Metal−Insulator Transitions and Possible Quantum Effects in Supported Nickel Monolayers

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Theoretical considerations show that the adsorption of oxide, water, or CO on a close-packed monolayer of a group 10 element converts the substrate into an electrical insulator. (The result has been confirmed experimentally by Gomer and coworkers for oxide.) The electronic effect is separation of 3d and 4s bands of the metal by interaction with the orbitals of the adsorbate. One should be able to generate metallic and nonmetallic areas that may vary from the dimensions of a few surface atoms to much larger areas. Adsorption of benzene produces some metal atoms that are metallic and others that are insulating since it is not possible to pack benzene molecules on the surface so that the carbon atoms interact strongly with all nickel atoms of the monolayer. Quantum wires and other nanostructures are thought to be possible via this route. For an adsorbate such as CO, the process may be readily reversed by successive adsorption and desorption. For copper a metal is always found since, even when 3d and 4s bands are separated in energy, the latter is half full. Renormalization of the metal orbitals plays a vital role in the electronic picture.

Introduction

Metal−insulator transitions have long been of great interest to chemists and physicists alike. Recently we have identified theoretically[1] a particularly interesting transition in a monolayer of nickel supported on a layer of oxygen, itself supported on a tungsten surface. Experimental data[2-7] from the group of Gomer prompted the study. A nickel monolayer (presumably metallic when isolated) is converted to an insulator by adsorption on an oxide support. The effect is a particularly important one since the nickel monolayer is just that, a single atom thick with interesting possibilities for the construction of quantum devices if regions of metal and insulator may be specifically tailored. Several such systems are now known. With reference to **1** we will refer

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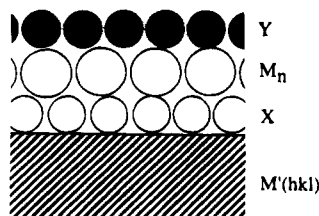
to them as M′(hkl)/X/M$_n$/Y or just as X/M$_n$/Y, the presence of the support being understood. Most of the experimental work has involved M′(hkl) = W(110); M = Ni,[2] Pd,[3,4] Cu,[5] Ag;[6] X = O$_x$, H$_x$, CO; Y = benzene,[7] CO, but other systems involving Ru(111)/CO/Cu are known too.[8] Some of the systems are insulators such as W(110)/O/Ni, others are metallic, such as W(110)/O/Cu.

Figure 1 shows the results of our LMTO calculations from ref 1 which investigated the interaction of nickel monolayer with the oxide layer, the tungsten support being regarded as electronically benign. Certainly in terms of geometry and electronegativity considerations the important interactions should be between nickel and oxygen. Before "adsorption" of the metal sheet on the layer of oxygen, the 3d and 4s bands overlap leading to a metal. This is just like the traditional electronic picture[9,10] of a bulk metal. This conclusion of a metallic monolayer for nickel with these dimensions is further confirmed by spin-polarized FLAPW calculations.[11] After adsorption the 4s band is pushed to higher energy, opening a gap between 3d and 4s bands. Elsewhere[1] we underline the validity of these calculations by showing the agreement between calculated ΔDOS (electronic density of states) and experimental ΔUPS (UV photoelectron measurements) on metallic and insulating materials. The essence of the electronic structure problem is shown in **2**. Electronically this is very similar to the common picture which describes the formation of a transition-metal complex, **3**. The weakest interactions between metal and nonmetal are associated with the nd orbitals of the metal. Interactions are generally much stronger with the metal ($n + 1$)s, p orbitals.

This paper will present theoretical evidence to show that it is possible to induce a similar transition from metal to insulator or the reverse by adsorbing a small molecule on the nickel monolayer. It is possible that at low coverage, islands of adsorbate may be created

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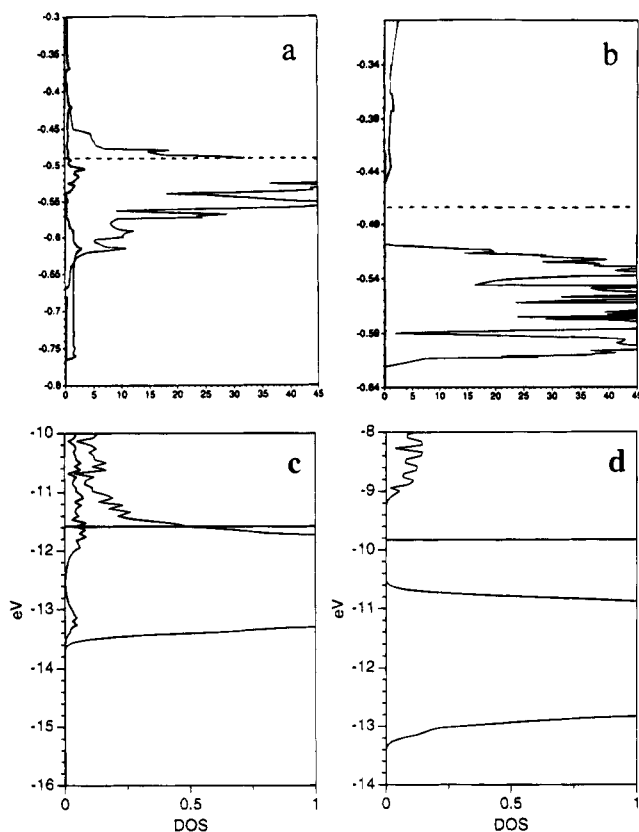(11) Green, M. T., unpublished.

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Figure 1. Top panels: (a) Calculated electronic density of states for a nickel monolayer and (b) that for a nickel monolayer lying on top of an oxide layer to mimic W(110)/O/Ni using the first principles LMTO method (from ref 1). The energies are in units of rydbergs. (c, d) Analogous results for charge iterated tight-binding calculations. In (a) and (c) the 4s orbital contribution is also shown. The 3d/4s band overlap typical of an elemental transition metal, is removed, creating a bandgap and thus an insulator when the oxide layer interacts with the nickel monolayer. In all of the densities of states shown in this paper the Fermi level is indicated by a horizontal line.

and that these may be small enough and may be able to be readily varied in size, to be of interest in terms of quantum size effects. This has been a topic of interest for several years among chemists and physicists alike.[12-14] The properties of nanoclusters have perhaps received most attention, but effects such as quantum confinement in cesium suboxides[15] and the reduction in work function this engenders[16] are also noteworthy. One of the interests here is the possibility of a quantum-confinement device that can be controlled by simple chemical means by manipulating Y. Specifically, this paper explores the properties of some of these M'(*hkl*)/X/M$_n$/Y systems further by using tight-binding calculations with parameters fit to the first principles LMTO computations described above. This enables study of systems where Y = benzene, for example, which are not readily accessible using the more accurate LMTO method. Although the examples discussed are for nickel, we find similar results by calculation for palladium and platinum.

