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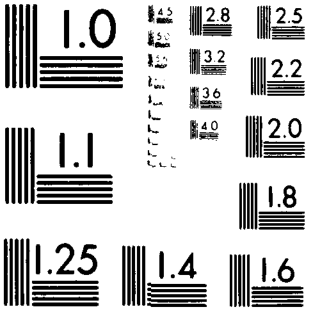

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Report

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Semi-empirical calculations were performed for small clusters modelling the adsorption of CO on nickel (100), (110), and (111) surfaces at low and high coverage levels and on nickel-copper alloy (100) surfaces at low coverage. The bearing of the results upon the understanding of experimentally observed faceting and magnetization (Hedvall) effects is discussed. A preference for adsorption at multifold sites is observed at low coverage, and the (100) and (111) surfaces are predicted to be enrgetically smooth at high coverages. The results for alloy surfaces are qualitatively in agreement with experiment.

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Further Studies on the Kinetics of $Ni(CO)_4$ Formation

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by

Lynn T. Redmon
Principal Investigator

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Introduction

Transition metals and their molecular complexes comprise an area of chemistry which is of critical importance to both industry and government. They are the key element of most catalytic processes, which account for 90% of all chemical substances produced [1]. Catalysis affects the quality of the air we breathe, the cost of gasoline, and many other aspects of daily life. In addition to catalysis, transition metal complexes may also be potentially important as novel laser pumping sources [2].

Although the effects of catalysis are often macroscopic, the specific mechanisms responsible for each process are molecular in origin. For this reason, the field of theoretical chemistry has much to offer towards understanding catalysis and, ultimately, aiding in the design and development of new and improved catalysts.

The detailed study of catalysis is still in its infancy, both theoretically and experimentally. Either method encounters difficulties in treating such phenomena that often involve the interaction of one (or more) molecule(s) with other molecules or atoms adsorbed on or comprising a solid surface or film. The study of carbon monoxide (CO) adsorption on nickel (Ni) surfaces has often been chosen as a prototypical case because it has some simplifying features: Ni is a common catalyst, CO does not dissociate on Ni, and the reaction product $Ni(CO)_4$ forms only at high coverages and leaves the surface in gaseous form (although it is extremely toxic).

Various techniques are available to experimentalists for the study of adsorbed species. However, no single method gives enough information for a complete description of the chemisorptive bond [3], and the interpretation of data is always dependent upon the theoretical models adopted. Quantum chemistry offers an alternative approach, at an atomic an molecular level, which should be applied along with experimental procedures to enhance the understanding of complex phenomena [4,5].

This report describes the results of a series of calculations performed on various cluster models of CO adsorption on Ni and Ni/Cu alloy surfaces. The method employed is a semi-empirical one, the modified Huckel method of Anderson [6]. The investigations were designed to provide insight into the mechanism(s) of the formation of nickel carbonyl, $Ni(CO)_4$, with particular emphasis toward explaining experimentally observed magnetic [7] and orientational effects [8].

The main content of this report is in the form of two papers which will be submitted for publication in The Journal of Physical Chemistry. The first of these describes calculations for clusters modelling the (100), (110), and (111) surfaces of Ni at low and high levels of CO coverage. These studies were designed to provide information relevant to explaining the observed formation Ni of (111) facets on (100) and (110) surfaces [8] during $Ni(CO)_4$ formation. The second paper gives the results of calculations examining CO adsorption at various sites on thirty different nine-atom Ni/Cu clusters. It includes a tabulation of the average and localized-site magnetizations, as measured by orbital population analysis, and discusses trends observed in ligand and ensemble effects.

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Comments on Accurate Calculations for NiCO

Methods such as the modified Huckel method employed for the investigations described in this report are not well suited for the determination of the spin states of atoms or molecules. Since they do not treat the correlation problem explicitly (i.e., they do not include configuration interaction), any open shell specification of occupation numbers will always yield a higher total energy than the closed shell (or most-nearly closed shell) configuration. This is not necessarily the proper result. Therefore, in our calculations we have specified the occupation numbers intuitively. Unfortunately, the treatment of surface adsorption models is not feasible with sophisticated methods.

However, the more rigorous quantum chemical methods have been applied to small Ni systems. It turns out, though, that these studies are far from trivial. Indeed, only recently and with great effort has the ground state of the Ni atom been correctly obtained[1]. The calculations used the CI method and required a large basis of STO´s (Slater type orbitals) including three sets of _f_ functions and one set of _g_ functions. Previous work involving substantial effort still reversed the two lowest states [2-4].

NiCO has also been treated by _ab-initio_ methods[5-8]. The earliest of these works reported its ground state to be a triplet delta state, bound by 1.1 eV [4]. More recent calculations predicted this state to be a shallow relative minimum, unbound relative to its separated limit involving ^3D Ni by 0.1 eV, and predicted the lowest state to be a singlet sigma state separating to a $\underline{d}^{10}$ ^1S Ni atom and to be bound, relative to that limit, by 2.7 eV [8]. This result is particularly interesting in regard to the question of the magnetic state of the species leaving the surface during $Ni(CO)_4$ formation if that species is NiCO.

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Comments on the Relationship between Cluster Size and Bulk Properties

For some time, theoreticians have realized that predictions of bulk properties from calculations on small clusters could be considerably in error[1-6]. The convergence of various properties to their bulk values with increasing cluster size has been studied for several methods: the modified Huckel[1], SCF[2,3,5,6], and X-alpha[6,7] methods. Although the rate of convergence is different, depending on the specific property[2,4], a qualitatively similar convergence for densities of states has been demonstrated for the HFS (Hartree-Fock-Slater) application of X-alpha and the SCF and Huckel methods, as opposed to MS (multiple-scattering) X-alpha[7]. Thus, the use of one of the former methods is advocated. Another relevant conclusion reached is that the study of the interaction of metal surfaces with electronegative species (which involves the modelling of the ionization potential) can be achieved with smaller clusters than those needed for the case of electropositive species[2]. Therefore, we hope that the modified Huckel method applied to CO adsorption on small Ni clusters will be useful.

