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The interaction of CO with a nickel (100) surface was examined theoretically via semi-empirical calculations. The energetics of nickel clusters (of 1 to 18 atoms) interacting with 1 to 3 CO molecules were examined. A model for the high coverage regime of CO on Ni(100) was developed. Studies with this model suggested that nickel dicarbonyl might be the desorbing species initially formed in the carbonylation process. Preliminary transition state calculations of an empirical nature indicated a large activation energy requirement for formation via a nickel monocarbonyl intermediate. Bonding of a single CO (low coverage regime) was examined on (100), (110), and (111) surfaces of nickel. In general, sites allowing multiple coordination were preferred.

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KINETICS OF $Ni(CO)_4$ FORMATION

to

U.S. AIR FORCE
OFFICE OF SCIENTIFIC RESEARCH

November 26, 1980

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Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

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Columbus Laboratories
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November 26, 1980

Dr. Mike Stroscio
Air Force Office of Scientific
  Research/Physics
Bolling Air Force Base
Washington, D.C. 20332

Dear Mike:

Enclosed are six (6) copies of our final scientific report on Contract F49620-77-C-0004.

Our immediate efforts (in December) will be to straighten out some minor errors, such as the not-quite-optimal s-exponent and reparameterize the CO (I will do an *ab initio* CO dimer potential curve). Then the corrected calculations will be incorporated into a paper for publication. I do not think these changes will alter the conclusions of the report, except of course the calculated coverage limit. The corrections probably will not take long and will bring the contents of the paper closer to my usual standards of publication. I have been tied up with final reports lately, and I am looking forward to computing again soon.

Sincerely,

Lynn

Lynn T. Redmon
Research Scientist

LTR:sld

Enclosures (6)

Battelle
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201
Telephone (614) 424-6424
Telex 24-5454

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I. INTRODUCTION

The adsorption of carbon monoxide on nickel surfaces has been the subject of a number of experimental and theoretical investigations. Most of the experimental work and all of the theoretical studies have involved the low coverage regime. However, conditions in the high coverage regime (CO pressure > 5 mm) lead to the reaction of CO with the surface to form nickel carbonyl:[1]

$$Ni + 4\ CO \rightarrow Ni(CO)_4(g) \quad . \tag{1}$$

This reaction is an intermediate step in the commercial purification of nickel.[2] Furthermore, it serves as a prototype for most of the technologically important catalytic surface reactions, which typically take place under high coverage conditions. This system has the advantage that dissociative chemisorption and accumulation of product species are not primary sources of surface contamination.

One area of particular interest in the nickel carbonylation reaction, as well as other catalytic reactions, involves magnetic effects. Enhancement ("Krinchik effect") of the reaction by external magnetic fields has been reported by Soviet workers,[3,4] but has not been verified by others.[5-7] Also, a Hedvall effect (dependence of the activation energy upon the substrate's magnetic state) has been observed for this reaction.[8]

The detailed mechanism of nickel carbonyl formation has not been directly determined. Although the overall reaction is given by (1), it almost certainly does not proceed directly. There is evidence that terminally adsorbed carbonyl leads to NiCO as the first intermediate species.[9] This would presumably be followed by the reaction of CO(g):

$$Ni_{Surf} + CO \rightarrow NiCO$$

$$NiCO + 3\ CO \rightarrow Ni(CO)_4 \quad . \qquad (2)$$

However, other mechanisms are possible, such as

$$Ni_{Surf}(CO)_{ads} + CO \rightarrow Ni(CO)_2$$

$$Ni_{Surf}(CO)_2 + 2\ CO \rightarrow Ni(CO)_4 \qquad (3)$$

The fact that these reactions only occur under high coverage conditions limits the sophistication of theoretical treatments. For this reason it is not now feasible to address the magnetic state problems which would require a precise treatment of spin and electron correlation. We instead have conducted the first theoretical examination of the high coverage regime of CO adsorption on nickel in order to gain insight into determining the species leaving the surface and details of the reaction mechanism.

II. DISCUSSION OF THE ELECTRONIC STRUCTURE METHOD

In problems such as the one involving many transition-metal atoms and CO molecules, the application of the usual first-principles methods of molecular quantum mechanics becomes impracticable. The large number of basis functions, N, required in this case results in a numerical problem of such a magnitude, $O(N^4)$, that it exceeds present computer capacity. In these cases one must resort to more approximate methods which, while practical, retain the prospects of yielding a realistic physical description.

