COMMENTARY

Chemical and Electronic Properties of Bimetallic Surfaces

We recently read a very interesting Account by Ruckman and Strongin on the subject of bimetallic bonding at surfaces.[1] Ruckman and Strongin focused their discussion on photoemission and CO-chemisorption studies for the Pd/Ta(110) and Pd/Nb(110) systems. The studies they describe provide evidence for the complex type of phenomena that can occur when two different metals are bonded on a surface. A more general description of bimetallic bonding at surfaces is provided by systematic studies of the chemical and electronic properties of a given admetal on different kinds of metal substrates.[2-6] From this type of work, it has become clear that the chemical and electronic perturbations induced by bimetallic bonding on an admetal (Pd, Ni, Cu, or Au) depend strongly on the properties of the metal substrate. For example, Cu atoms bonded to Ta(110) show core and valence levels shifted toward higher binding energy, while Cu atoms in contact with Pt(111) exhibit core and valence levels shifted toward lower binding energy.[2,3] In the case of Pd adatoms, the electronic and chemical perturbations observed after adsorption on early transition metals are much larger than those seen on late transition metals.[2,3] These trends cannot be explained in terms of simple "covalent" bonds between the admetals and metal substrates. They indicate that, in general, bimetallic bonding is accompanied by an important redistribution of electronic charge.

Ruckman and Strongin[1] mention that Rodriguez and Goodman support "the idea that charge transfer from one metallic element to another is responsible for the behavior of bimetallic systems." This statement is misleading, since it does not take into account studies carried out in

our laboratories in the last three years.[3,7-10] In our recent work, we show that in many cases the properties of a bimetallic surface are determined by the changes in electron density produced by atomic rehybridization or volume renormalization.[3,7-10] In photoelectron spectroscopy, initial and final state effects need to be taken into consideration. We do not believe, as Ruckman and Strongin interpret our work, "that significant amounts of charge are transferred from the Palladium monolayer to the substrate and that this accounts for the reduced CO−metal interaction." Adsorption of Pd on a transition or (s,p) metal induces a reduction in the electron population of the Pd(4d) orbitals by charge transfer from Pd to the metal substrate *and* rehybridization of the Pd(4d, 5s,5p) levels.[3,8,9] The d → s,p rehybridization "moves" 4d electrons from the Pd center into the region around the bimetallic bond. In general, the net loss in the Pd(4d) population increases when the fraction of empty states in the valence band of the substrate rises.[3,8,9] The reduction in the Pd(4d) population decreases electron−electron repulsion within the Pd adatom, and this contributes to an increase in the binding energy of the core and valence levels of Pd.[3,8,9] The electronic perturbations induced by the metal substrate on Pd reduce the CO-chemisorption ability of the admetal by weakening simultaneously the Pd(4d)−CO(2π) and Pd(5s,5p)−CO(5σ) bonding interactions.[3,8,9] Results of work function measurements and MO-SCF calculations indicate that the net charge transfer from Pd to the metal substrates is generally small (<0.2e).[3,8,9] For Pd/Ru and Pd/Zn, the charge transfer between metals is negligible and the electronic and chemical perturbations in Pd reflect a Pd(4d) → Pd(5s,5p) rehybridization that concentrates Pd

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electrons in the region around the bimetallic bond.[3,8,9] The behavior observed for the Pd overlayers is similar to that seen for bulk alloys, where bimetallic bonding induces a decrease in the Pd(4d) population and an increase in the Pd(5s,5p) populations.[11] The inverse photoemission studies described by Ruckman and Strongin for Pd/Nb(110) *do not* necessarily indicate an increase in the Pd(4d) population, since a clear separation of the unoccupied s, p, and d states of Pd and Nb is not observable from the results of these experiments.

Ruckman and Strongin, together with other investigators,[1] neglect the possibility of a Pd → Ta(110) charge transfer (as the work function suggests[8]) due to the positive core-level shifts observed for Pd and Ta.[1] In our opinion, this type of criterion *cannot* be used to determine the existence of charge transfer within a bimetallic bond. In many bimetallic systems significant charge transfer between the metals occurs, and the core levels of both elements are shifted in the same direction.[7,8,12,13] The core-level shifts of each metal are dominated by different phenomena.[7b,8,12,13] For Pd/Ta(110), a Pd-induced Ta(5d) → Ta(6s,6p) rehybridization could be moving the Ta core levels toward higher binding energy, overcoming the effects of a shift of electrons from the Pd overlayer toward the Ta substrate.[8]

The importance of the relation between the occupancy of the valence d band and the shifts in the core levels of a metal is illustrated by the behavior of Au atoms supported on Ru(0001). Work function measurements and the results of MO-SCF calculations are consistent with a net Ru → Au charge transfer that increases the electron population of the Au(6s,6p) orbitals.[10,14] In spite of this, the 4f levels of Au atoms bonded to Ru are shifted ~0.15 eV toward higher binding energy with respect to those of the surface atoms in metallic Au,[15] as a result of a Ru-induced decrease in the Au(5d) population.[10] Similar electronic perturbations have been found for Au in bulk alloys.[10,13,16,17] Usually, the core levels of a metal are more sensitive to variations in the population of the valence nd orbitals than to changes in occupancy of the valence (n+1)s,p orbitals.[12,13,16,17] For AuTa alloys, bimetallic bonding induces inter- and intraatomic electron transfers that decrease the valence d populations of Au and Ta and shift the core levels of both metals toward higher binding energy.[17,18] A similar phenomenon is probably taking place in the Pd/Ta(110) system.[8] First principles quantum-mechanical calculations for a Pd monolayer supported on a Ta(110) slab show a significant decrease in the electron density around the Pd and Ta atoms, with an accumulation of charge in the Pd–Ta interface and bonds that cannot be described as either "ionic" or "covalent".[19]

In summary, the bonding of Pd, Ni, Cu, and Au atoms to surfaces of transition and (s,p) metals leads to an important redistribution of electronic charge that affects the population and stability of the valence d orbitals of the admetals.[3,8-10] These changes in the d band of the admetal depend strongly on the occupancy of the valence band of the metal substrate, and in general, they cannot be predicted using standard scales of electronegativity. The very good correlation found between the changes in the core levels of an admetal and variations in its ability to adsorb CO[2,9,10] arises from the fact that both properties are very sensitive to perturbations in the valence d levels of the admetal.

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