Origin of the Coverage-Dependent Vibrational Shift for O on Ni(100)

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The $p(2\times2)$ and $c(2\times2)$ coverages of O on Ni(100) are studied with a cluster model. The $p(2\times2)$ coverage is modeled by the addition of a single O at a fourfold site. The $c(2\times2)$ is modeled by the explicit inclusion of four additional O atoms. Consistent with electron energy-loss spectroscopy results, the O-Ni vibration is 85 cm^{-1} lower for the $c(2\times2)$ cluster than for the $p(2\times2)$. The height of O above the surface is 0.11 Å smaller for the $c(2\times2)$ coverage. The nature of the O-to-Ni bonding is similar for both coverages.

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Measurement of the electron energy-loss spectra[1] (EELS) for O on Ni(100) has shown a shift in the O vibration normal to the surface, ω_e, from 430 to 310 cm^{-1} as the oxygen coverage changes from a $p(2\times2)$ to a $c(2\times2)$ low-energy electron-diffraction pattern. Upton and Goddard[2] (UG) have suggested that the electronic nature of the chemical bond between the O and the Ni(100) surface was very different for the $p(2\times2)$ and $c(2\times2)$ coverages of O on Ni(100). For the lower $p(2\times2)$ coverage, they claimed that the bond involved an open shell which was essentially localized on O; UG denoted this open shell state as a "radical" state. For $c(2\times2)$ coverage, they claimed that the bond was one for which all the O electrons were in closed shells; they denoted this as an "oxide" state. The equilibrium vertical distance of O from the surface, $R_\perp$, was very different for these two states. For the "radical" state, UG found $R_\perp = 0.88$ Å; for the "oxide" state, $R_\perp = 0.26$ Å. This was based on cluster calculations for oxygen at the center of a fourfold site. The UG potentials for the O-Ni interaction as a function of the O-Ni distance were used by Rahman, Black, and Mills[3] in a lattice-dynamics study, which included a treatment of the surface phonons; they were able to obtain excellent agreement with the specular EELS data.

The large difference for $R_\perp$ between the $p(2\times2)$ and $c(2\times2)$ coverages of O on Ni(100) are not consistent with a large body of results obtained with several different techniques. The only tentative support for a short $R_\perp$ at high coverages of O is from angular-resolved x-ray photoelectron spectra.[4] The early low-energy electron-diffraction analyses[5] showed the same $R_\perp \sim 0.9$ Å for both coverages. This has been confirmed by recent extended x-ray-absorption fine structure,[6] and normal photoelectron diffraction[7] which also give $R_\perp \sim 0.9$ Å for both $p(2\times2)$ and $c(2\times2)$ coverages. There is further support from experimental[8] and theoretical[9] analyses of He diffraction from O/Ni(100) which give strong evidence against a short $R_\perp$ for $c(2\times2)$ O/Ni(100). Other measurements give evidence for only one kind of electronic structure for both $p(2\times2)$ and $c(2\times2)$ coverages of O chemisorbed on Ni(100). These include a linear change in the work function with O coverage,[10] x-ray absorption-edge fine structure,[6] and photoemission spectra of O-related features.[11] A recent off-specular EELS[12] study has shown that this spectra can be explained by $R_\perp \sim 0.9$ Å for $c(2\times2)$ coverage; however, the authors concluded that the chemical nature of the oxygen must be different to account for the large observed shift for the oxygen ω_e.

We have recently performed a small-cluster (Ni_5O) study[13] of the "radical" and "oxide" states of chemisorption. This work showed the importance of a proper treatment of (1) the $4s$-$4p$ near degeneracy and (2) the electron affinity of O. The latter is rather important because chemisorbed oxygen is significantly negatively charged (Refs. 2 and 13). In this cluster study, we took these factors correctly into account and showed that the closed-shell, "oxide," chemisorbed state is considerably more stable, ≥ 1.0 eV, than the open-shell, "radical" state. However, in this work we did not explicitly treat coverage changes and considered a cluster with only one O atom. In their work, UG also studied clusters with no more than one O atom. In the present work, we include a treatment of coverage. For $p(2\times2)$ coverage we add only one O atom to the Ni cluster but to simulate the higher coverage, we add five O atoms in $c(2\times 2)$ geometry. Our results show that this explicit consideration of coverage explains the reduction of the O-Ni vibrational frequency between $p(2\times 2)$ and $c(2\times 2)$ O coverages. This large change in frequency is accompanied by only a small decrease in $R_\perp$.

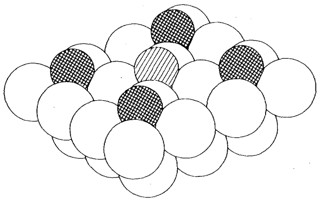

FIG. 1. The $Ni_{25}O_5$ cluster; the O atoms are cross hatched. The central O, singly cross hatched, is used for $p(2\times 2)$ coverage, and the four doubly cross hatched O's are added for $c(2\times 2)$ coverage.