One approach which has been quite actively applied to electronic structure problems of this magnitude is the approach of Anderson.(10,11) This is a semi-empirical method which combines Hellmann-Feynman electrostatic forces and molecular one-electron orbital energies to construct an estimate of the total electronic energy of a system. This method has been applied to the study of the structures of clusters of transition-metal atoms,(12) to the study of chemisorbed molecules on surfaces,(11,13) and to the study of organometallic molecules.(14)

Procedurally the method of Anderson has two steps. The first step is the calculation of pair-wise repulsive energies among the atoms

$$E_R = \sum_{A>B}\sum \left(\frac{Z_A Z_B}{|\underset{\sim}{R}_A - \underset{\sim}{R}_B|} - Z_B \int \frac{\rho_A(\underset{\sim}{r})}{|\underset{\sim}{r} - \underset{\sim}{R}_B|} \, d\underset{\sim}{r} \right)$$

where ρ_A is the electronic charge density of atom A, Z_B is the charge of the nucleus of atom B, and $\underset{\sim}{R}_A$ is the position vector of atom A. The second step is the calculation of molecular one-electron energy levels by solution, in an atomic orbital basis, of the matrix wave equation

$$\sum_{j=1}^{N} (H_{ij}-\varepsilon_k S_{ij})\, C_{j,k} = 0 \qquad i = 1,\ldots,N; \qquad k = 1,\ldots,n \leq N$$

In this secular equation, the ε_k's are the molecular orbital energies, the S_{ij}'s are the overlap matrix-elements between two atomic orbitals, and the H_{ij}'s are the interaction matrix-elements between two atomic orbitals. Anderson defines the diagonal elements by

$$H_{ii} = -I_i$$

and the off-diagonal (two-center) elements by

$$H_{ij} = \frac{1}{2}k\ (I_i+I_j)\ S_{ij}$$

where I_i is the experimental atomic ionization potential corresponding to removal from an atom of an electron in the i-th atomic orbital. The factor k has usually been taken as 2.25 exp(-0.13 D) where D is the distance between the two atoms.

The final step in Anderson's method is to use the molecular energy levels, ε_k, to construct the energy term

$$E_D = \sum_{k=1}^{n} \rho_k\ \varepsilon_k$$

where ρ_k is the occupation number of the k'th molecular one-electron energy level. This energy tends to be an attractive energy as the atoms approach each other. It is combined with the previously defined repulsive energy, E_R, to obtain Anderson's estimate of the total electronic energy, i.e.,

$$E = E_R + E_D$$

The application of this method to large molecules has been shown to yield useful predictions of structure, force constants, and relative bond strengths.(11,15) There is thus some empirical basis for its validity. The evidence of its validity on purely theoretical grounds has been sparser. Anderson explains the physical reasoning motivating his approach as follows:(16) One first envisions constructing the molecule by superposing rigid atoms. This results in E_R by neglecting in the Hellmann-Feynman force-formulae all terms in the exact one-electron density not arising from the superposition of atomic densities, and integrating the remaining force terms. The physical effect which has been neglected in the first step, according to Anderson, is the effect on the energy due to the "tunneling" of the electron from one atom to the next. This effect, as is well known, is expressed in the off-diagonal Hamiltonian matrix-elements, H_{ij}, connecting basis states describing electrons moving about alternative nuclei. This is the source for the binding force between atoms,(15) and is also often referred to as the "delocalization" energy in chemistry. In the second step of the method, Anderson then identifies the delocalization energy contribution to the total energy as the net energy lowering in the orbital energies obtained by solving the secular equation. This is subjected to the additional simplifying assumption that, for this purpose, field effects due to neighboring atoms may be neglected.

A comparison of Anderson's method with the standard approaches is very difficult and complex. There are a few simple examples, however, for which some contact can be made with the more conventional approximations. Consider the case of the H_2^+ molecular ion. This is a one-electron system.

