Electronic Interactions in Bimetallic Systems: An X-ray Photoelectron Spectroscopic Study

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The electronic interactions in Cu/Rh(100), Cu/Ru(0001), Ni/Ru(0001), Ni/W(110), and Pd/W(110) have been examined by means of X-ray photoelectron spectroscopy (XPS). The shifts in core-level binding energies indicate that the adatoms in a monolayer of Ni, Cu, or Pd are electronically perturbed with respect to the surface atoms of Ni(100), Cu(100), or Pd(100). The magnitude of the electronic perturbations is larger for Pd/W(110) and Cu/Rh(100). The present results show a correlation between the shifts in the XPS surface core-level binding energies and the variations in the desorption temperature of CO from metal adlayers.

I. Introduction

The catalytic properties of metal surfaces can be altered greatly by the addition of a second transition metal. In many cases, bimetallic systems are superior over their single-metal counterparts in terms of catalytic activity and/or selectivity. Many fundamental studies have focused on the identification of those electronic and structural properties of bimetallic systems which can be related to their superior catalytic properties. In gathering information to address this issue, it has been advantageous to simplify the problem by modeling bimetallic catalysts via the deposition of metals onto single-crystal surfaces.

Previous work on ultrathin-metal films supported on well-defined metal surfaces has demonstrated the unique properties of bimetallic systems toward adsorption of CO. Figure 1A shows a typical results of thermal desorption experiments. In Figure 1A we compare the desorption temperature of CO adsorbed onto a monolayer of Pd supported on W(110) with that for adsorption onto bulk Pd substrates. These data show clearly that there is a substantial reduction (≈180 K) in the desorption temperature of CO from bulk Pd compared to desorption from monolayer Pd on W(110). For CO adsorption on Cu/Rh(100) (Figure 1C), an increase of ≈70 K in the CO temperature-programmed desorption (TPD) maximum with respect to the peak maximum on Cu(100) has been observed. The results of Figure 1 then suggest that the electronic properties of a metal atom bonded to a different metal can be significantly perturbed.

In the present study we examine the electronic interactions that occur in the Ni/W(110), Pd/W(110), Ni/Ru(0001), Cu/Ru(0001), and Cu/Rh(100) systems using X-ray photoelectron spectroscopy (XPS). Our results show a correlation between the shifts in the XPS surface core-level binding energies and the variation in the desorption temperature of CO from the corresponding monolayer films.

II. Experimental Section

The ultrahigh-vacuum system (base pressure ≤4 × 10⁻¹⁰ Torr) used in our experiments is described in detail elsewhere. The Ni(2p₁₂), Cu(2p₁₂), and Pd(3d₁₄₂) XPS spectra were recorded with Al Kα radiation. The variations in the binding energies of the Ni(2p), Cu(2p), and Pd(3d) XPS regions were determined by referencing against a core level of the substrate W(4f₁₂) peak for W(110), Ru(3d₁₄₂) for Ru(0001), and Rh(3d₁₄₂) for Rh(100). For adsorbate coversages (film thicknesses) in excess of 1 monolayer, the XPS peak positions reported in section III represent a product of the combination of electrons emitted from subsurface and surface atoms.

The Ru(0001), Rh(100), and W(110) crystals were cleaned following procedures reported in the literature. The cleanliness and structure of the surfaces were checked by means of XPS, Auger electron spectroscopy (AES), and low-energy electron diffraction (LEED). Ni, Cu, and Pd were evaporated onto the Ru(0001), Rh(100), and W(110) substrates (sample temperature ≈50 K) after deposition to 500 K to desorb any accumulated CO; no impurities were detected subsequently by AES and XPS. The Cu, Ni, and Pd coverages were determined by TPD area analysis and AES. In this work, adsorbate coverages are reported with respect to the number of substrate surface atoms (W(110), 1.43 x 10¹⁵ atoms/cm²; Ru(0001), 1.64 x 10¹⁴ atoms/cm²; and Rh(100), 1.38 x 10¹⁵ atoms/cm²). One adatom per substrate surface atom corresponds to θ = 1.