Renormalization and Charge Iteration

Of particular importance in tight-binding studies of metals is the adjustment of the metal d and s orbitals to the local environment "renormalized" orbitals.[10,17] In this renormalized model, the atomic s and d levels are adjusted in terms of both orbital energy and exponent in order to accommodate the different degrees of d–s mixing that occur in the extended structure, a comment which that equally well to surfaces as to bulk solids. For example, for the first-row transition metals the electronic configuration[9] in the bulk metallic state is $3d^{\sim n-1}4s^{\sim 1}$. It is not possible to reproduce this situation, either in the bulk or for the monolayer, using the normal atomic parameters. Within the tight-binding approximation, such renormalization is accomplished by an iterated charge calculation.[18,19] If H_{ii} is set equal to $Aq^2 + Bq + C$, where the A, B, and C parameters are obtained via spectroscopic data, then the calculation may be run to self-consistency. This is an important aspect of the studies reported here, especially for the calculations involving benzene and CO. The renormalized orbital parameters in addition to being charge consistent must meet the following three criteria: (i) They must give a similar DOS and Fermi level location as the previous LMTO calculations. (ii) They must therefore show a metal–insulator transition in the W(110)/Ni and W(110)/O/Ni systems that mimics the results of previous LMTO calculations.[1] (iii) They must make good intuitive sense in terms of the differences between three-dimensional bulk Ni and molecular Ni. In addition we are required to change the Slater coefficients on the s and p orbitals on Ni to obtain the proper orbital mixing in the same manner as in other calculations[18] of the bulk Ni parameters.

The charge-iterated orbital parameters used (see Appendix) for the nickel monolayer meet all three of these requirements. First the actual energies of the orbitals (most noticeably for d) lie between the values for molecular and bulk Ni, which is what one would expect for a two-dimensional nickel sheet. Second, the Fermi level location and total electronic density of states (DOS) picture make a satisfactory comparison with the LMTO calculations as can be seen in Figure 1. It will be noted though that the LMTO calculations has a portion of 4s-band electronic density below the 3d band that our tight-binding fit does not show. We discovered that it was possible to mimic this feature of the DOS but that the parameters thus obtained did not satisfy the other two criteria. Finally, the tight-binding approximation gives a robust result for the W(110)/O/Ni system, showing clearly nonmetallic behavior and a DOS that is comparable to that of the LMTO calculation. This comparison can be seen in Figure 1.

Results

W(110)/O/Ni, W(110)/O$_x$/Ni, and W(110)/O/Cu. A comparison between the LMTO calculations described

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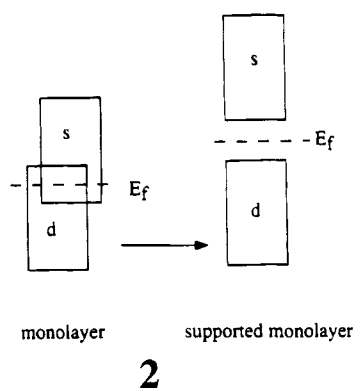(15) Ebbinghaus, G.; Simon, A. *Chem. Phys.* **1979**, *43*, 117.

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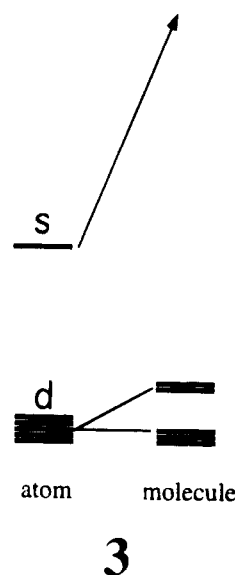(19) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006.

earlier and the results obtained from a tight-binding fit to them using the charge-iteration approach is shown in Figure 1 as noted above. As expected the computed bandgap between 3d and 4s bands decreases as the oxide coverage of the surface decreases. In Gomer's experiments[2] for Ni deposited on clean W(110), the Ni grows pseudomorphically up to a coverage of 1 Ni per surface W atom (what we would call 0.78 monolayers of Ni). For additional Ni deposition, the Ni begins to pack more tightly on the surface and is no longer pseudomorphic with the W(110). By the time the first monolayer of Ni on top of W(110) is completed, there are 1.29 Ni atoms per surface W atom. At this point, the Ni layer is a strained or distorted Ni(111) layer as seen by LEED. The calculations both at the LMTO level and using the tight-binding fit for the Ni(111) layer are very similar to those already described. The 3d band is a little wider for nickel in the W(110) geometry than in the Ni(111) calculation. Notice from the model that a very clear prediction is made that this adsorbate-induced metal—insulator phenomenon is restricted to the group 10 metals. For copper, for example, although a similar calculation leads to the opening of a gap (2)

s

d

atom   molecule

3

value chosen here (1.88 Å) is close to that expected for strongly adsorbed water. The gap decreases as the Ni—O distance increases. The question of the choice of metal—nonmetal distances in these unusual electronic systems is taken up in general in the Appendix.

The results so far have been from calculations which ignored the tungsten underlayer. More extensive calculations which include a tungsten slab five metal atoms thick as in **4** show very similar results. Figure 2

Ni

O

W

4

monolayer   supported monolayer

2

between 3d and 4s bands, the 4s band contains one electron and the monolayer will always be a metal. This is found to be the case experimentally.[5] As described earlier, a copper monolayer is always metallic under these conditions.
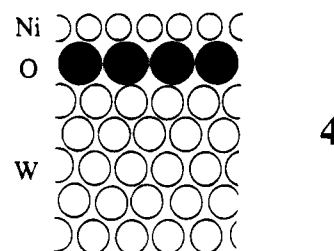
Although the Gomer experiments are carried out under high vacuum on a monooxidized W(110) surface, there is no electronic reason the (111) oxide surface of an alkaline earth oxide should not behave analogously. In terms of the dimensions of the pseudo-close-packed W(110) surface, MgO (O—O = 2.98 Å) would be satisfactory. A solid solution of two alkaline earth oxides could be used to get a perfect match. The metal monolayer would then be a (111) close-packed layer rather than the pseudo-close-packed layer used here. Mica is another candidate. It is a good substrate for the support of films of group 10 elements. On the basis of cubic close-packing, the O—O separation on a cleavage plane of 2.79 Å is close to that for the adsorbed oxide on the W(110) surface (2.95 Å). So, although we generally refer to W(110) as a support in this paper, one of these other alternatives is probably just as good. There are certainly several other possibilities.

We find results similar to those for oxide for the adsorption of water on a metal monolayer. This result will become of interest in the next section. The results of course depend on the Ni—O distance which controls the overlap between nickel and oxygen orbitals. The

compares the computed densities of states for the W/Ni/O and Ni/O systems and show effectively the same picture for the nickel layer in terms of a gap between 3d and 4s levels. The W and Ni atoms are far enough apart to preclude strong direct interactions. (Although the actual distance between the W and Ni layers is not known from experiment, reasonable estimates may be made.) The general picture is that the tungsten slab is sufficiently electropositive that its major role is to contribute electrons to the surface oxygen atoms. The important interaction is then between nickel and oxygen. The extreme case where the metal atoms contained in the underlayer can be completely neglected occurs of course for the MgO and related supports. A different electronic picture, one where the metal underlayer is not quite so innocent is thus expected for the situation where the electronegativies of M' and M are closer.