Let us consider just two basis states. Each basis state consists of two protons and one electron moving about one or the other proton, i.e.

$$|1\rangle = N \exp(-|\mathbf{r}-\mathbf{R}_A|)$$

$$|2\rangle = N \exp(-|\mathbf{r}-\mathbf{R}_B|$$

where N is a suitable normalization factor. The secular equation is

$$\begin{pmatrix} H_{11}-\varepsilon S_{11} & H_{12}-\varepsilon S_{12} \\ H_{21}-\varepsilon S_{21} & H_{22}-\varepsilon S_{22} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = 0$$

In this case $S_{11} = S_{22} = 1$, $H_{12} = H_{21}$, $H_{11} = H_{22}$. The lower energy is

$$\varepsilon = \frac{1}{(1+S_{12})} (H_{11}+H_{12})$$

The Hamiltonian operator in this example is

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{|\mathbf{r}-\mathbf{R}_A|} - \frac{1}{|\mathbf{r}-\mathbf{R}_B|} + \frac{1}{|\mathbf{R}_A-\mathbf{R}_B|}$$

with the property that

$$\hat{H}|1\rangle = -I|1\rangle$$

$$\hat{H}|2\rangle = -I|2\rangle$$

where $I = -13.6$ eV is the first ionization potential of H atom. It follows that

$$H_{11} = -I + \langle 1| \frac{-1}{|\mathbf{r}-\mathbf{R}_B|} + \frac{1}{|\mathbf{R}_A-\mathbf{R}_B|} |1\rangle$$

The second term is indeed the E_R term in Anderson's approach. Therefore we write

$$H_{11} = -I + E_R$$

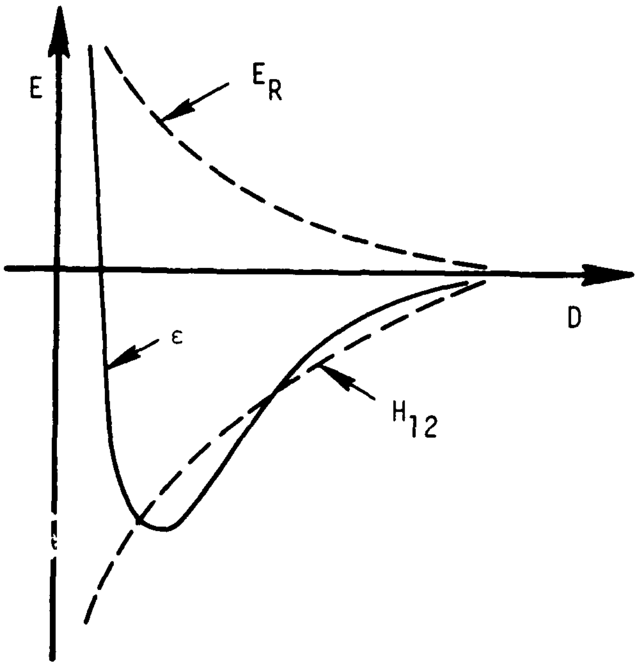
In reducing E_R one finds

$$E_R = \int_D^{\infty} \rho(r) \left(\frac{1}{D} - \frac{1}{r}\right) r^2 dr$$

where $D = |\underset{\sim}{R}_A - \underset{\sim}{R}_B|$. This shows that $E_R \geq 0$ and is thus indeed always a repulsive energy term. The off-diagonal term is

$$H_{12} = -I\,S_{12} + \left\langle 1 \left| \frac{-1}{|\underset{\sim}{r} - \underset{\sim}{R}_B|} + \frac{1}{|\underset{\sim}{R}_A - \underset{\sim}{R}_B|} \right| 2 \right\rangle$$

Since H_{12} is exponentially dependent on the distance between the atoms, one can see that H_{12} will give a progressively attractive energy lowering which we identify as the source of binding energy. Schematically the variation of these energy terms with interatomic distance, D, is



Anderson's energy expression in this case would have been

$$\varepsilon = E_R + \frac{1}{(1+S_{12})}(\bar{H}_{11}+\bar{H}_{12})$$

where

$$\bar{H}_{11} = -I$$

$$\bar{H}_{12} = -I\, S_{12}$$

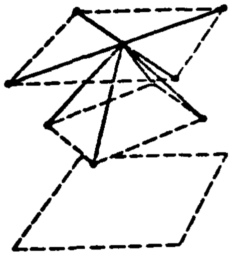
One can see that this is almost identical to the variational result. The approximation lies in the approximate relation

$$\langle 1|\frac{-1}{|\underset{\sim}{r}-\underset{\sim}{R}_B|} + \frac{1}{|\underset{\sim}{R}_A-\underset{\sim}{R}_B|}|2\rangle \cong E_R\, S_{12}$$

This shows that at least in a simple case one can discern, among the energy terms of a more conventional approximation, the physical effects which underlie Anderson's method, and that they do take on approximately the form he postulates.