Experimentally, metallic properties, such as ferromagnetism in Ni, are found to be particle-size dependent[8]. For example, the Curie temperature appears to vanish for grain sizes smaller than 60 A. Not only is the size of our clusters inadequate to study this phenomenon, but, more importantly, the method employed does <u>not</u> attempt to treat temperature effects. However, to the extent that local site effects predominate in adsorption processes and are decoupled from the bulk[9], we hope to provide theoretical insight into the role of CO adsorption in nickel carbonyl formation using small cluster model calculations.

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Semi-Empirical Studies of CO Adsorption at Low and High Coverages on Ni (100), (110), and (111) Surfaces

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Abstract

The modified Huckel method of Anderson is applied to CO chemisorption on small Ni clusters. The adsorption energies of a single CO at all possible sites on the (100), (110), and (111) surfaces are calculated. The results indicate that at low coverage levels multifold sites are preferred. Calculations for models of high coverage are performed to provide insight into the possible mechanisms of $Ni(CO)_4$ formation.

Introduction

Over the past several years, the adsorption of CO on various Ni surfaces has been addressed by a number of experimental and theoretical investigators: (100)[1-8], (110)[8-10], and (111)[10-14], among others. In general, researchers agree that the absolute coverage limit for CO is about 1 x 10^{15} molecules/cm^2, and it is independent of the surface orientation. Since the densities of surface atoms vary according to the orientation, the coverage ratios for the (100), (110), and (111) surfaces are approximately 2/3, 1/1, and 4/7, respectively. Low-energy electron diffraction (LEED) studies have shown that the coverage is ultimately limited by CO-CO repulsions[8], and, as a result, the high coverage LEED patterns correspond to hexagonal structures or structures that can be considered to be distorted hexagons[1,9,12]. Although LEED studies provide the relative angular orientation of the overlayer relative to the substrate lattice, they do not determine the absolute bonding sites. Other experimental methods, such as ultraviolet photo-emission spectroscopy (UPS) and electron energy loss spectroscopy (EELS)[3], have sought to identify the symmetry of the adsorbate-substrate interaction by examining spectral shifts. However, it has been pointed out [2] that comparisons of this type could lead to erroneous conclusions when the adsorptive process involves large relaxation effects.

The characterization of CO adsorption on Ni is an important step toward understanding the mechanism of $NI(CO)_4$ formation. Although the species leaving the surface in this reaction has not been identified, a Hedvall effect has been observed[15]; i.e., the activation energy is dependent upon the magnetization of the substrate. Also, a very interesting faceting process has been observed[16]: Ni

(100) and (110) surfaces are transformed into regularly arranged (111) facets upon reaction. The exact cause of this faceting is not known. The studies described herein were designed to provide information useful in understanding these phenomena.

Low Coverage Studies

The parameters used in these studies are given in Table 1. The standard values (in parentheses) were used for some subsequent calculations. The Ni s exponent was adjusted so that the equilibrium position of the central surface atom of a two layer cluster model of Ni (100) or (111) [the exponents were nearly identical] lay in the surface plane. The cluster for (100) consisted of a five-atom "domino"-pattern layer and the four nearest neighbors (NN) of the central atom in a layer below these. Because of the emphasis on CO-CO repulsions (see Ref. 8, for example), the C and O s exponents were proportionately adjusted so that the semi-empirical CO-CO repulsivity matched an *ab-initio* calculation at the Ni NN distance (2.49 Å). The Ni lattice distance used was 3.52388 Å and the C-O distance was fixed at 1.15 Å for all calculations. The occupation numbers for the Ni clusters were specified by the nearest possible integral value corresponding to 0.6 unpaired electrons/atom. Thus for the nine-atom clusters six electrons were unpaired.

Terminal (T), i.e. linear, adsorption on Ni (100) was modelled by CO approaching the central atom of the five-atom layer of the cluster described above. The same cluster was used to study the four-fold (4) site by approaching from the second-layer side. The two-fold, or bridge (B), site used was one on the five-atom layer. Figure 1 shows the results of these studies and corresponding calculations for

Table 1. Parameterization

atom	orb.	coef.	exponent	energy
Ni	3d	0.5683 0.6292	5.75 2.0	-10.0
	4s	1.0	2.0±.04	-7.63
	4p	1.0	1.5	-4.0
C	2s	1.0	1.375(1.61)	-16.6
	2p	1.0	1.57	-11.3
O	2s	1.0	1.925(2.25)	-28.5
	2p	1.0	2.23	-13.6