W(110)/O/Ni₂ and W(110)/O/Ni₂/O. Addition of a second layer of nickel to W(110)/O/Ni to give W(110)/O/Ni₂ leads to a metal by calculation (Figure 5a). All of the metal atoms in the O/Ni₂ bilayer were charge iterated in this calculation. The computed result is at variance with experiment[22] where an insulator is identified. From the calculations the metallic electronic density of states involves contributions from orbitals on both types of metal atom. The situation is rather
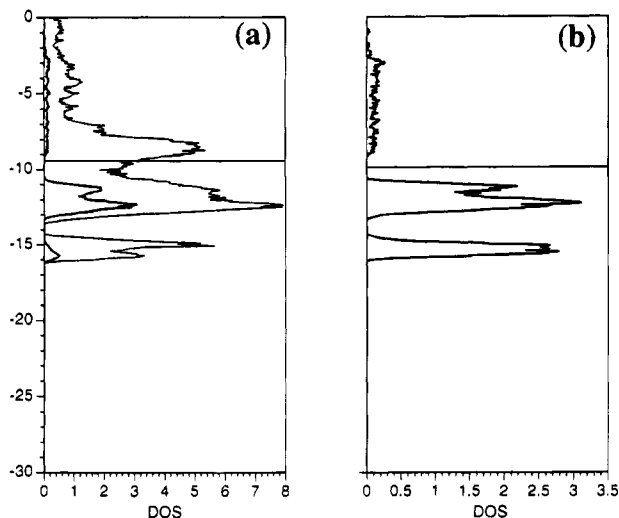
Figure 2. Computed densities of states for (a) W(110)/Ni/O (a five-layer slab of W was used) and (b) Ni/O. The partial nickel electronic density of states is shown in (a) as the smaller amplitude plot.

different for the case of W(110)/O/Ni$_2$/O, where the nickel bilayer is sandwiched by a pair of oxide layers. Our calculated results (using the charge-iterated metal parameters for the free bilayer) show a very small band-gap semiconductor, a semimetal, or a poor metal (Figure 5b). Certainly the size of the gap will be quite sensitive to the metal—oxygen distance. A very similar result is found for W(110)/O/Ni$_2$/H$_2$O. This result can be compared with that of in Figure 1 for the metal monolayer. The major difference is associated with the increase in metal d band width in W(110)/O/Ni$_2$/O over that in W(110)/O/Ni. This is a straightforward consequence of the increased metal coordination number in the bilayer. A schematic is shown in **5**, where, in accordance with

5

monolayer	bilayer	bulk
6	9	12 neighbors
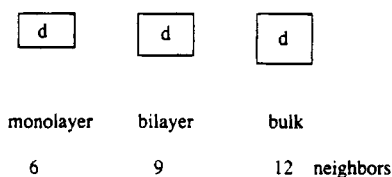
well-known results, the bandwidth varies as the square root of the average coordination number. A theoretical prediction is that the systems W(110)/O/Ni$_n$/O (with $n \geq 3$) should be metals, but this theoretical result should be set in light of the incorrect prediction for W(110)/O/Ni$_2$. Certainly for a large enough number of nickel layers a metal will surely be found.

The interpretation of the calculations described above is relatively simple. The orbitals of the adsorbate (on top) or the support (beneath) interact with those of the nickel sheet to open a gap between 3d and 4s bands as long as the interaction is large enough. The gap may be closed by interaction with sulfide or by adsorption of more metal layers. The situation is not always as simple though. As we describe below, the interaction of benzene with the nickel sheet is more complex since

not all nickel atoms interact with the adsorbate in the same way.

LiF/Ni, LiF/Ni/O, and LiF/Ni/H$_2$O. By comparison with molecular transition-metal chemistry, the interaction of fluoride ion with the metal 3d and 4s levels is expected to be smaller than that for oxide. Indeed a calculation on F/Ni to mimic W(110)/F/Ni using a fully occupied fluoride layer shows that the interaction is small enough that no gap opens up between 3d and 4s bands for this system. There is however, a nonzero interaction between the nickel and fluoride orbitals since a calculation on F/Ni/O to mimic W(110)/F/Ni/O shows a larger gap than for W(110)/O/Ni. One could envisage supporting the nickel monolayer on the (111) surface of an alkali metal fluoride such as LiF (F−F = 2.84 Å). The F−F distance in NaF (F−F = 3.27 Å) is possibly too large to mesh with the Ni−Ni distance in the monolayer, however, solid solutions of two alkali metal fluorides could be used to provide a perfect match. A Teflon surface might be one with a lower electronic density of surface fluorine atoms and there are other possibilities. No experiments have been carried out on this system. One experimental problem with this support may be that the smaller interaction with the metal for fluorine compared to oxygen may be insufficient to bind the metal to the surface. The metal might then not remain as a monolayer and would roll up into balls as found for some W(110)/O/M systems.[2-7] Certainly, whether one can generate monolayers of this type at all becomes less likely as the metallic cohesive energy increases.

Recalling the result of the previous section it is clear that the system LiF/Ni/H$_2$O will be an insulator too. This is indeed the case by calculation on F/Ni/H$_2$O. As before the results depend on the Ni−OH$_2$ distance.

LiF(111)/Ni/(CO). The adsorption of CO on metal, especially nickel, surfaces is well-known. For the (111) surface there is an extensive theoretical treatment.[20] However, it has not proven successful to make W(110)/(CO)/Ni. We performed calculations on a LiF(111)/Ni/(CO)$_x$ system, with a coverage geometry similar to that characterized[21] for CO on metal surfaces with the adsorbate located in some of the 2-fold bridging sites and on some of the on-top sites. Although the W(110)/CO system has the carbon, rather than oxygen, atom bound to tungsten, the calculations on Ni/(CO)$_x$ were for a system where the carbon is bound to nickel in the usual way. We showed above that the fluorine atoms of the LiF(111) surface have little electronic effect on the nickel monolayer and thus can be ignored in a first approximation. The result is shown in Figure 3. It represents a coverage of $x = 0.5$ with CO molecules in both 2-fold and on-top sites. As may readily be seen, the monolayer has again been converted from a metal to a nonmetal by the adsorption of a small molecule. For the CO's located in on-top sites it is the nonzero interaction between the 4σ orbital on CO and the Ni 4s band which leads to the creation of the bandgap. For those COs that reside in the 2-fold sites in the close-packed monolayer there is also the interaction between the π-bonding orbitals on CO and the Ni 4s orbitals.

