( \sim 300 \text{ K} \) at this CO background pressure. For Cu in a well mixed Pd(45\% Cu(55\%)) \{111\} surface alloy, Bertolini et al., observed only a 5.6 kcal/mol increase in the heat of adsorption for CO on Cu (\( \sim 60-70 \text{ K} \) increase in the desorption maximum in TPD) due to the interaction with Pd.\(^{36}\) This moderate increase observed in that experiment would be insufficient to account for the difference noted here in thermal stability between CO bound on pure Cu and Cu in a Pd surface if the peak at \( 2060 \text{ cm}^{-1} \) in fact arose from CO bound on electronically modified Cu. This indicates that this peak must be related to Pd.

Also, it seems doubtful that the feature could be associated with CO multiply bound between Cu and Pd, as the stretching frequency is too high. Additionally, high-resolution electron-energy-loss spectroscopy (HREELS) studies of CO bound on the Cu(001)c(2x2)-Pd surface (a well ordered 50\%-50\% Cu-Pd alloy surface) by Lu et al., provided no indications of CO multiply bound to both Cu and Pd.\(^{37}\) Comparisons with pure Pd model supported catalysts and the Pd(111) single crystal may yield some insight into the origin of this feature.

As noted above, for pure Pd particles, the peak in the region associated with atop-bound CO begins to undergo a shift from \( \sim 2100 \) to \( \sim 2074 \text{ cm}^{-1} \) at \( \sim 200 \text{ K} \) as temperature increases (Fig. 1); this feature persists in the spectrum up to surface temperatures of \( \sim 400 \text{ K} \). This similarity in the position and the thermal behavior suggests that the feature at \( \sim 2060 \text{ cm}^{-1} \) for the bimetallic catalyst is related to atop CO bound on Pd in an uncompressed overlayer. A similar IRAS feature at \( 2065 \text{ cm}^{-1} \) for CO bound on a 75\% Pd(Cu)/SiO\(_2\) powder catalyst in a study by Hendrickx and Ponec has been attributed to CO bound atop on Pd.\(^{38}\) However, the stretching frequency is \( 10-15 \text{ cm}^{-1} \) lower than that observed on the pure Pd catalyst, and the feature is sharper and more intense. One explanation of this feature is an enhancement in the coverage of the uncompressed CO bound atop on Pd due to a dilution in the concentration of Pd atoms in the surface layer by Cu, an ensemble effect. The frequency redshift of this feature relative to that observed for the single crystal and the pure Pd model supported catalyst could be a result of either a reduction in the dipole-dipole interaction of CO or an electronic modification of Pd by Cu that alters the Pd-CO bond.

Ligand effects on the CO stretching frequency are diffi-
cult to interpret. For Cu overlayers deposited on transition metal substrates that result in increased Cu 3d electron density and CO–Cu bond strength, the changes in the CO stretching frequencies do not reflect the electronic modification to Cu in a manner one might anticipate based on the Blyholder model. For example, Cu supported on Pt (111) exhibits a large negative core-level shift (CLS) and a 70 K increase in the CO TPD maximum, and yet the C–O stretching frequency is ~20 cm⁻¹ higher than for CO bound on Cu(111). Besides being sensitive to the degree of π back-donation to the 2π* CO antibonding orbitals, the stretching frequency is also influenced by the electrostatic interaction between the partial charge residing on the metal center and the CO dipole moment and also by the repulsive interaction between the vibrating CO and the rigid surface to which it is bound. The complex interplay between these various contributing factors makes interpreting this small frequency shift for the bimetallic difficult. Hendrickx and Ponce concluded, based on CO isotopic dilution experiments, that no ligand effect was apparent in the CO stretching frequency for the 75% Pd(Cu)/SiO₂ powder catalyst.

Figure 4(b) shows the IRAS spectra for saturation coverages of CO at 105 K after the sample has been annealed to successively higher temperatures in the CO background and recooled. The unannealed sample and the sample annealed to 250 K display only slight differences, but for the 400 K annealing temperature, notable changes have occurred. The Pd bridge-bound peak has increased significantly, the high frequency atom feature has decreased, and a shoulder at approximately 2060 cm⁻¹ has appeared. The emergence of the Pd bridge-bound peak at saturation indicates an increasing concentration of Pd on the surface. As the annealing temperature is further increased to 600 K, the ratio of the Pd bridge bound to the atom feature also increases. These results are consistent with ISS results for Cu deposited on multilayer Pd films supported on Mo(110) that indicate significant Cu diffusion into the bulk Pd as the annealing temperature is increased across a similar range. For those systems, Cu deposited at 330 K effectively wets the surface, and then immediately begins to diffuse into the film as the temperature is raised. By 600 K, ISS indicates significant alloying has occurred. The appearance of the shoulder at 2060 cm⁻¹ at 105 K is again suggestive of CO bound atop Pd atoms relatively dispersed in a Cu surface in such a way as to preclude the formation of the compressed CO overlayer that blueshifts the frequency. The large peak widths probably result from the increased inhomogeneity that one would expect in a well mixed, disordered alloy.