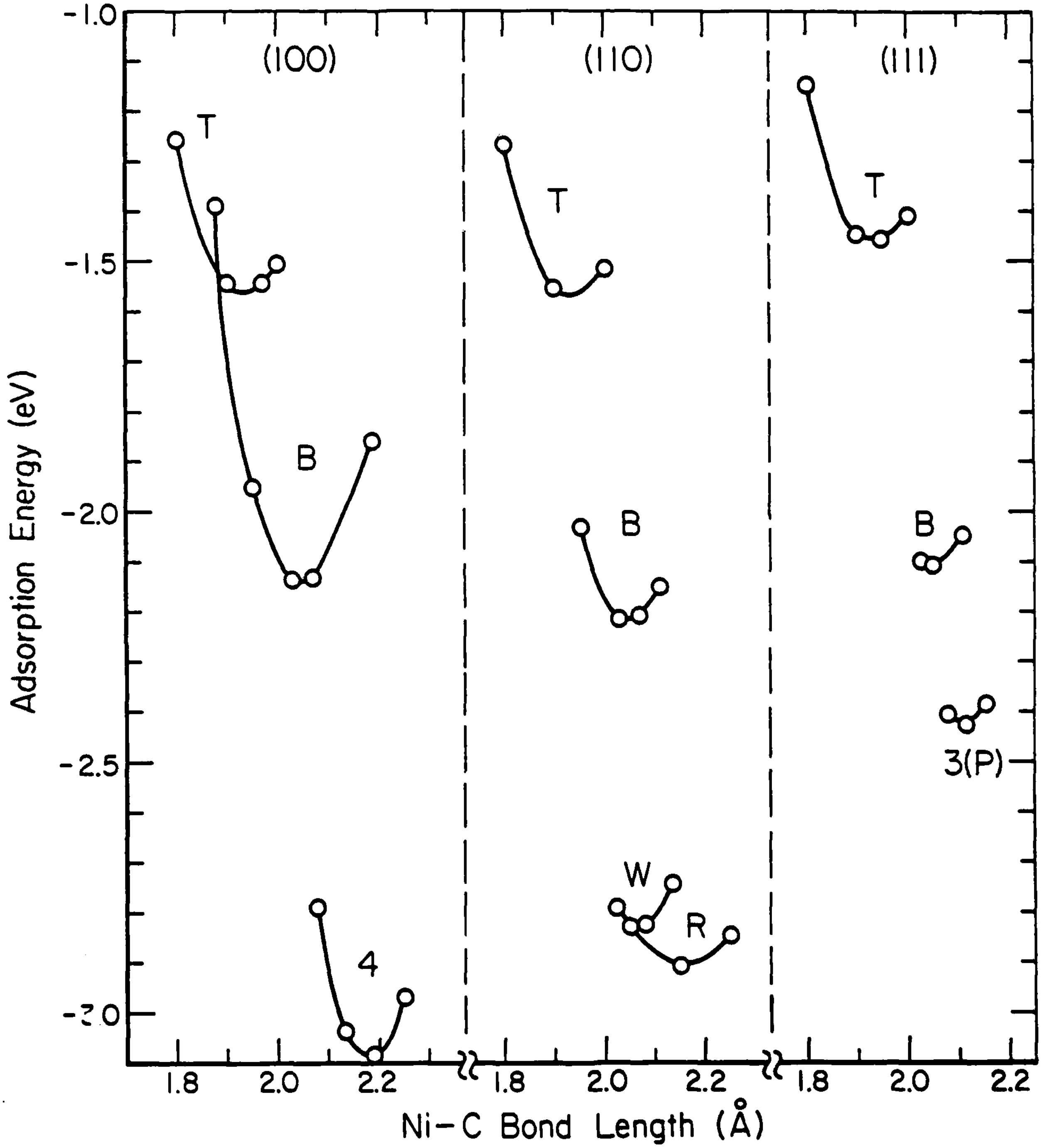

Figure 1. CO Adsorption on Ni at Low Coverage

the (110) and (111) surfaces.

For the (110) surface a ten-atom cluster with three layers having 5,4,1 atoms respectively was used for the T, B, and wide (W) bridge (between two next-nearest neighbors) sites. This was necessary to provide all 7 NN to the central Ni atom, which we adopted as our basic cluster definition. The rectangular (R) site used a similar ten-atom cluster (1,5,4) with the lone atom moved to the opposite side. The W site has 4-fold character because the layers of (110) are closer together than those of (100) and allow the possible interaction with two more Ni atoms. Similarly, the R site has 5-fold character because of the underlying "central" atom.

A ten-atom two-layer cluster with seven atoms in the top layer was used for these (111) studies. The P in the figure indicates that the three-fold (3) site was one situated over a particle (Ni atom) rather than a hole in the lattice, although the energies were very similar because the layers are fairly far apart.

The results in the figure show that multifold sites are preferred on each face. Although the energies do not quantitatively agree with the experimental value of 1.3 eV, we hope that their relative values are meaningful. The T and B site adsorption energies are less than any of those for multifold sites, and they are independent of the Ni face. Thus, the "roughness" of a surface is indicated by the stability of its characteristic multifold site(s). These calculations predict (111) to be the "smoothest". The preferred multifold site in each case agrees with the empirical theory that adsorption should occur at the site which would be occupied by a Ni atom if the lattice were extended.

High Coverage Studies

The Ni cluster used for the (100) studies at high coverage consisted of a single layer of nine atoms arranged in a 3 x 3 square. The model of the CO overlayer was based on the LEED studies of Tracy[1]. The compressed hexagonal structure was represented by a triangle of three CO molecules. The distance of approach of each CO was specified by a linear fit to the optimum distances determined in the low coverage studies. Calculations were performed which corresponded to θ=3/5 for six translational positions of the overlayer relative to the Ni surface. The CO's were moved as little as possible, in order to minimize edge effects. In some cases, two calculations were done and their energies were averaged to obtain a representative energy. Because the hexagonal packing of the overlayer results in misregistration with the substrate, the resultant calculated energies for these clusters differed by only 0.2 eV. The average adsorption energy per CO molecule was 1.6 eV, which might be reduced further if the correct number of neighboring CO's could be modelled.

Studies were also done on (100) for θ=2/3 at three positions. This degree of compression of the hexagonal pattern reduces the misregistration. The variance here was slightly more, 0.3 eV, and the adsorption energy hardly changed. The model with "hybrid" (i.e., half-way between) T/B and B/4 sites was slightly preferred over the B-and-T/4 or the 4-T-and-T/4 combinations.

For Ni (110) we used model clusters consisting of ten Ni atoms in two layers and 2 CO molecules. At 100% coverage on Ni ('10) there are two registered coverage geometries consistent with the LEED structure determined in Ref. 9; one involving equal numbers of B and R sites and the other involving T and W sites. We also did calculations for three intermediate orientations. The B&R position was predicted to be the most stable. The adsorption energy was 1.5 eV per CO, and the least favorable cluster we tried (one of the intermediate ones) was almost 4 eV less stable. Thus, the (110) surface is not very smooth.

The rotated hexagonal coverage structure [12] for CO on Ni (111) also has two likely geometric possibilities. One has mostly B sites with some T sites in the ratio B_3T, and the other has mostly hybrid T/3 sites with some 3-fold sites, $T'_3 3$. Our model cluster consisted of a single layer of eight Ni atoms and 4 CO′s. We found the B_3T orientation to be preferred by 0.7 eV, in agreement with Ref. 13. The adsorption energy was 1.3 eV per CO molecule. It should be noted that using more CO′s in the model increases the number of CO-CO interactions, thereby tending to decrease the calculated adsorption energy.