These results are important because, unlike water or benzene, CO is known to be readily removed from the surface. Thus with this molecule, a switchable system can be envisaged. CO can be deposited on LiF(111)/Ni to create an insulating monolayer and thermally des-

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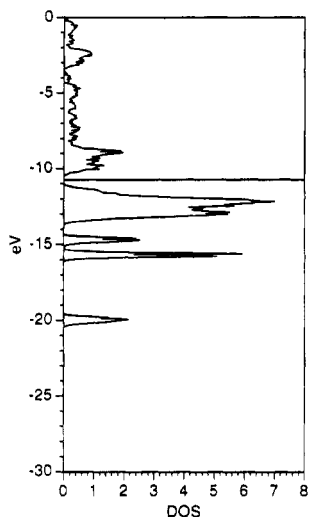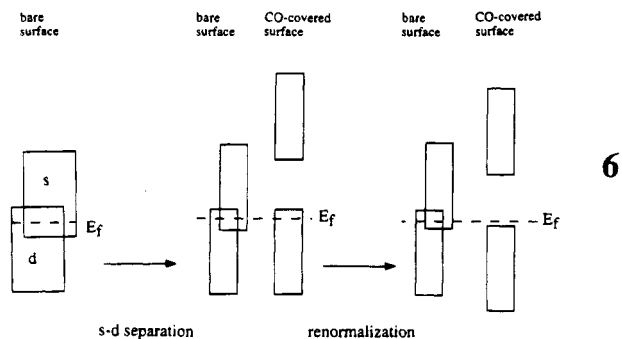(22) Whitten, J. E.; Gomer, R. *Surf. Sci.* **1994**, *316*, 1.

Figure 3. Computed densities of states for Ni/(CO)$_{0.5}$ showing an insulating state.

Figure 4. Computed densities of states for (a) S/Ni and (b) for S/Ni/H$_2$O.

Figure 5. (a) Calculated electronic density of states for two layers of nickel lying on top of an oxide layer to mimic W(110)/O/Ni$_2$. (b) Calculated electronic density of states for a nickel bilayer sandwiched by oxide, O/Ni$_2$/O, to mimic W(110)/O/Ni$_2$/O.

orbed to regenerate the metallic monolayer. Although these systems have yet to be experimentally realized, our results here are suggestive enough to indicate that the relevant experiments should be encouraged.

We have also investigated the situation at higher coverages of CO. Both all on-top sites and all 2-fold sites were studied up to $x = 1$. Here with closer intermolecular contacts leading to stronger intermolecular interactions, a broad π-bonding band is formed from the adsorbate molecules. This interacts with the d band on Ni to form a wide band with a nonzero electronic density of states at the Fermi level. Such a broadening of the band is associated with a steric repulsion between adjacent molecules which in practice limits the maximum possible coverage. The interaction will be of interest again later when considering some of the benzene systems that are discussed later. Here we just remark that the metallic/insulating behavior of CO adsorbed on a nickel monolayer in principle depends on the coverage although very high coverage may not be possible as we have just noted.

These results on the adsorption of CO on a metallic nickel monolayer highlight the importance of renormalization of the metal levels. We can imagine a situation where the surface is partially covered by islands of CO (a topic taken up further later) in which the areas containing the adsorbate are insulating but the rest metallic. Electronically this occurs through the process shown in **6**. Notice that without renormalization,

6

although the region covered by CO is described by separation of 4s and 3d bands, the system overall is still metallic. Only after renormalization, when that part
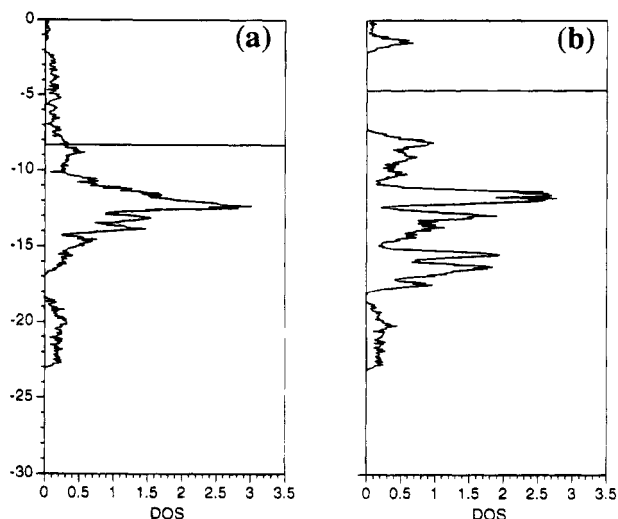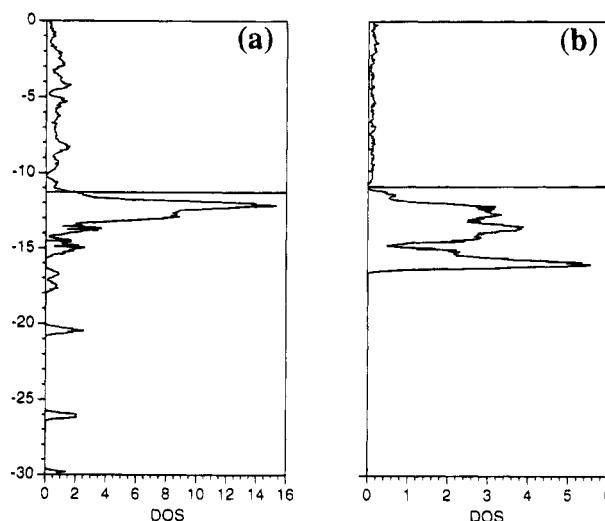
of the surface covered by CO becomes more "molecular", are separate metallic and insulating regions found. Similar situations are found for almost all of the systems studied in this paper. Recall, however, that using the tight-binding model, charge iteration is a way of reproducing the renormalization process automatically included in the high-quality calculations of Figure 1.

S/Ni and S/Ni/(H$_2$O)$_x$. The interaction between oxygen and transition metals is quite different from that between sulfur and these metals. Sulfur interacts much more strongly with both 4s and 3d levels than oxygen. This is in part due to the fact that the metal 3d/S 3p separation is much smaller than the 3d/O 2p separation and in part due to the larger overlap integrals involved. That sulfides often give rise to metals whereas the corresponding oxides are insulators is a longstanding observation. Although both one- and two-electron terms in the energy are important, the larger bandwidth found for sulfides is a dominant feature.

The calculated electronic density of states for a S/Ni system is shown in Figure 4a. The result is an interesting one in that the calculation suggests that interaction

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of sulfur with the metallic sheet, rather than leading to an insulator by band separation as in the oxide, broadens the 3d band sufficiently that no 3d—4s separation occurs. Such a state of affairs might apply to the case of a metal monolayer supported on a (111) surface of a rocksalt sulfide such as BaS or one of the lanthanide sulfides. As in the oxide and fluoride cases an optimal distance may be achieved by synthesis of the appropriate solid solution.

Adsorption of water on the opposite side of the metal layer (S/Ni/(H$_2$O)$_x$) leads to the dramatic results shown in Figure 4.