We model the (100) surface with a two-layer, 25-atom cluster, shown in Fig. 1. The cluster contains a four-atom by four-atom square top layer and a three-atom by three-atom second layer. We place the adsorbed O atom(s) in the center(s) of some of the fourfold sites and vary its vertical distance from the first-layer Ni atoms. We model the $p(2\times 2)$ coverage by adding a single O atom to the central fourfold site to form the $Ni_{25}O$ cluster. We model $c(2\times 2)$ coverage by adding five O atoms to the fourfold sites as shown in Fig. 1. For Ni, we use the same modified effective potential (MEP)[14] as UG. This potential includes the Ar core and the nine $3d$ electrons in an effective core potential; it reduces Ni to a one-electron problem and has a term added to bring the energy difference between the atomic ^3F ($d^8 4s^2$) and ^3D ($d^9 4s^1$) states into agreement with experiment at the self-consistent-field (SCF) level. The Ni contracted Gaussian-type orbital basis set includes two functions to describe the $4s$ and one to describe the $4p$ atomic orbitals. The oxygen basis set[15] is a double-zeta contracted Gaussian-type orbital set, which includes a diffuse p function to describe O^- Previously,[13] we noted the importance of the Ni $4p$ functions and the need to be able to describe O^-. Our previous work also showed that it is very important to include correlation to obtain the open-shell state energy correctly relative to the closed-shell state; however, $R_\perp$ and ω_e for the correlated wave functions are very similar to those obtained with SCF wave functions (see Table I and Ref. 13). Therefore, we have used the SCF technique to treat the $Ni_{25}O$ and $Ni_{25}O_5$ clusters.

For $Ni_{25}O$, we vary the height of the O atom above the surface and obtain $R_\perp$ as the location of the minimum of the SCF potential curve. For $Ni_{25}O_5$, four atoms are placed at the outer fourfold sites and fixed at the equilibrium $R_\perp$ found for $Ni_{25}O$. The position of the central atom was varied in the presence of these four atoms and a new $R_\perp$ was determined for it. A quadratic fit of the potential curves for the motion of the central atom was used to obtain the O-Ni vibrational frequencies, ω_e; the mass of Ni was assumed to be infinite.

TABLE I. Summary of cluster results for $R_\perp$, ω_e, and force constant.

Method	$R_\perp$ (Å)	ω_e (cm^{-1})	Force constant[a]
Ni_5O all electron	1.05	380	0.0897
Ni_5O MEP	0.68	290	0.0514
Ni_5O CI[b]	0.74	320	0.0624
Ni_5O corrected MEP	0.93	400	0.0963
Ni_5O corrected CI[b]	0.99	390	0.0914
$Ni_{25}O$ MEP	0.58	280	0.0479
$Ni_{25}O_5$ MEP	0.45	230	0.0319
$Ni_{25}O$ corrected MEP	0.83	400	0.0977
$Ni_{25}O_5$ corrected MEP	0.72	315	0.0603
$p(2\times 2)$O/Ni(100), experiment	0.86 ± 0.07[c]	430[d]	
$c(2\times 2)$O/Ni(100), experiment	0.86 ± 0.07[c]	310[d]	

[a] The second derivative of the total energy with respect to the variation of $R_\perp$, in hartree/bohr^2.

[b] Correlation added through configuration interaction (CI).

[c] Ref. 6.

[d] Ref. 1.

It is clear that neglecting the d electrons of Ni and treating it as a one-electron atom is a drastic approximation. We have tested the seriousness of this approximation by performing both MEP and all-electron SCF calculations for the Ni_5O cluster. The differences between these calculations are dramatically large for $R_\perp$ and ω_e as shown in Table I. The MEP $R_\perp$ is 0.37 Å or 35% smaller than the all-electron value; the MEP ω_e is 90 cm^{-1} or 24% smaller. The $3d$ electrons are not inert; they are involved to some extent in the bonding of Ni to O. One assumption of the MEP is that the O atom moves in a field of a Ni nucleus of charge +1. This is not true, in particular, because of the reasonably large spatial extent of the $3d$ shell. The radial part, $rR(r)$, of the $3d$ and $4s$ SCF orbitals of the Ni atom in the ^3D $(3d^94s^1)$ state are plotted in Fig. 2; clearly the $3d$ orbital extends into the valence region where the $4s$ has most of its density. As the oxygen atom approaches the Ni surface, it gets inside some of the $3d$ charge and a Z_{eff} greater than +1 is necessary for the Ni atom. The use of a larger Z_{eff} will lead to a longer bond length because of the larger electrostatic repulsion between the Ni and O nuclei. This problem is discussed for Cu_2 and CuH by Jueng and Barthelat[16] who find that the use of a suitably varied Z_{eff} improves the agreement between theory, based on a one-electron pseudopotential for Cu, and experiment. Similar improvements have also been found for other systems.[17] We have included a correction for this failing of the one-electron MEP for Ni by using a $Z_{\text{eff}}(R)$ which is determined by considering the penetration of the atomic $3d$ orbital by a point charge. When this corrected MEP is used for the Ni_5O calculation, the results are much closer to the all-electron values. Clearly the $3d$ orbital is not so inert that it can be neglected, but the agreement between the all-electron (with $3d$'s) and the corrected MEP suggest that it may be possible to treat the $3d$ as perturbation to a valence-only treatment. However, we regard this correction as empirical since other errors of the one-electron MEP, including the direct involvement of the Ni $3d$ electrons in the Ni-O bonding,[18] are neglected. Because of the empirical nature of this correction, we report both the corrected MEP and uncorrected MEP results in Table I. While the corrected MEP results are in better agreement with experiment, both sets of calculations have similar differences between $Ni_{25}O$ and $Ni_{25}O_5$ for $R_\perp$ and ω_e.