Higher Coverage Studies

Since $Ni(CO)_4$ is only formed at very high coverages and it is not known whether the reaction involves adosrbed species alone or with impinging gaseous molecules, we designed studies to examine the energetics of CO approaching an already covered surface. Because the pattern of CO adsorption on the primary surfaces of Ni is hexagonal, or nearly so, the cluster models we used consisted of a single Ni layer, three CO′s situated in a preferred orientation, and a fourth CO "approaching". The X-Y position of the fourth CO was initially presumed to be centered on the original three CO′s. All of the calculations on clusters of this form were mostly repulsive (even though the "standard" orbital exponents in Table 1 were used and would have given rise to less repulsion than the fitted ones) so the X-Y positions were subsequently optimized. Composites of the cluster geometries used are illustrated in Figure 2. Separate calculations were done for each arrangement of the three "original" CO's (indicated by circles connected by lines) in order to investigate the possible "landing sites" for the fourth CO (indicated by a dashed circle) on each surface. Nickel atoms are indicated by small black dots, except for the second layer atoms required in the (110) calculations, which are indicated by small circles. Terminally adsorbed CO appears as a concentric circle about a dot; see (111). The concentric circles on (110) represent CO at an R site. Shaded bonds indicate interactions which might be important in the $Ni(CO)_4$ reaction. These studies suggest that either NiCO or $Ni(CO)_2$ might be involved. However, particularly for (100) since several arrangements were almost equally preferable, other arrrangements not investigated here could be possible.

Figure 3 shows the energy as a function of the Z-coordinate of the approaching CO molecule. For (110), Z=0 corresponds to the upper layer. It should be noted that the original three CO molecules were not allowed to relax during this process. The solid curves shown are for each of the more favorable alternatives given in Figure 2, and they are labelled by the site being approached by the incoming CO for each surface. Both curves for (110) have been shown because they were so different.

Discussion

The studies we have described provide some evidence to be considered in attempting to understand the process of nickel carbonylation. In order to aid in the interpretation of the results in

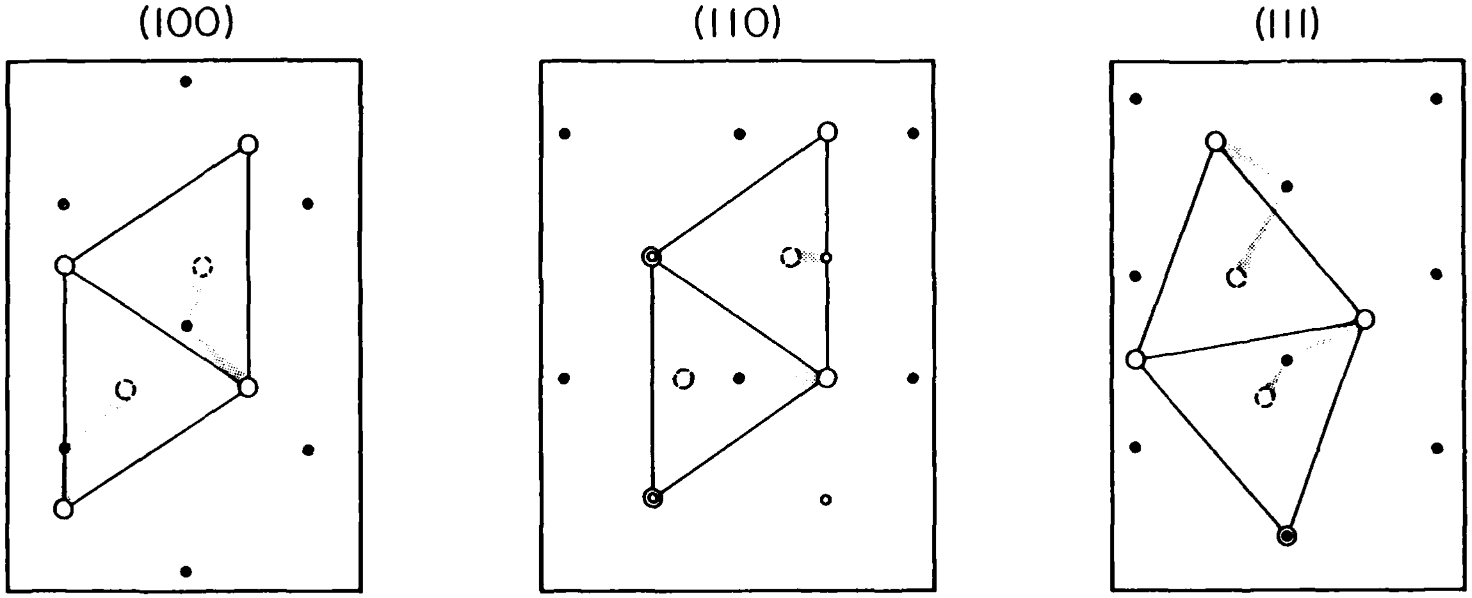

Figure 2. CO Adsorption on Ni at High Coverage

Ref. 16 we did a few simple calculations that supported the assumption that Ni atoms in lower coordinated sites (imperfections) are less tightly bound, although the binding energies obtained were not quantitatively correct. Thus, the rate of reaction on (110) might be the fastest since its surface atoms have only 7 NN. However, it is possible that "accessibility" of the surface atoms is important. At high coverages, we have seen that the (110) face is 100% covered, whereas the (100) and (111) faces are only approximately 67 and 57% covered. Furthermore, an impinging CO molecule would encounter a repulsive barrier which would be less likely to relax because of the greater roughness of the (110) surface (i.e., the more well-registered nature of the coverage).