W(110)/Bz/Ni, W(110)/Bz/Ni/Bz, and W(110)/Bz$_x$/Ni. These are interesting systems, different from the oxide case and much more complicated. Not only is there little experimental information[7] concerning the geometrical arrangement within the benzene layers, especially in W(110)/Bz$_x$/Ni, but there is no information at all as to how the nickel atoms are arranged on the adjacent layer. Recalling experience with electronic structure results from many different areas of chemistry and physics, the results are almost invariably strongly controlled by geometry and the reader should bear this in mind. Experiments by Gomer and co-workers have shown[7] a lack of significant order in the W(110)/Ni/Bz system through the use of high-resolution electron loss spectroscopy. If such results imply metal clustering, then an insulating state is a possibility from this route. Our calculations here will use the geometries determined experimentally for benzene adsorption on metal surfaces, as well as some other possibilities. These are restricted by the fact that the benzene molecule has a definite two-dimensional shape which has to fit with its neighbors. The benzene molecule lies flat, parallel to the surface. The calculations on the Ni/Bz system have been performed with idealized geometries. (We recall that coadsorption of benzene with CO sometimes leads[21] to well-ordered adsorbate layers on bulk metal surfaces, a result that will be used below.) Experiments have also been performed[7] on W(110)/Bz$_2$/Ni. Since the interaction of the first benzene layer is probably stronger with the tungsten, but the second with the nickel, the presence of this "insulating" benzene layer makes calculations on Ni/Bz a particularly good mimic of W(110)/Bz$_2$/Ni.

Initial computations were performed using a coverage (Ni$_8$Bz) that matched experimental measurements, a coverage of approximately one benzene molecule for every eight Ni atoms. Cluster calculations by Anderson[23] have shown sites with local C_{3v} or C_{2v} to be preferred for benzene adsorbed on a Ni(111) surface with a C_6 site somewhat higher in energy although on different faces and different metals the relative stabilities may be reversed.[24] Figure 6 shows the C_{2v} and C_6 sites we chose to study in this work. (Since the W(110) surface is pseudohexagonal close-packed, these site symmetry designations are not exactly correct here.) Figure 7 shows calculated results for the C_6 sites. These calculations used the renormalized metal parameters for the nickel monolayer from Figure 1c for all metal atoms. In all of our calculations, a nickel—benzene
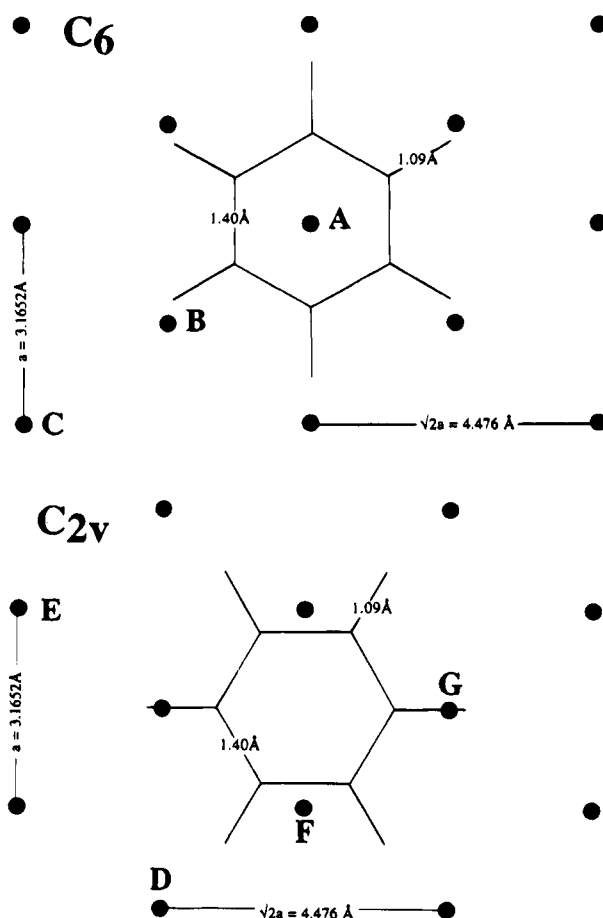
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(24) Anderson, A. B.; McDevitt, M. R.; Urbach, F. L. *Surf. Sci.* **1984**, *146*, 80.

Figure 6. C_6 and C_{2v} sites for benzene on close-packed metal surfaces. The different types of metal atoms are labeled.

plane perpendicular distance of 1.86 Å was used. The results proved relatively insensitive to minor changes in this distance. The results of these tight-binding calculations shown in Figure 7a for Ni$_8$Bz indicate that although there is no gap at the Fermi level, there is a region of low density of states for a system with two electrons more (per Ni$_8$Bz unit). The other panels give some insight into this state of affairs. It shows the 4s orbital projections of the three different types of nickel atom in the unit cell. Notice that one of the metal atoms (the central one, A) behaves quite differently to the others. We have selected two in this figure (B, C). It is easy to see why. For the W(110)/Ni/Bz system, in the ideal C_6 geometry of Figure 6, six carbon atoms make close contact with one nickel atom (A) but there are longer contacts to the other nickel atoms. A gap opens for atoms A but not for the others. As a result there is a considerable difference in the interaction of the metal orbitals on different atoms with the carbon atoms of benzene, and thus a significant charge difference between the different nickel atoms. The Ni atoms close to benzene are much more positively charged than those that are further away. This type of electronic situation is exactly the type that demands renormalization of the nickel parameters as indicated for CO adsorption in **6**. Charge iteration was then used to renormalize all of these nickel orbitals lying on atoms in chemically different environments and led to results which are chemically satisfying. The "molecular" nature (close to the free atom parameters) of those Ni atoms that are closer to the benzene and the "bulk" nature (more like
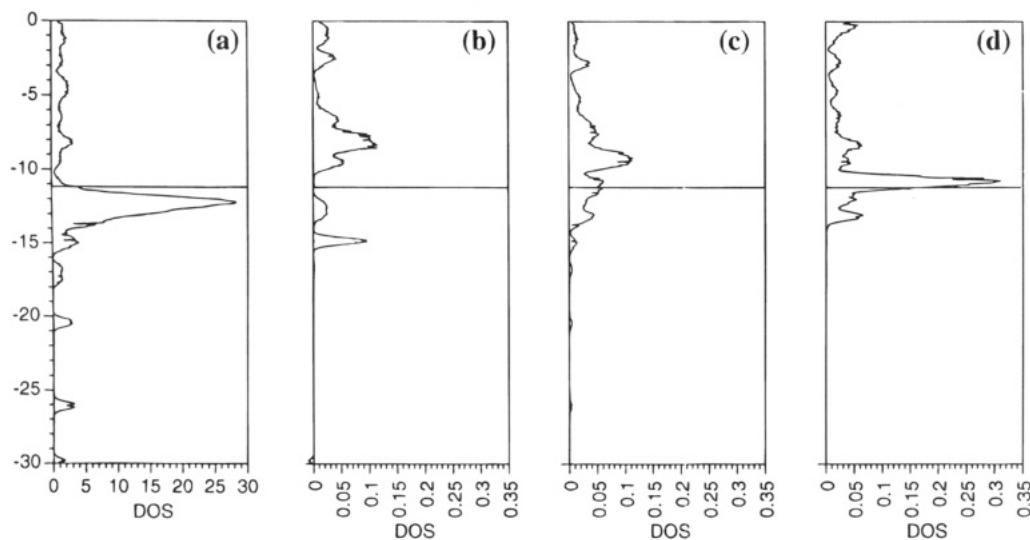
Figure 7. (a) Total electronic density of states for benzene on a metal monolayer in a C_6 site with a Ni_8Bz stoichiometry. (b)–(d) Metal 4s partial density of states for the three different atoms A, B, C (see Figure 6). The calculations used the renormalized metal levels from Figure 1c.
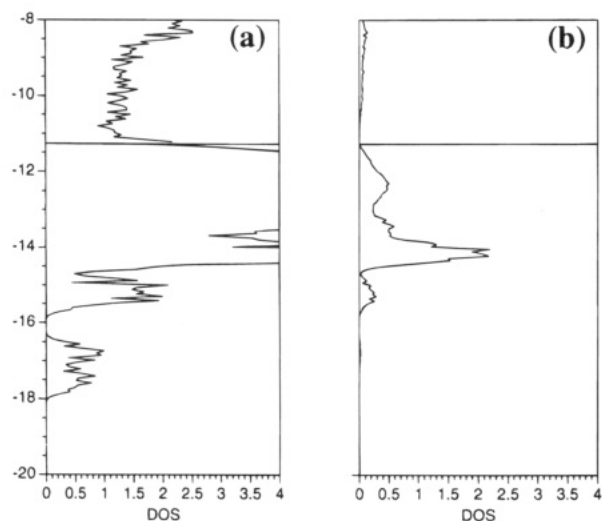