An annealing series for a Pd(1.0 ML)/Cu(6.0 ML)/Al₂O₃/Mo(100) catalyst is presented in Fig. 5(a). The Cu was deposited at 500 K and annealed to 600 K, followed by Pd deposition at 120 K with no annealing prior to CO exposure. At 105 K, the spectrum looks very similar to that of a pure 1.0 ML Pd catalyst, with a large peak in the region associ-
ated with atop bound CO and a smaller peak in the bridge-bound region. The peaks for the unannealed saturation coverage are broad, again suggestive of a poorly ordered unannealed surface and possibly also due to disorder in the CO overlayer that results from the low temperature initial adsorption conditions. As the sample is annealed, an intensity shift from the high frequency atop peak to a peak at ~2060 cm⁻¹ begins at 220 K. By 300 K, a single peak at 2065 cm⁻¹ can be seen in this frequency region, in addition to the lower energy peaks attributed to CO multiply bound on Pd at 1980 and 1920 cm⁻¹. At 350 K, three features are evident at 1974, 1920, and 1840 cm⁻¹, associated with bridge- and threefold hollow-bound CO. By 450 K, these multiply bound CO peaks have almost been completely attenuated. Since these features persist in the spectrum at temperatures up to ~550 K on pure Pd catalysts, this indicates that the concentration of Pd on the surface is decreasing with heating due, again, to diffusion of the admetal into the bulk dissimilar metal onto which it has been deposited. This is consistent with ISS results for the Pd(1.0 ML)/Cu(10.0 ML)/Mo(110) system that shows that significant diffusion of surface Pd into the Cu film has occurred at an annealing temperature of 500 K for Pd deposited at 325 K.⁴¹

A second temperature series for the same catalyst, after being annealed in CO to 600 K, is presented in Fig. 5(b). At 110 K, the peak at 2112 cm⁻¹ has narrowed significantly, indicative of the different initial adsorption conditions, and possibly of a decrease in the heterogeneity of the binding sites relative to the unannealed sample. The peak intensity for the bridge-bound CO has been attenuated dramatically, which is consistent with thermally stimulated Pd diffusion into the Cu particles. In fact, throughout this entire postannealed temperature series, no features associated with multiply bound CO on Pd are apparent.

As the temperature is increased, the peak at 2112 cm⁻¹ is attenuated, demonstrating thermal stability consistent with the atop feature observed on the pure Cu catalyst. Concurrently, a feature at 2061 cm⁻¹ appears and grows in intensity, virtually identical to the corresponding feature in the Cu(1.0 ML)/Pd(7.0 ML)/Al₂O₃/Mo(100) catalyst. Again, this peak must be related to Pd, as the thermal stability is too high for CO on Cu, but the peak position is shifted relative to the uncompressed atop CO feature on the pure Pd catalysts.

Finally, a Pd(1.0 ML)/Cu(1.0 ML)/Al₂O₃ catalyst was prepared by vapor depositing 1.0 ML of Pd at 120 K onto 1.0 ML Cu deposited at 500 K and annealed to 600 K prior to Pd dosing. A CO annealing series for CO introduced at 120 K is presented in Fig. 6(a), followed by a series for the catalyst after annealing to 600 K in CO in Fig. 6(b). These results are qualitatively identical to those for the larger bimetallic Pd/Cu and Cu/Pd particles just presented. For the unannealed sample at 110 K in Fig. 6(a), the spectrum features broad peaks at 2112 and 1974 cm⁻¹, representing atop and bridge-bound CO. As the sample is annealed in CO, a shift in
the position of the broad top feature above 2100 cm\(^{-1}\) towards the peak at \(~2060\) cm\(^{-1}\) is apparent. At the higher temperatures, low intensity peaks below 2000 cm\(^{-1}\) associated with CO bridging and threefold-hollow-bound CO are clearly present, indicating imperfect mixing of Pd and Cu on the surface of the particles. For the sample annealed to 600 K in the CO background, the peaks are much sharper, the feature near 2060 cm\(^{-1}\) being very distinctive. Significant amounts of CO multiply bound on Pd are still apparent.

The IRAS results for these three Cu–Pd/Al\(_2\)O\(_3\)/Mo(100) catalysts revealed no conclusive ligand effects on the CO stretching frequencies relative to the pure metals, in spite of the electronic changes to each constituent that have been indicated by x-ray photoemission spectroscopy (XPS) studies.\(^{41}\) The spectra for the bimetallics exhibited basically the same features observed for the single metal catalysts with roughly the same thermal behavior. For all three catalysts, in the temperature range from \(~200\) to \(~400\) K, a sharp peak attributed to CO bound atop on diluted Pd in a mixed Pd–Cu surface is evident in the spectrum.