Researchers have speculated that NiCO, associated with T-bonded CO, might be the critical species in $Ni(CO)_4$ formation. Although the correlation of available experimental and <u>ab-initio</u> [17] data indicates that the removal of NiCO would have an activation barrier significantly larger than that observed [15], it is still possible that the presence of T-bonded CO is important for some other (less obvious) reason. If so, the (110) surface would be at a disadvantage because its predicted preferred high coverage geometry does not involve T sites. It might also be at a disadvantage if an impinging mechanism were involved because of the barrier described above and, furthermore, half of its "higher coverage landing sites" (i.e., the dashed circles in Fig. 2) are directed toward a lower layer Ni atom (which would presumably be less likely to react because of its binding to 11 NN). However, if more than a single CO were required, the (110) surface would seem to be at an advantage because of its already high coverage ratio and the $Ni(CO)_2$ interaction (indicated in Fig. 2)

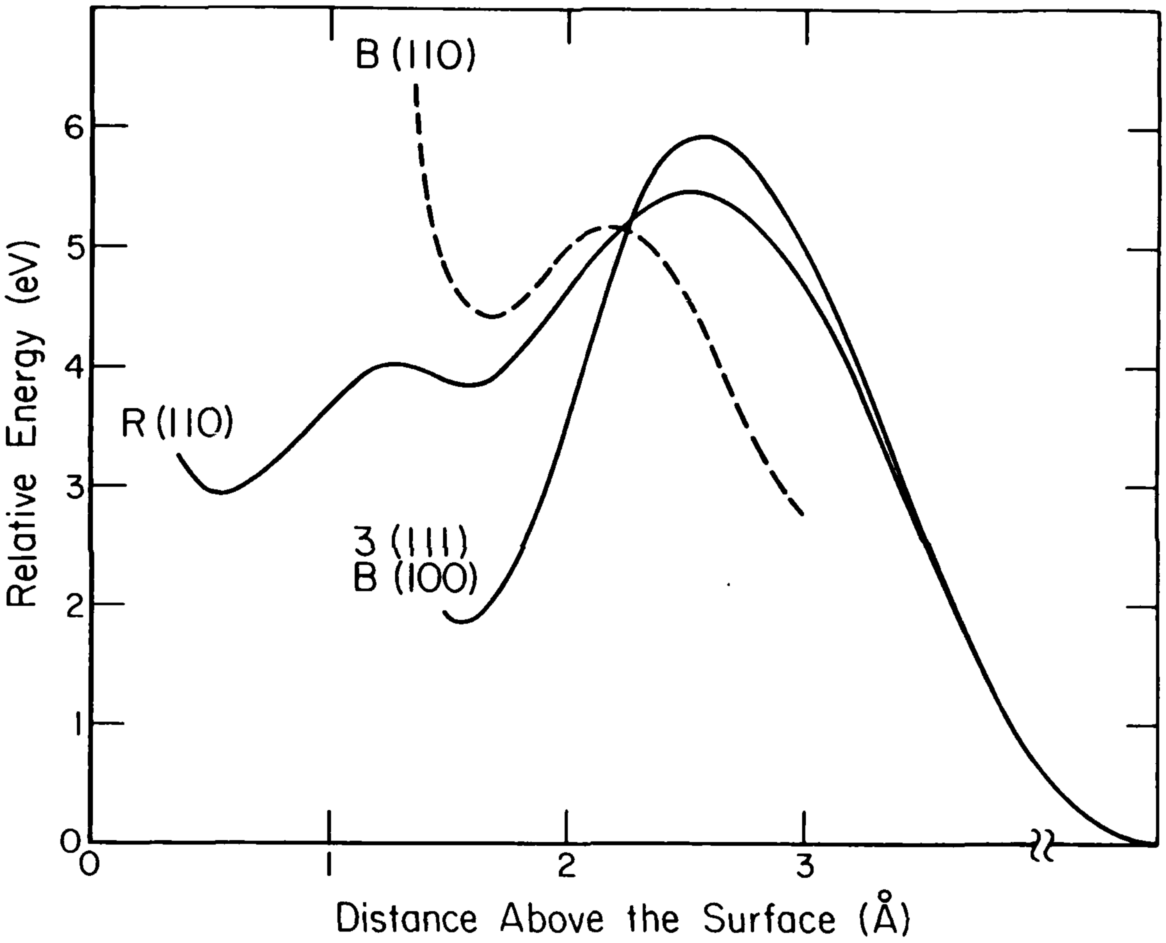

Figure 3. Approach of CO to an Already Covered Ni Surface

involving a Ni atom with only 7 NN, although the barrier might still be a problem.

On the other hand, the predicted (111) surface coverage at high levels includes some T-bonded CO, as well as some possibilities for $Ni(CO)_2$ interactions. The geometry investigated for (100) also has some $Ni(CO)_2$ possibilities, and configurations allowing T-bonding might be easily accessible energetically. The barrier toward incoming CO molecules should be more easily relaxed for either of the latter surfaces because of their enhanced smoothness at high coverages.

In general, we have been able to find several ways in which the (110) surface differs from the (100) and (111) surfaces. However, the latter two seem fairly similar.

Acknowledgements

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Semi-Empirical Studies of CO Adsorption on (100) Faces of Ni/Cu Alloys

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Abstract

Semi-empirical calculations using the modified Huckel method of Anderson have been performed for 30 nine-atom Ni/Cu clusters. Ensemble and ligand effects on the magnetic character of the clusters and on the adsorption of CO at terminal and 4-fold sites have been examined. The presence of Cu is found to decrease the magnetization of Ni terminal sites and to degrade the multifold adsorption sites.

Introduction

Metal catalysts are critical components of many commercial and technological processes. The characteristics of metals responsible for their catalytic properties and the details of the mechanisms involved are still the subject of many experimental and theoretical investigations.[1] Some processes, such as the formation of nickel tetracarbonyl, have been found experimentally to exhibit magnetic-phase-dependent activation energies.[2] The origin of this so-called Hedvall effect is uncertain, as is the determination of the surface species involved and the reaction mechanism. This reaction has also been studied for Ni/Cu alloys, for which the Curie temperature can be varied over a convenient range. In order to better understand these reactions, we have undertaken a semi-empirical investigation of the magnetic effects in CO adsorption on Ni/Cu alloys.

Ni/Cu alloys have been the subject of a number of investigations. Although they should be potentially useful for studying magnetic effects, in practice a variety of phenomena which complicate the interpretation of the experiments are encountered. First, Cu atoms migrate to the surface at a visible rate, even at room temperature[3,4]. Furthermore, there is a definite possibility of clustering of like atoms [5,6]. It has even been suggested [3] that the determination of the Curie temperature might be uncertain; in particular, that it might be different for thin films than for macrocrystals. Surface conditions and alloy composition are known variables when theoretical methods are employed.