Figure 8. (a) Total electronic density of states in a C_{2v} site with a $Ni_{24}Bz$ stoichiometry. (b) Partial density of states for atoms F.

the free monolayer) of those further away is apparent in the new parameters (see Appendix).

There are interesting results associated with both C_{2v} and C_6 adsorption site in the Ni_8Bz system and also in a more dilute coverage which we have studied ($Ni_{24}Bz$). We discuss a selection from our calculations here. Although the C_6 location for adsorption is believed to be an energetically unfavorable site,[23] the results show that if a benzene molecule were to adsorb on a flat monolayer in this fashion the central atom (Figure 7a) would make no contribution to the electronic density of states at the Fermi level, and would become nonmetallic, if one can use this description for a single atom. The result of the charge iteration is then exactly that of **6** with one atom showing a gap. This single monolayer would then behave just as a slice through one of the cesium suboxides,[15] namely, it would contain a small insulating region in the middle of a metallic sea. This result comes about since it is not possible to pack benzene molecules on the surface so that the carbon atoms interact strongly with all nickel atoms of the monolayer.

An analogous, but more extended result is found for the C_{2v} site in a cell with $Ni_{24}Bz$ stoichiometry, shown in Figure 6. This is a particularly large system for a charge iteration calculation with a tendency to be numerically unstable. The H_{ii} parameters used for this system thus came from renormalization of Ni_8Bz. We used the higher coverage renormalized parameters for those atoms that are nearest the benzene and the original renormalized monolayer parameters for those Ni atoms that are further away. The results for this system can be seen in Figure 8. The nickel atoms F are insulating, but clearly some nickel atoms are metallic since from (a) the total DOS is nonzero. These are those furthest from the carbon atoms of the benzene molecule (Figure 6). At the same time, those Ni atoms arranged near benzene (atoms G) have a low density of states. This is shown pictorially in **7**, a conducting
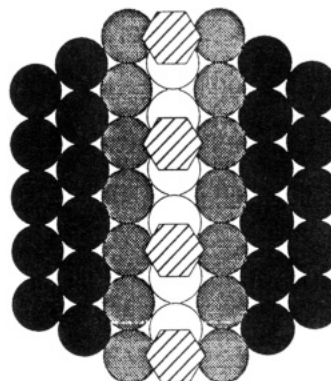
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region (solid circles), a quantum wire, and an insulating (open circles) chain one atom wide separating them. The shaded atoms are those (G) that are metallic but with a low density of states. There are nine "black" rows of atoms in $Ni_{24}Bz$ between insulating chains and one "black" row for Ni_8Bz.

Gomer and co-workers find[7] that the $W(110)/Bz_x/Ni$ system is an insulator for all x. However, in trying to compare theory and experiment in these systems, it should be borne in mind that our knowledge of the detailed structure of the underlying benzene layer(s) is limited. The experimental evidence suggests[7] that the

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first two layers are arranged flat on the surface but later layers are arranged in a perpendicular fashion, in a manner reminiscent of crystalline benzene. How the nickel actually lies on the jagged surface presented by these side-on benzene molecules is difficult to imagine. LEED data for the nickel overlayers is nonexistent for many of the systems described in this paper and which have been studied experimentally indicating surface disorder. In much larger systems, such as $Ni_{large}Bz$, which current calculational methods will not allow us to examine explicitly, we would expect rigorous metallic behavior in the Ni atoms that were far from the nonmetallic wire and that nonmetallic behavior for the Ni atoms nearest the benzene molecule. Of course, many other arrangements of benzene on the surface may produce similar results.

One question that should be asked here is whether or not such idealized systems would in fact hold together. Recall that the situation here is different from that of that of the bulk surface where the surface atoms are also bound to those lying in the penultimate layer. Our charge iterated results show the insulating atoms more and more "molecular"-like. One way to investigate the strength of the various Ni—Ni linkages is examination of the appropriate overlap populations for the relevant calculations. Although the population between insulating and metallic nickel atoms for systems containing adsorbed benzene (0.0662) is smaller than that between the atoms of the bare monolayer (0.0784), it is still significant, suggesting that these systems might not cluster or break apart. We note, however, that on warming[7] $W(110)/Ni_n/Bz_x$ systems, benzene is not regenerated but hydrogen is produced and graphite is formed.

The W(110)/Ni/Bz system contains insulating and metallic regions because of the geometrical demands of the adsorbate. Judicious addition of benzene to both sides of a nickel sheet such that all metal atoms interact with benzene should thus lead to an insulator. Indeed our computations on Bz/Ni/Bz to mimic $W(110)/Bz_x/Ni/Bz$ shows that there is sufficient interaction to give a gap between 3d and 4s bands. The calculated electronic density of states is shown in Figure 9a. The calculated ΔDOS W(110)/Bz/Ni—W(110)/Bz/Ni/Bz of Figure 9b looks just like that calculated earlier[1] for W(110)/Ni—W(110)/O/Ni and of the same general form as the observed ΔUPS spectrum of the latter. It is a characteristic signature of a metal—insulator transition of the type shown in **2**.