III. Results and Discussion

Figure 2 shows representative spectra of the Cu(2p₁₂) XPS region for various coverages of Cu on Rh(100). There are not any extra features or changes in line shape with increasing Cu coverage. A clear shift in the Cu(2p₁₂) peak position can be observed. Spectra with similar characteristics were found for Cu

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This phenomenon can be attributed to the formation of two-dimensional islands of the metal on the surface. For Cu/Rh(100) the total shift in the Cu(2p$_{3/2}$) peak position up to a value of 932.9 eV is smaller than that measured for the combined peak of bulk and surface atoms in 20 ML of Cu. If we reference the combined Cu(2p$_{3/2}$) peak of 20 ML of Cu on Rh(100) to that of Cu(100) (see Figure 4A), a difference of $\sim-0.43$ eV is obtained between the Cu(2p$_{3/2}$) binding energy of a monolayer of Cu on Rh(100) and that of the surface atoms of Cu(100). For the case of Pd(100), theoretical calculations suggest that the Pd(3d$_{5/2}$) XPS binding energy of the surface atoms should be shifted by $\sim-0.4$ eV with respect to that of bulk palladium. The predicted shift is in quantitative agreement with the shifts observed experimentally for Ni and Pt surfaces. Applying the same type of analysis used above for the Cu/Rh(100) XPS data to Pd/W(110) (see Figure 4B), we obtain a difference of $\sim-0.85$ eV between the Pd(3d$_{5/2}$) binding energy of a monolayer of Pd on W(110) and that of the surface atoms of Pd(100).

Figure 5 shows the calculated shifts in surface core-level binding energies in going from the pure metal (Ni(100), Cu(100), or Pd(100)) to a monolayer supported on various substrates. For comparison, we also plotted the variations in the desorption temperature of CO observed in Figure 1. A qualitative correlation clearly exists between the increase or decrease in CO desorption temperature and the relative shifts in surface core-level binding energies. That is, a reduction in the binding energy of a core level is accompanied by an enhancement in the strength of the bond between CO and the metal overlayer. Likewise, an opposite relationship is observed for an increase in the surface core-level binding energy.

In order to fully understand the phenomena responsible for the correlation observed in Figure 5, it is necessary to have a very detailed knowledge about (1) the orbitals of the metal overlayer involved in CO chemisorption bonding and (2) the effects of the metal–metal interaction on the valence levels of the metal overlayer. The data of Figure 3 do not provide this type of information. The values reported in Figure 3 represent relative binding energies, and their exact positions with respect to the vacuum level are unknown. Furthermore, the shifts in binding energies could be in part a consequence of variations in the final-state relaxation energy or changes in the shape of the surface dipole. In the following paragraph we describe a simple model that explains the correlation observed in Figure 5.

The chemisorption bond of CO on metals is dominated by transfer of electron density from occupied metal orbitals into the lowest unoccupied $\pi$ orbitals of the CO molecule ($\pi$ back-bonding). Experimental results for Cu(100) show that the core levels and the valence $d$-band centroid of the surface atoms shift in the same direction with respect to the vacuum level. For CO adsorption on Cu(100), the Pd/W(110) system shows a decrease in the Pd(3d$_{5/2}$) peak position with Pd coverage, giving a total shift of $\sim-0.55$ eV. In Figure 3E, the variation of the position of the adsorbate core level with coverage is much more gradual than in Figure 3A,B,D. For this particular system an $\sim6$–8 equivalent monolayer coverage is required to achieve a bulklike binding energy.

XPS data for Cu(100) show that the Cu(2p$_{3/2}$) binding energy of the surface atoms is $0.22$ eV lower than that of bulk Cu. A recent work has shown that surface XPS shifts can provide useful information about the electronic properties of the surface atoms. The data of Figure 3A show that the Cu(2p$_{3/2}$) binding energy of a monolayer of Cu on Rh(100) is $0.6$ eV smaller than that measured for the combined peak of bulk and surface atoms in 20 ML of Cu. If we reference the combined Cu(2p$_{3/2}$) peak of 20 ML of Cu on Rh(100) to that of Cu(100) (see Figure 4A), a difference of $\sim-0.43$ eV is obtained between the Cu(2p$_{3/2}$) binding energy of a monolayer of Cu on Rh(100) and that of the surface atoms of Cu(100). For the case of Pd(100), theoretical calculations suggest that the Pd(3d$_{5/2}$) XPS binding energy of the surface atoms should be shifted by $\sim-0.4$ eV with respect to that of bulk palladium. The predicted shift is in quantitative agreement with the shifts observed experimentally for Ni and Pt surfaces. Applying the same type of analysis used above for the Cu/Rh(100) XPS data to Pd/W(110) (see Figure 4B), we obtain a difference of $\sim-0.85$ eV between the Pd(3d$_{5/2}$) binding energy of a monolayer of Pd on W(110) and that of the surface atoms of Pd(100).