Calculations using the modified Huckel method of Anderson [7] have been carried out for 30 nine-atom Ni/Cu clusters, from pure Ni to pure Cu. We examine changes in the magnetic moment of the bare surface model cluster as evidenced by a population analysis and changes in the adsorption energy of CO at various sites on the cluster while varying the Cu content and geometrical arrangement. The cluster geometry used was a model of (100) nickel consisting of a 5-atom layer in a "domino" pattern and a 4-atom layer providing nearest neighbors (NN) to the central atom of the first layer. This model could be used to study terminal (T) and 4-fold (4) adsorption sites by approaching the appropriate layer. It provided all eight NN for the T site surface atom. Of course it was less adequate in this regard for the 4-fold site atoms, which each had only five NN. Since Ni/Cu alloys are solid solutions whose lattice dimensions vary with constitution by less than 0.1 Å, [8] the nickel dimension (3.52388 Å, or a NN distance of 2.49 Å) was used for all clusters, even though Cu atoms were eventually substituted for all of the Ni atoms.

The calculations for the Ni_9 cluster used a valence region occupation with six unpaired electrons. This was consistent with the experimental magnetic moment of 0.6 m_B/atom, and led to an average Mulliken population of $\underline{s}^{0.6}$ $\underline{d}^{9.4}$. Our spin convention for the alloy clusters was to pair up these valence electrons as Cu atoms were substituted for up to six Ni atoms. Beyond this point, the number of unpaired electrons was either zero or one, depending on whether the number of Cu atoms was even or odd, respectively. However, a complication arose in the straightforward application of these conventions for the Cu_8 and Cu_9 clusters. It has been documented [9] that the pi* levels of CO lie too low in energy when conventional parameters are employed in Huckel methods.[10] Occupying the lowest energy orbitals resulted in a potential energy curve for CO adsorption that separated to CO^{-4}. Our arbitrary resolution of this problem was to disallow occupation of the pi* orbitals.

Bare Cluster Calculations

The simplest study of magnetic effects is to examine the bare cluster calculations (i.e., without the presence of CO). We obtained results for 30 different clusters, shown in Table 1. Each cluster is defined by its location in the table; the 5-atom layer is given by the row heading, and the 4-atom layer by the column heading. Thus, the all-Cu cluster is in the upper-left-most block, and the all-Ni one is in the lower-right-most block. Clusters having the same Ni/Cu ration lie in blocks along diagonal lines drawn from left to right and rising (with unit slope). Table 2 provides the key to the data in Table 1. Clusters for which occupation of the pi* orbitals was explicitly disallowed are indicated in Table 1 by an asterisk in the lower right corner of their blocks. Table 1 gives a measure M of the magnetic moment defined to be ten minus the total population of the d-orbitals for each atom. Since the clusters were also used to study both T and 4-fold site adsorption of CO, M is given separately for these cluster atoms and for the average over the entire cluster.

Examination of Table 1 reveals that, indeed, the "extra" s electron on Cu does tend to fill the d-band of nickel, as had been presumed[11]. This is the only type of transfer that occurs; i.e., there is no s to s, d to d, or d to s transfer. This process takes place readily. In fact, the cluster s population drops from 0.94 electrons(e)/atom(at) to 0.68 e/at as soon as one Ni atom is present, compared to the weighted average of the pure cluster values of 0.9 e/at. It continues dropping, to less than 0.6 for 4 Ni atoms (compared to 0.77), and becomes constant at 0.54±.01 e/at for 5 to 9 Ni atoms.

The so-called "ligand" effect [12] (which we prefer to refer to as indirect or environmental) of alloying Ni with Cu is apparent in the M_{avg} and $M_T(Ni)$ values. M_{avg} is never exactly zero, even for the

TABLE 1

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            |    (Cu)    |    (Cu)    |    (Cu)    |    (Cu)    |    (Ni)    |
            |   /    \   |   /    \   |   /    \   |   /    \   |   /    \   |
            |(Cu)    (Cu)|(Cu)    (Cu)|(Ni)    (Ni)|(Ni)    (Ni)|(Ni)    (Ni)|
            |   \    /   |   \    /   |   \    /   |   \    /   |   \    /   |
            |    (Cu)    |    (Ni)    |    (Cu)    |    (Ni)    |    (Ni)    |
--------------------------------------------------------------------------------
Cu        Cu| 0.08  0.66 | 0.08  0.54 | 0.09  0.54 | 0.11  0.55 | 0.11  0.56 |
  \      /  | 0.06  0.79 | 0.08  0.71 | 0.11  0.71 | 0.14  0.71 | 0.20  0.62 |
     Cu     | 0.05  0.94 | 0.06  0.86 | 0.08  0.77 | 0.09  0.69 | 0.12  0.60 |
  /      \  |  XX    XX  |            |            | 0.26       | 0.18  0.95 |
Cu        Cu| 1.08     * |          * |          * |            | 2.58       |
--------------------------------------------------------------------------------
Cu        Cu| 0.35  0.54 | 0.38  0.65 | 0.32  0.55 | 0.38  0.55 | 0.33  0.56 |
  \      /  | 0.06  0.69 | 0.08  0.78 | 0.14  0.70 | 0.18  0.62 | 0.20  0.56 |
     Ni     | 0.08  0.68 | 0.09  0.77 | 0.09  0.70 | 0.13  0.62 | 0.14  0.54 |
  /      \  | 1.18       | 1.29       | 1.37       | 1.25       | 1.11  1.45 |
Cu        Cu|          * |          * |            | 2.35       | 2.20       |
--------------------------------------------------------------------------------
Cu        Ni| 0.10  0.55 | 0.12  0.56 | 0.11  0.56 | 0.12  0.56 | 0.11  0.57 |
  \      /  | 0.06  0.73 | 0.09  0.72 | 0.14  0.64 | 0.22  0.56 | 0.41  0.57 |
     Cu     | 0.07  0.77 | 0.09  0.69 | 0.11  0.61 | 0.13  0.53 | 0.25  0.54 |
  /      \  |            |            |            |            | 0.09       |
Ni        Cu|          * |            | 2.29       | 2.12       | 2.92       |
--------------------------------------------------------------------------------
Cu        Ni| 0.34  0.56 | 0.34  0.56 | 0.35  0.57 | 0.57  0.57 | 0.74  0.57 |
  \      /  | 0.06  0.71 | 0.10  0.63 | 0.14  0.56 | 0.31  0.56 | 0.49  0.57 |
     Ni     | 0.10  0.69 | 0.11  0.61 | 0.13  0.53 | 0.25  0.54 | 0.37  0.55 |
  /      \  | 1.29       | 1.15       | 0.99       | 1.44       | 1.51       |
Ni        Cu| 2.05       | 1.97       | 1.85       | 2.65       | 2.66       |
--------------------------------------------------------------------------------
Ni        Ni| 0.12  0.57 | 0.12  0.57 | 0.16  0.58 | 0.12  0.58 | 0.12  0.58 |
  \      /  | 0.07  0.65 | 0.07  0.57 | 0.27  0.57 | 0.51  0.58 | 0.80  0.58 |
     Cu     | 0.09  0.60 | 0.10  0.52 | 0.24  0.53 | 0.31  0.54 | 0.48  0.55 |
  /      \  |            |            |            |            | 0.29       |
Ni        Ni| 1.78       | 1.62       | 2.54       | 2.91       | 3.19       |
--------------------------------------------------------------------------------
Ni        Ni| 0.37  0.58 | 0.69  0.58 | 1.03  0.58 | 1.16  0.58 | 1.39  0.59 |
  \      /  | 0.07  0.56 | 0.14  0.56 | 0.28  0.57 | 0.48  0.57 | 0.64  0.58 |
     Ni     | 0.12  0.53 | 0.24  0.53 | 0.36  0.54 | 0.48  0.55 | 0.60  0.55 |
  /      \  | 0.89       | 1.38       | 1.48       | 1.48       | 1.55  2.15 |
Ni        Ni| 1.11       | 1.94       | 2.47       | 2.77       | 3.08       |
--------------------------------------------------------------------------------
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TABLE 2