Ni/Bz and CO. We have already noted that the coadsorption of benzene and CO on a metal surface leads to ordered systems in several cases (most notably on Ru(111)).[21] Bearing in mind the suggestion of quantum wires in the Ni/Bz system and ready removal of CO, such coadsorbed molecules on a group 10 monolayer have interesting possibilities. Recall that the calculations on the Ni_8Bz system above with the benzene on the C_6 site show that the central Ni atom (A) is insulating and that although the total electronic density of states is not very high, the whole system is metallic, indicating that the other Ni atoms in the monolayer are metallic. Coadsorption of CO in the hollow sites surrounding the benzene molecule leads to very interesting results. The CO molecules interact with benzene through each of their π-bonding orbitals, leading to formation of a π-band which mixes with the d orbitals
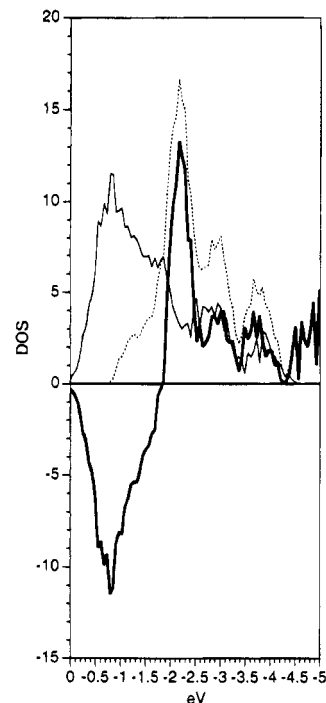

Figure 9. Calculated difference electronic density of states (ΔDOS, heavy line) from the total densities of states for W(110)/Bz/Ni (solid line) and W(110)/Bz/Ni/Bz (dotted line).
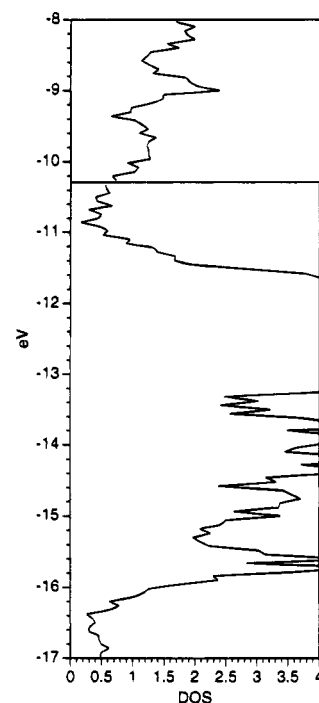

Figure 10. Calculated total electronic density of states for Ni/Bz, CO using the C_{2v} sites of the Ni_8Bz system with CO located in the gaps between the organic molecules as in **8**.

on Ni, effectively closing the gap for the central atom—making it metallic once again. The results of a charge-iterated calculation (where all metal atoms are included in the iteration) are shown in Figure 10. What has happened to the metallic or otherwise behavior of the metal atoms is shown pictorially in **8**. The effect is similar to that noted earlier for CO adsorbed on the monolayer at high coverage. These conclusions are easily extended to the more dilute system presented by the $Ni_{24}Bz$ cell. Note that the CO molecules are placed

Table 1. Summary of Theoretical Results and Comparison with Experiment

	theory	experiment[a]
O/Ni	insulator	reduced met. (W(110)/O/Ni)
$O_{0,x}$/Ni	insulator	reduced met. (W(110)/$O_{0,x}$/Ni)
O/Cu	metal	metal (W(110)/O/Cu)
F/Ni	metal	
F/Ni/O	insulator	
F/Ni/H_2O	insulator	
F/Ni/CO	insulator	
S/Ni	metal	
S/Ni/H_2O	insulator	
W(110)/Bz/Ni	reduced met.	reduced met. (W(110)/Bz/Ni)[b]
Bz/Ni/Bz	insulator	reduced metallicity
O/Ni_2	metal	reduced metallicity (W(110)/O/Ni_2)
O/Ni_2/O	semimetal?	
O/Ni_2/H_2O	semimetal?	

[a] The experiments which have been performed often see a loss of metallic character, but are unable to conclusively state that an insulator is formed. [b] See text.

Table 2. Metals and Insulators

| metal	→	insulator	→	metal
Ni	→	O/Ni		
F/Ni	→	F/Ni/CO	→	F/Ni
S/Ni	→	S/Ni/H_2O	→	S/Ni
F/Ni	→	F/Ni/O		
O/Ni_2	→	O/Ni_2/O[a]		

[a] Perhaps a semimetal.

on the 2-fold bridging sites and surround the benzene molecules.

Metals to Insulators. Table 1 shows a summary of the theoretical results described above, and Table 2 some metal−insulator transitions that may be generated by adsorption. Particularly interesting is the reversibility of the adsorption of CO, which is calculated to dramatically change the properties of the system. In the Ni_{24}Bz cell described above one can envisage insulating wires one atom apart acting as insulating boundaries to conductivity across the monolayer, which can be "opened" by coadsorption with CO as in **8**. This effect

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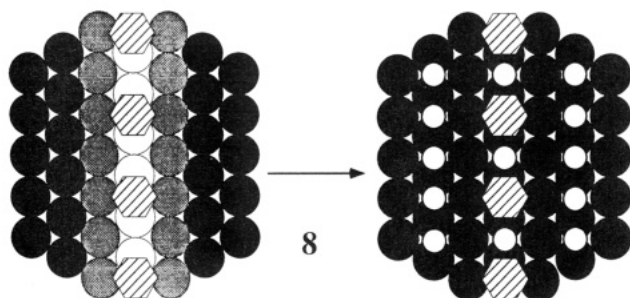
is reversible since CO is readily added or removed from the surface. It does rely, however, on ordered benzene molecules on the surface without the presence of the CO which is often not the case for a variety of metal surfaces.

Quantum Confinement and Other Effects. The electronic results described above we believe are robust enough for us to be able to make some comments concerning possible quantum effects in these systems. Recalling the results for the cesium suboxides[15,16] noted above, we can envisage partial coverage of a nickel monolayer LiF(111)/Ni/X_x (X = oxide, CO, water, etc.) with $x < 1$, which will give similar results (**9**). There will be regions of the surface that are insulating and regions that are conducting. They are one nickel atom