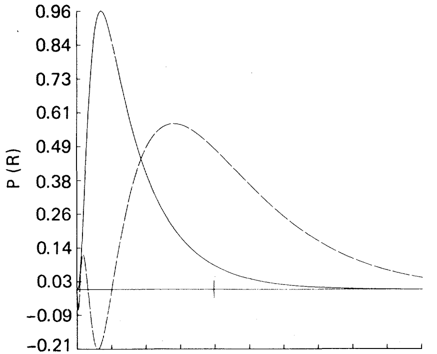

FIG. 2. The radial density of the $3d$ and $4s$ orbitals for Ni ^3D. The mark at about 2 Å indicates the Ni-O distance for $p(2\times 2)$ O/Ni from Ref. 6.

The corrected MEP $Ni_{25}O$ results are in good agreement with both the EELS[1] ω_e and the extended x-ray-absorption fine-structure $R_\perp$ for $p(2\times 2)$ coverage. The ω_e results for $Ni_{25}O_5$ agree with the EELS changes for the $c(2\times 2)$ coverage; however, they show a 0.11-Å shortening of $R_\perp$ from that for $Ni_{25}O$. Although this shortening of the bond length from $p(2\times 2)$ to $c(2\times 2)$ coverage is not outside of the error bounds of the extended x-ray-absorption fine-structure determination for $R_\perp$ (see Table I), it does suggest that there is a difference, albeit not large, for $R_\perp$ between $p(2\times 2)$ and $c(2\times 2)$. Recent lattice-dynamics calculations[19] suggest that about half of the observed coverage-dependent shift in ω_e is due to direct changes in the Ni-O interaction and half is due to an indirect change related to the coupling, at $p(2\times 2)$ coverage, of the Ni-O vibration with surface phonons. Therefore, our computed shift in ω_e which takes into account only the direct changes should be too small.

Considering the approximations made in our model studies, we do not expect to be able to reproduce experiment; in particular, we have not made any attempt to include the effects of phonon coupling. However, we believe that the changes we have observed are real effects; there is a shift in ω_e to lower frequency and there is a small reduction in $R_\perp$. Our calculations are quite consistent with the observed values[5-9,12] of $R_\perp$ and ω_e and their changes from $p(2\times 2)$ to $c(2\times 2)$. For both the $Ni_{25}O$ and $Ni_{25}O_5$ clusters, the O atoms are in a closed-shell state; that is all O electrons are in fully occupied orbitals, either bonds or lone pairs. Thus, we conclude that there is only one electronic state of O for all coverages of O/Ni(100). This is consistent with our conclusions based upon studies of a smaller cluster.[13] The changes in $R_\perp$ and ω_e with coverage are not the result of major changes in the bonding of O to Ni; rather they are due to small changes in bonding as a result of larger lateral interactions at the higher, $c(2\times 2)$, coverage. We believe that the most important effect is an indirect lateral interaction because of the different surface stoichiometry for $p(2\times 2)$ and $c(2\times 2)$. Since the interaction of O with the Ni surface has some covalent character, it should not be surprising that changing the ratio of O to surface Ni atoms results in some, small, changes in the bonding.

In summary, calculations modeling the change in O coverage from $p(2\times 2)$ to $c(2\times 2)$ show that both coverages have the same ground electronic state, one in which all of the O electrons are in closed shells. The increase in O coverage results in a small shortening of the O distance above the surface and a shift to lower frequency of the O vibration normal to the surface. We conclude that the observed shift in vibrational frequency is not due to a major change in the electronic state; small changes in the bonding are the result of the change in ratio of O atoms to surface Ni atoms.

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