M_T S_T

M_4 S_4

M_{avg} S_{avg}

E_T E_B

E_4

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all-Cu cluster, but it has nearly constant values along the diagonals of constant Cu/Ni ratio, and is small for all clusters with five or fewer Ni atoms. As the amount of Ni increases, M_{avg} increases, gradually at first. However, the slope of its linear dependence changes abruptly at 5 Ni atoms, or 44% Cu. This matches the point of change in slope of the average moment/atom measured and calculated by Robbins et al.[13], and has the appearance of a Hedvall effect. We note, also, that M_T(Ni) never falls below 0.32, although it is low, 0.35±.03, for all clusters with fewer than 5 Ni atoms. It also begins to increase rapidly beyond 5 Ni atoms, and its dependence is fitted fairly well by a straight line. Since our clusters do not include second NN for even the central Ni atom, we cannot address the theory of Ref. 14 regarding their effect. We expect that our results will still be useful in light of evidence that adsorptive properties are strongly influenced by local sit effects which are decoupled from the bulk[15]. In contrast to the Ni case, the M values for the Cu T site are all about 0.10±.02 and are not affected much by their cluster environment. Similarly, the Cu M_4 values in the first column are practically identical.

The direct site effects of substituting Cu for Ni can best be examined along the diagonals of constant composition. In this way the environmental ligand effects are eliminated. Under these conditions the M_4 values follow a general pattern of being larger when there are more Ni atoms in the site. This result is not surprising. When the composition varies, this effect is superimposed upon the ligand effect. We also note that the Ni M_4 values in column 5 vary considerably. Also, larger M_4 values seem to occur when the central atom of the 5-atom layer is a Cu atom. (Notice the fourth and fifth elements of the fourth row in comparison to their respective diagonally related blocks.) This may be an artifact of the finite cluster. When the Cu atom is central, its electron donation is more widely distributed because it has all eight NN; whereas corner atoms of this layer have only three, and the 4-atom layer atoms have five. Even so, these two blocks seem somewhat anomalous, as it is difficult to explain why M_4 should be larger for the Ni_8Cu cluster in row 4 than for $Ni_9$and for Ni_7Cu_2 in row 4 than for Ni_8Cu in row 5; unless it is due to finite cluster effects causing the M_T values of the last row to be so large. By this we imply that the relative lack of NN by corner and second layer atoms might cause them to all draw an unrealistic amount of electron density from the central surface atom.

Adsorption Calculations

Adsorption studies on the Ni_9 cluster predict that the 4-fold site is preferred, but that bridge (B) and terminal sites can also adsorb CO. Our Cu_9 calculations predict binding at only the 4-fold site; although there is a slight local minimum in the curve for bridge-site adsorption. The 4-fold curve for Cu exhibits an activation barrier of 0.2 eV. This feature is not observed for clusters containing Ni and, particularly in light of the occupation number difficulties mentioned earlier, may not be reliable. Additionally it is obvious that the method overestimates the adsorption energies on Ni, so that CO might not be bound on Cu when this type of error is taken into account.

Although T bonding is not preferred, examination of T site adsorption energies for various clusters allows the study of environmental effects alone. Also, the T site is of interest in regard to the formation of $Ni(CO)_4$, for it has been proposed that the presence of T site bonding, which occurs for pure Ni at high coverages when the

CO-CO repulsions force a misregistration of the CO overlayer with respect to the surface symmetry, might be crucial to the mechanism of formation. Our studies indicate that Ni T bonding is as favorable under any circumstances as Cu 4-fold bonding or hybrid bridge bonding. Therefore, one would expect to be able to conduct experimental studies with alloys such that few Ni multi-fold sites would be available (unless the formation of Ni islands[5,6] is unavoidable). Then, if the carbonyl were formed, it would indicate that NiCO is the primary intermediate in the mechanism. On the other hand, if the reaction did not proceed, it would indicate that more than an isolated Ni atom is required or that some other aspect of the high CO coverage is critical.

In general, we look for indirect effects upon 4-fold adsorption as we go down a column, or upon T-adsorption as we go across a row, of Table 1. We can also examine environmental effects on adsorption at T sites by examining alternant blocks going down a column since changes of the corner atoms are of the same class as changes in the second layer. If we examine only the last row and column of the table, a trend of adsorption energies at specific sites paralleling the M values of those sites is apparent. However, other parts of the table do not seem to follow these trends. For example, the first column has an almost constant M_4 value, but the adsorption at this site varies by a factor of two! Similarly, while the Ni M_T values for clusters with fewer than 6 Ni atoms are $0.35\pm.02$ the adsorption energies appear to range haphazardly from 0.89 to 1.37 eV. The reasons for this behavior are rather complex. They involve specific shifts in orbital energies, particularly for the valence orbitals, and the occupation numbers of these valence orbitals.