III. CO ADSORPTION ON Ni(100) AT LOW COVERAGE

Our first studies examined the binding of nickel atoms in the (100) crystal face. A nine atom cluster was chosen for this study:



With this structure, the central upper layer nickel atom modeled a typical surface atom complete with its eight nearest neighbors.

Because the orbital occupation on a nickel atom in the solid is approximately d^9s the repulsions between atoms can be modified by changing the s-orbital exponent.(18) Since one of the energies of interest is the energy to remove a single surface nickel atom, the s-orbital exponent was adjusted so that the equilibrium position of the central upper layer nickel atom (as it was moved up or down with all other atoms fixed) lay in the plane with the other four upper layer atoms. The same exponent was used for all nine atoms. Figure 1 shows this procedure. With an exponent of ≥ 2.2, the repulsions are too small and the central atom contracts below the surface. Conversely, at 1.9, the atom pops out of the surface plane. A value of 1.97 was found to be nearly optimal.[†] The binding energy for removing the central nickel atom ($Ni_9 \rightarrow Ni_8 + Ni$) was found to be 0.5 eV. This does not agree well with the experimental bulk value of 5.6 eV. This problem is

---

[†] An error in tabulation led us to believe that this value was closer to the optimum than 2.0. Either of these values is reasonable, but the final result may be slightly ≥ 2. This point will be corrected in future studies. It should be noted that the difference in binding energies calculated with 1.97 and 2.0 is only .03 eV. See also the results in Section VI.