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Figure 3. Adsorbate core-level binding energies as a function of adsorbate coverage (film thickness): (A) Cu(2p3/2) peak for Cu/Rh(100), (B) Cu(2p3/2) peak for Cu/Ru(0001), (C) Ni(2p3/2) peak for Ni/W(110), (D) Ni(2p3/2) peak for Ni/Ru(0001), and (E) Pd(3d3/2) peak for Pd/W(110).

Figure 4. (A) Relative Cu(2p3/2) XPS binding energies of bulk Cu, the surface atoms of Cu(100), and a monolayer of Cu on Rh(100). (B) Relative Pd(3d3/2) XPS binding energies of bulk Pd, the surface atoms of Pd(100), and a monolayer of Pd on W(110).

the bulk atoms. An identical result has been observed for polycrystalline Au,32 for Cu, Ag, and Au deposited on Al(100),33 and for Au supported on Pt(100).34 On the basis of this previous work and the results of Figure 3, we anticipate a shift toward lower binding energy for the Cu valence levels of the Cu/Rh(100) and Cu/Ru(0001) systems. This shift could reduce the separation between the occupied valence bands of Cu below the vacuum level and the empty 2π orbitals of CO at ~1.8 eV above the vacuum level,34,37 leading to an increase in π back-bonding and a subsequent enhancement of the strength of the Cu–CO bond with respect to Cu(100). On the other hand, for Pd/W(110) the expected shift (see Figure 3E) in the valence levels of Pd is toward higher binding energy. This agrees very well with results of UPS which show that the valence d levels of a Pd monolayer on W(110) are at higher binding energy than those of pure Pd substrates.35 An increase in the separation between the occupied valence bands of Pd and the CO(2π) orbitals can cause a reduction in π back-

Figure 5. Correlation between the shift in surface core-level binding energy and the shift in CO TPD maximum. The properties of the Pd, Ni, and Cu monolayers are compared with the corresponding values for the (100) face of the pure metals.

donation and a weakening in the Pd–CO bond. These simple arguments, based on "initial-state" effects, are sufficient to explain the general trends found in Figure 5. The overall contribution of "final-state" effects is as yet unclear. Further work on other bimetallic systems is in progress to address this issue.

IV. Conclusions

Our results show a correlation between the shifts in the XPS surface core-level binding energies and the variations in the desorption temperature of CO from metal adlayers. An "initial-state" argument suggests that this correlation arises due to changes in the density of states of the overlayer metal near the Fermi level from the bulk metal upon adsorption onto a dissimilar metal. This, in turn, affects the magnitude of the back-bonding from the overlayer metal to adsorbed CO and thus the metal–CO bond strength. These data then show that shifts in core-level binding energies can provide useful information about the electronic interactions that occur in bimetallic systems and, as well, successfully predict changes in certain chemical properties of metal overlayer systems.

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23Na MAS-NMR and FT-Mid-Far-IR Cation/Proton Probes of the Phototopotactic Oxidation of Intrazeolite Hexacarbonyltungsten(0) to Tungsten(VI) Oxide Quantum Dots and Supralattices: Exploring Anchoring Sites and Aggregation Processes

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Adsorption-induced 23Na MAS-NMR chemical shifts and far-IR Na+ translatory mode frequency shifts provide direct and complementary evidence for the anchoring of W(CO)6 and WO3 moieties to α-cage Na+ cations in the precursor nWO3-nαcage, as well as in the intrazeolite phototopotactic oxidation product nWO3-nαcage. Similar experiments, in conjunction with mid-IR spectroscopy conducted in HzNa56Y (where m = 8, 16), allow one to clarify W(CO)6 and WO3 homogeneity questions, as well as to map details of W(CO)6 precursor loading effects on the intrazeolite aggregation processes of the WO3 photooxidation product. In this way one is able to monitor the birth and population growth of WO3 dimers, which at half-loading (n = 16) constitutes an intrazeolite (WO3)2 quantum supralattice and at full-loading (n = 32) creates an intrazeolite (WO3)4 quantum supralattice.

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