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□ insulating or metallic	▨ metallic or insulating
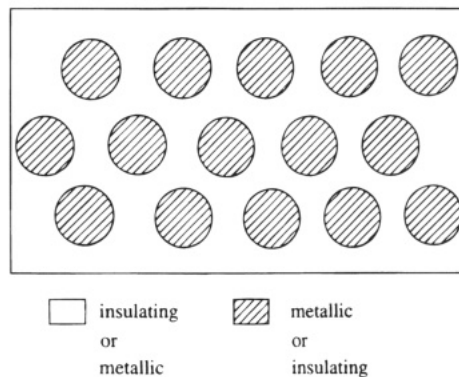
thick. The relative expanse of each may be controlled by the nature and formal coverage of X. (An attractive pair potential of the adsorbate ensures that they cluster rather than distribute themselves randomly over the surface.) The types of patterns that can be imagined are varied. They include conducting pathways through the surface of the width of a few atoms and one atom deep (quantum wires), ordered regions of insulating material generated by adsorption (nanoclusters) that could be several atoms wide or much larger, a two-dimensional analogue of the electronic picture in the cesium suboxides or the recently characterized system[25] $Nb_7S_2I_{19}$ which contains insulating NbI_5^{5+} monomers in a metallic matrix. In both of these "molecular" examples the size of the insulating unit is of the order of a few atomic dimensions. For the systems described in this paper the size of the units should be controllable via the coverage. It may well be possible to generate arrays of close-packed regions of metal or insulator. In some cases the type of pathway will be determined by the geometry of the molecule and how it is ordered on the surface. The W(110)/Bz/Ni and LiF(111)/Ni/Bz systems are cases of this type. **7** shows a possibility for a row of benzene molecules adsorbed in C_{2v} sites. The back atoms are metallic, the white atoms insulating, and the shaded atoms metallic but with a low density of states. The calculated behavior for LiF(111)/Ni/Bz described above indicates quantum wires a few atoms wide. Molecular wires have been made (e.g., ref 26). Certainly some of the predicted properties of such systems, such as enhanced electron mobility, are of considerable interest.[27]

Benzene is not readily desorbed from a nickel surface; during "desorption" it chemically degrades. However, it might be possible to find other molecules that retain their chemical integrity on adsorption and desorption. If such species may be adsorbed and desorbed at will, then there is control over the consequent change in properties. We have suggested the CO molecule from our calculations on CO and benzene mixtures. Perhaps they may be "swept" into patterns using an AFM.

Extensions of these results are several; to three dimensions, to other systems as adsorbates; large organic molecules such as pentacene, for example, to segregated alloy surfaces and to more complex chemical and geometrical structures. The recent development of new methods[28] of surface microfabrication using arrays

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Table 3. Renormalized Nickel Parameters

monolayer	H_{ii} (eV)	bilayer	H_{ii} (eV)	Ni/Bz C6 A	H_{ii} (eV)
4s	−8.47344	4s	−9.43411	4s	−8.94553
4p	−4.60874	4p	−5.35413	4p	−4.97322
3d	−12.39218	3d	−13.92496	3d	−13.13452
Ni/Bz C6 B		Ni/Bz C6 6		Ni/Bz C2v D	
4s	−9.42126	4s	−8.23175	4s	−8.30023
4p	−5.34311	4p	−4.42127	4p	−4.47406
3d	−13.89440	3d	−11.99771	3d	−12.10660
Ni/Bz C2v E		Ni/Bz C2v F		Ni/Bz C2v G	
4s	−8.52212	4s	−9.32665	4s	−8.59783
4p	−4.64535	4p	−5.26942	4p	−4.70389
3d	−12.45967	3d	−13.74314	3d	−12.58025

[a] These are all double-ζ wave functions with the d orbitals having $\zeta_1 = 0.5683$, $\zeta_2 = 0.6292$, and weighted with $c_1 − 5.75$ and $c_2 − 2.00$. The s orbitals were weighted with $c_1 − 1.60$ the p orbitals with $c_1 − 1.55$.

of identical particles with a variety of shapes might be particularly important too.

Conclusions

The results described in this paper suggest that there are some very interesting electronic effects associated with the adsorption of small molecules on monolayers of group 10 metals. The dimensionality of the metal sheet is crucial for these experiments to work, as is the electron count. Similar effects are not usually seen with the surfaces of bulk solids. Elsewhere[29] we have examined the effect on the Fermi surface of monolayers of the group 6 elements of adsorption on small molecules. Quite dramatic effects are seen here too. The idea of opening a gap between two overlapping bands by chemical means, the underlying theoretical basis of the paper is, of course, found elsewhere in the solid state. For example,[30] increasing the separation of the arsenic-like (SnSb) sheets in K(SnSb) by a layer of potassium ions ensures that valence and conduction bands do not overlap in contrast to the situation in elemental (grey) arsenic itself.

Appendix

All calculations were performed using the extended Hückel implementation of tight-binding theory.[30] Standard orbital parameters were used, with the exception of those for nickel as discussed in the text. Standard structural parameters were used for CO, water, and benzene molecules, with the observed[2] dimensions of the nickel monolayer, itself that of the (110) face of bulk tungsten. Choice of metal−X, −Y distances is frequently not straightforward since these are unusual systems. We have considered a range of interatomic distances, taking into account ionic radii, van der Waals radii and the atomic radius of Ni, which is 1.60 Å. The choice of internuclear separation is very important, for at a short enough distance, almost any substrate or adsorbate of the main group will create a bandgap in the nickel.

W/O/Ni: A typical W−O distance in a solid metal oxide is about 1.70 Å, but we expect our distances in the surface system to be longer because the bulk W is effectively W(0), which we would expect to have a longer bond to oxygen. We used a W−O distance of 1.99 Å, but our calculations showed similar results at even shorter distances. At distances of lower than 1.50 Å, the W−O interaction became so large that the band picture of a separate Ni layer was lost, but these distances are unrealistic. For the Ni−O distance we note that typical distances are within the 1.80−2.20 Å range in both molecules and solids. A standard Ni-(II)−O distance, as in NiO, is 2.08 Å. However, since we are dealing with a Ni(0)−O^{2-} linkage here, we might expect that it may be even longer than this. Our calculations shown in Figure 1 used a bond length of 1.91 Å, but the results are qualitatively the same for distances up to at least 2.4 Å in that a bandgap is created by interaction of the oxygen orbitals. Of course at longer the longer distances this bandgap is smaller. We used the same distance for the Ni−OH$_2$ case.

F/Ni: For fluorine, the van der Waals and ionic radii are very similar (1.35 and 1.36 Å, respectively), which when added to the nickel atomic radius gives us an upper limit of about 2.9 Å for a Ni−F distance. However, the Ni(II)−F distance can be smaller than 2.0 Å in molecules. We find from calculation that the fluorine layer itself produces a bandgap in the nickel monolayer at distances of 2.5 Å or shorter. This is a distance between the two extremes just noted.

S/Ni: A typical S−Ni bond length (for Ni(II)) is approximately 2.40 Å. Again with the monolayer, we expect slightly longer bond lengths. We found that sulfur, when used as a substrate, produced a bandgap in Ni at lengths shorter than 2.0 Å, but in the intermediate range 2.0−3.0 Å the metallicity of the monolayer was retained.

Ni/CO: Similar to the Pt(111) + 2CO system,[21] we used a CO coverage of 0.5, which led to an occupation of one on-top site and one bridge (or 2-fold site) for every four nickel atoms. This arrangement produces the (c2 × 2) type of surface. The Ni−CO distances were 2.15 Å in the bridge site and 1.74 Å in the on-top site, values comparable to adsorption on bulk metal surfaces.

Ni/Bz: In the C_6 site, the Ni−C shortest distance (for atom A) was 2.3 Å, in the C_{2v} site the Ni−C shortest distance was 2.0 Å for all four atoms nearest the benzene molecule. As described in the text, the results proved relatively insensitive to minor (∼0.10 Å) in this distance.

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