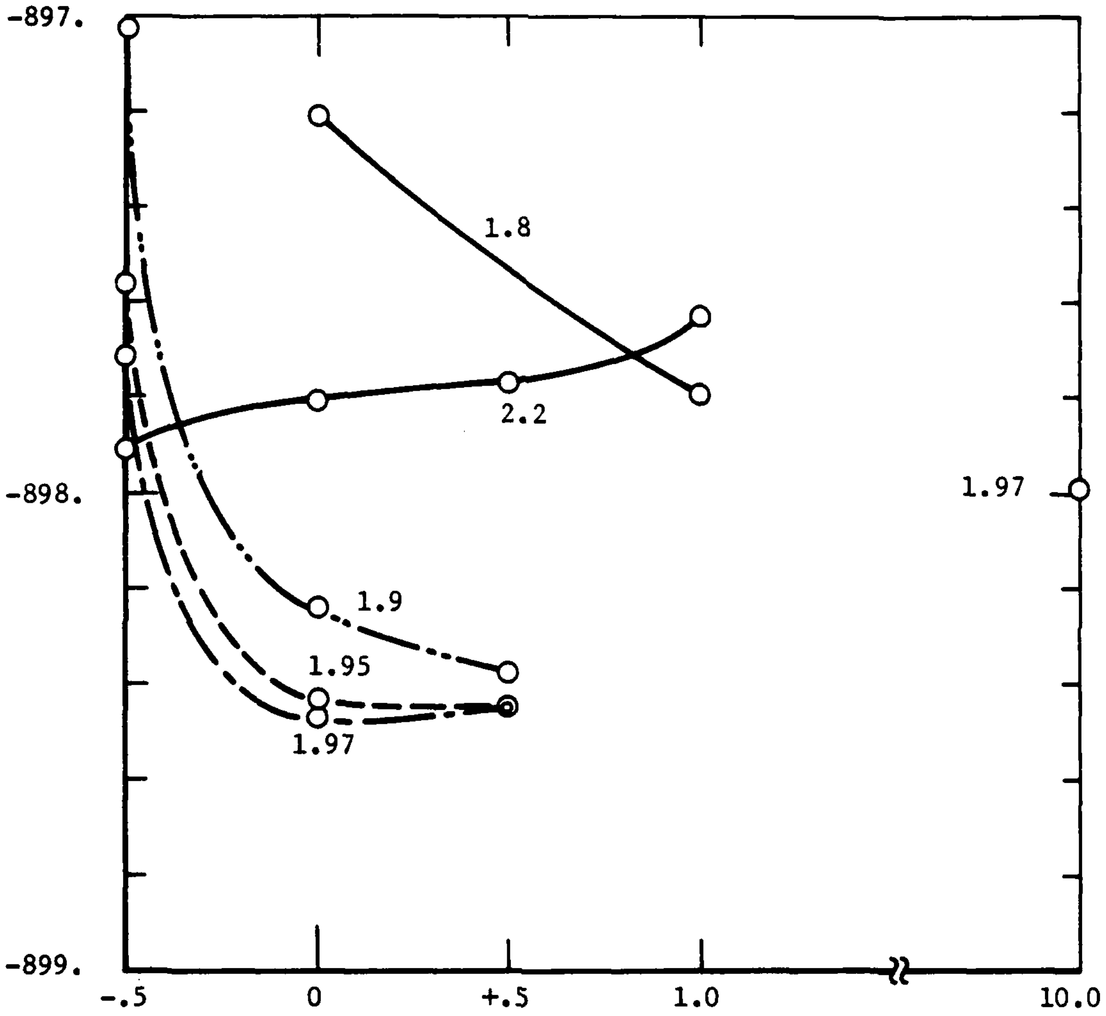


Figure 1. Surface Atom Equilibrium Position as a Function of the Nickel s-Orbital Exponent.

partly linked to problems in parameterization and in occupation numbers. In generating the potential curve the d-orbital energy was kept fixed at the bulk value -10.00 eV. Since the s-orbital energy was -7.63 eV, this resulted in a d^{10} nickel atom (with total energy -100 eV) being removed. If the gas phase nickel parameters were used for the single atom, its total energy would be only -77 eV, a difference of 23 eV! Thus, even switching parameters smoothly along the curve would not lead to a reasonable result. This problem is less noticeable in the removal of bonded species where orbital mixing occurs or the d^{10} configuration becomes plausible. For example, the tetrahedral geometry of $Ni(CO)_4$ can be interpreted as nickel in a d^{10} configuration with its vacant s and p orbitals sp^3 (tetrahedrally) hybridized to participate in bonding to the CO lone pairs. However, the binding energy is known, both theoretically[18] and experimentally[19], to be a function of the cluster size. Thus, it is not surprising that the nine atom calculation does not yield the bulk value.

Standard parameters were used for C and O. The set of parameters is given in Table 1. The bond length for CO was never varied. A value of 1.15 Å was used. For the nickel surfaces a nearest neighbor distance of 2.4918 Å (lattice edge = 3.52388 Å) was employed throughout.

Using these parameters and bond lengths, the adsorption of CO at various sites on the (100) surface was examined. (See the left-hand part of Figure 2.*) The optimal height above the surface was determined for each site. The curves in the figure are plotted as a function of the resultant

---

* Figure 2 will be discussed further in Section V.

Table 1. Orbital Exponents and Energies

	Orbital	Exp	ε(eV)
Ni	4s	1.97	-7.63
	4p	1.5	-4.00
	3d[*]	5.75	-10.00
	"	2.0	
C	2s	1.61	-16.6
	2p	1.57	-11.3, -11.2[†]
O	2s	2.25	-28.5
	2p	2.23	-13.6

[*] Contraction coefficients were 0.5683 and 0.62922

[†] Inadvertently, a value of -11.2 eV was used for the low coverage (100) studies. This oversight was corrected in subsequent calculations.