We do not attribute this variation in $E_4(Cu)$ to an environmental effect since M_{avg} is fairly constant, if not linear, going down the column. It is not a direct site effect since the column is labelled by the site, and, furthermore, the right-most column, which would have the same site variations , displays different trends. Examination of the Ni_3Cu_6 and Ni_5Cu_4 calculations in column 1 reveals that the energies of their two highest occupied orbitals are nearly identical before adsorption (which fits in with their similar M_{avg} values) and are shifted by identical amounts with adsorption. The only difference is that these orbitals are doubly occupied for the Ni_3Cu_6 cluster and singly occupied for the Ni_5Cu_4 cluster. When weighted by the occupation numbers, these shifts account precisely for the adsorption energy in each case. Although the calculational method used is not well suited for the absolute determination of spin states, so that these occupation numbers were merely specified rather than derived, this result points out the definite possibility that localized states may play a large role in adsorption processes. Even if the Ni_5Cu_4 cluster were closed shell, its predicted adsorption energy would only be -1.2 eV. A similar but smaller fluctuation occurs in column 1 for the Ni T-site adsorption energy. The Cu T-site adsorption is negligible for those clusters checked, even for high Ni content.

It is then natural to ask why the same variations are not observed for the clusters in the fifth column. Here, with the higher spins specified for the Ni_7Cu_2 and Ni_9 clusters, the orbitals differing in occupation number are not the outermost valence ones and do not shift much upon adsorption of CO. Thus we do not see the large variations as in column 1. Also, it is interesting that the shifts of the two highest orbitals for each of these clusters are cancelled by larger shifts of the third orbital in the opposite direction. Thus the Ni 4-fold site adsorption energy does not arise from the same type of effects as the Cu 4-fold adsorption.

The previous comments were made with respect to simply counting orbitals and comparing their energies. However, a closer examination reveals considerable reordering of orbitals upon adsorption. This is a well known result of orbital interaction. When two orbitals interact, they form bonding and antibonding combinations having relatively lower and higher energies, respectively, than before interaction, but roughly equal in average energy to the original orbitals. Thus, when the orbitals under consideration are low-lying and are not split so far upon interacting that the upper one changes its occupation number, the overall effects on the total energy are small (or "nonbonding"), particularly in comparison to the magnitudes of the orbital energy shifts. However this is exactly what is happening. Thus, regardless of which scheme of orbital examination is employed, the valence occupation numbers are of critical importance. Unfortunately, since all of the orbitals shift to some degree, the final adsorption energy is the net result of many different shifts. Thus, the simple counting comparison is attractive for the cases in which it succeeds in accounting for adsorption. In other cases, we are forced to look beyond the valence orbitals. Indeed, the negative shifts of the CO orbitals do seem to be larger for the Ni 4-fold site than for the Cu (at least for the Ni_9 and Ni_3Cu_6 clusters). Overall, we conclude that indirect effects may prevail in some cases, but be overridden by electronic effects in others.

Examining Table 1 further, we may look for a direct or "ensemble" effect at 4-fold sites by going across a row. However, to try to eliminate indirect effects and the hard-to-predict electronic effects, we should compare clusters across a lower left to upper right diagonal. Then, with only one exception, our model calculations predict that the substitution of Cu atoms for Ni atoms in a 4-fold site degrades the binding energy at the site. In general, as a function of composition, the 4-fold adsorption energies range from the Cu_9 value to the Ni_9 value with considerable fluctuations (according to the presence of a central Cu atom, as previously mentioned), presumably due to electronic effects. This is in qualitative agreement with experimental work [16] done on (110) surfaces. We may also compare E_T (Ni) values along the diagonals if we select alternant block entries. In this case, we observe a consistent preference for the clusters with more Ni atoms in the second layer. Surprisingly, this trend is opposite to the trend in M_T (Ni) values for the bare cluster. However, the variation of the Ni E_T values is much less overall than the variation in M_T, in agreement with Ref. 17, to a degree. Although E_T(Ni) is largest for $Ni9$, it has a relative minimum for clusters with 5 Ni atoms, which might be associated with the Hedvall effect for nickel carbonylation. This trend would also mean that Cu migration to the surface would not only decrease the number of pure Ni sites and degrade the multifold sites, but it would enhance the adsorption energy at Ni T sites. Notice that our calculations predict for 44% Cu that $E_4(Cu) = E_T(Ni)$, presumably resulting in a surface relatively homogeneous to CO adsorption, regardless of geometry. However, this adsorption energy is less than that for any of the sites on pure Ni.

Unfortunately, examination of the M values after adsorption is not enlightening. The Mulliken population analysis is completely dominated by charge transfer to CO and yields very large M values. This result is not surprising since the Ni population in $Ni(CO)_4$ is $\underline{s}^{0.4}\underline{p}^{0.4}\underline{d}^{6.5}$. Experimental investigators are not in agreement on this subject. Some indicate a decrease in magnetization[18], while another has shown that at low temperatures CO adsorption causes a 5% increase in magnetization[19]. However, a substantial decrease in the magnetization of corner Ni atoms when CO is terminally bonded to Ni is predicted in two cases we examined. The qualitative investigation of this effect will require a more rigorous theoretical treatment of the spin and orbital moments.

Conclusion

Our calculations definitely do not support the idea that there are no differences between Cu and Ni surface atoms[20]. We predict that CO probably will not adsorb terminally to Cu, regardless of the compositional environment. We find that the Ni E_T varies (in agreement with Ref. 16, among others), but not by as much as the M_T values, and that T-adsorption on Ni might be enhanced by the presence of surface Cu. The substitution of Cu for Ni in the preferred 4-fold site on (100) degrades the adsorption energy as a direct site effect in addition to the indirect detrimental effect of increased Cu content. In general, the calculations are qualitatively consistent with much of the experimental literature[12,21].

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