E. Au–Pd/Al\(_2\)O\(_3\)/Mo(110)

Figure 7(a) shows an annealing series for a Au(1.0 ML)/Pd(5.0 ML)/Al\(_2\)O\(_3\)/Mo(110) model catalyst in a 2 \times 10^{-6} Torr CO background. The Pd was deposited at 500 K and then annealed to 800 K, followed by Au deposition at 120 K.

At 100 K, features attributed to both atop and bridge-bound CO are visible in the spectrum. The appearance of bridging CO [which was not seen for the unannealed Cu(1.0 ML)/Pd(5.0 ML)/Mo(110) catalyst] indicates that Au does not wet the surface of the Pd particles at low temperatures as efficiently as Cu. As the temperature is increased, the atop feature at 2118 cm\(^{-1}\) is attenuated, concurrently with the appearance of a peak at 2085 cm\(^{-1}\). This peak displays the same thermal behavior as the uncompressed atop CO peak on pure Pd catalysts, and as the peak at \(~2060\) cm\(^{-1}\) observed for the Pd–Cu bimetallic systems. These similarities suggest that the feature can possibly be attributed to CO bound on Pd diluted in a Pd–Au surface. As the surface coverage decreases, this peak shifts toward \(~2070\) cm\(^{-1}\). As the sample is annealed, features for CO bound on bridging and threefold hollow sites displaying ostensibly the same thermal behavior as on pure Pd are present.

After annealing to 600 K [Fig. 7(b)], the increase in the contribution from CO multiply bound on Pd indicates Au diffusion into the Pd particles, consistent with ISS results for Au supported on a Pd film on Mo(110).\(^{41}\) A peak at 2085 cm\(^{-1}\) is quite evident in the saturation coverage spectrum at 100 K. As the CO coverage decreases with increasing temperature, this feature shifts toward lower stretching frequency, consistent with CO bound on Pd.
Vapor depositing an additional 1.5 ML of Au onto this catalyst (for a total Au loading of 2.5 ML) at 120 K results in the spectra in Fig. 8(a). At 100 K, the CO bridging feature at 1973 cm\(^{-1}\) has been attenuated significantly. The atop feature at 2109 cm\(^{-1}\) is sharper than the analogous peak for the unannealed Au(1.0 ML)/Pd(5.0 ML)/Mo(110) catalyst, possibly indicating less heterogeneity of bonding sites; this might be expected if the surface was covered predominantly by Au.

For the second annealing series presented in Fig. 8(b) (after the sample has been heated to 600 K in the CO background and subsequently cooled), the ratio of the peak at \(\sim 2105\) cm\(^{-1}\) to the peak at \(\sim 2083\) cm\(^{-1}\) is larger than for the annealed Au(1.0 ML)/Pd(5.0 ML)/Mo(110) catalyst. This suggests that the peak at 2105 cm\(^{-1}\) is attributable to CO bound atop on Au, and the feature at 2083 cm\(^{-1}\) is due to CO bound atop on Pd diluted in the surface. Again, the features are sharper and more well resolved, possibly indicating less heterogeneity of CO binding sites. The resolution of the two peaks at 1987 and 1973 cm\(^{-1}\) in the temperature range from 150 to 200 K is interesting, indicating bridge-bound CO in two distinctly different types of sites.

The IRAS results for the Au–Pd/Al\(_2\)O\(_3\) catalysts are very similar to those for the Cu–Pd/Al\(_2\)O\(_3\) systems discussed previously. Both display IRAS spectra characterized by features associated with their monometallic counterparts, and both exhibit a feature in the region from \(\sim 2085\) to 2060 cm\(^{-1}\) assigned to CO bound on Pd atoms in a mixed metal surface.

IV. CONCLUSIONS

Structural information regarding specific binding sites and facet distribution can be obtained through the study of supported metal particles on thin film oxide model catalysts using IRAS with CO as the probe molecule. Comparisons with analogous single crystal studies indicate that larger Pd and Cu particles feature morphologies primarily characterized by high proportions of low index, low energy crystal planes, while smaller particles exhibit a higher density of low coordinated step/edge defect sites. For the IRAS studies of supported Pd–Au and Pd–Cu catalysts, no conclusive indications of ligand effects were apparent in the CO stretching frequencies. The spectra resemble combinations of both analogous monometallic catalysts, even though a significant degree of metal mixing is apparent from thermally induced changes in the IRAS, and from previous (ISS) studies. A peak possibly attributable to Pd diluted in the surface by the presence of a dissimilar metal is apparent for each of these bimetallic supported catalysts.

These results will be developed further in a future article extending the vibrational studies described here to well-defined bimetallic overlayers supported on a refractory metal single crystal substrate.
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