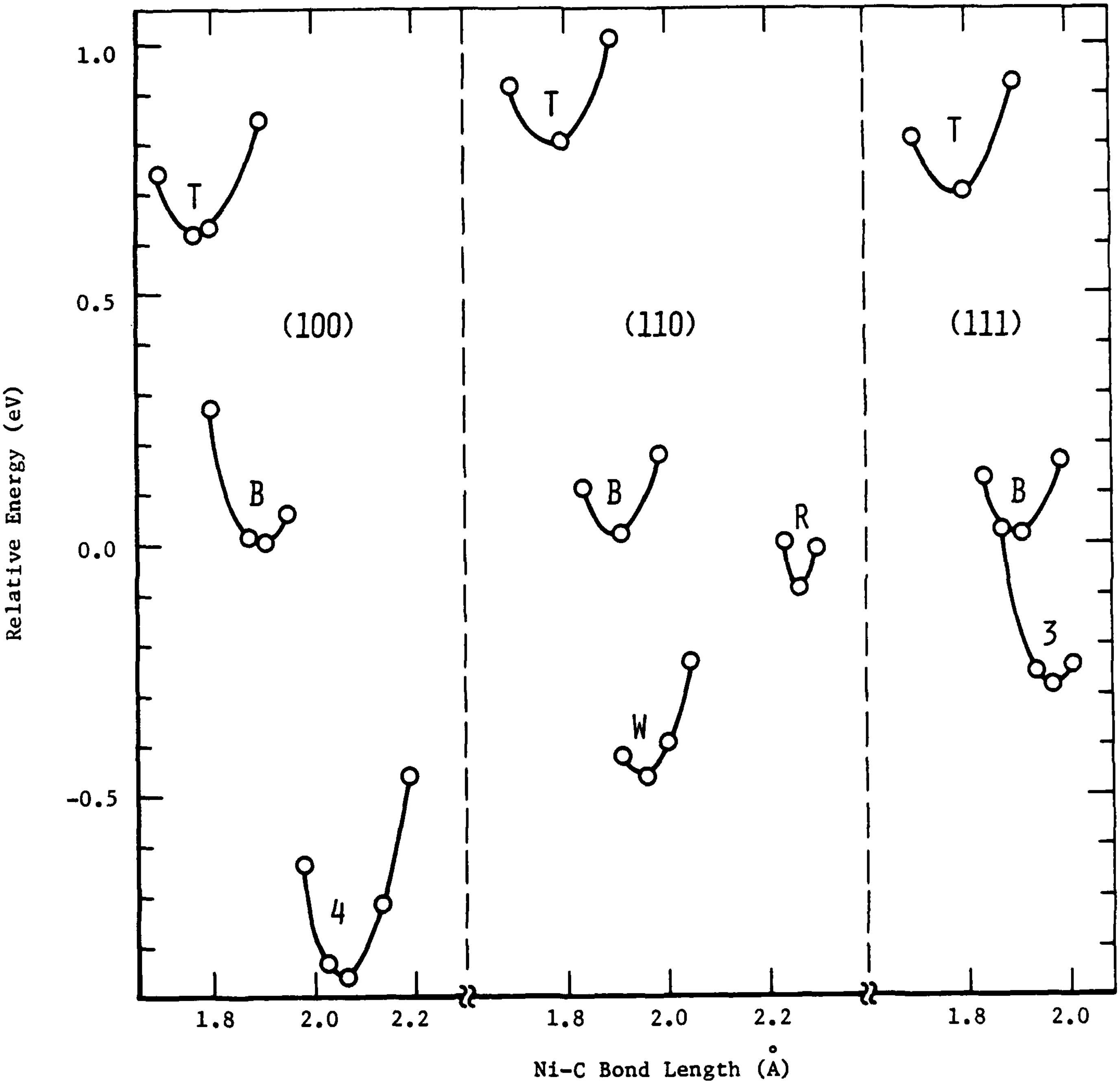


Figure 2. CO Adsorption Equilibria at Low Coverage.

Ni-C bond length(s). Even though the CO comes down to only 1.1 Å above the nickel surface for the 4-fold site, it still has the longest Ni-C bond lengths, 2.06 Å. The 4-fold site for the chosen 9 atom cluster was modeled by CO approaching from the underside. The bridge site used here was one of the ones on the top side. These optimizations were necessary because keeping the CO at a constant distance from the surface favors one site over the others.

The net energy (ΔH) required for the removal of a surface atom (from the same nickel cluster) by a terminally adsorbed carbonyl molecule ($Ni_9CO \rightarrow Ni_8 + NiCO$) was calculated to be $\sim$ 1.1 eV.

Using the same parameters, we conducted a series of calculations of the total energies (stabilities) of $Ni(CO)_n$ for n = 1-4. All spin configurations used were closed shell. The Ni-C bond length used was that of nickel carbonyl, 1.87 Å. The geometries for n = 2 and 3 were those of a similar study using the X_α method(20). Our results are shown in Table 2. These values are required for the energetic analyses in Section IV-D. They show $Ni(CO)_4$ to be the most stable, with stability decreasing as the number of bonded CO's decreases (in contrast to the X_α calculations). This seems only natural since the final product of reaction (1) is the tetracarbonyl.

Table 2. Binding Energies of Nickel Carbonyl Species

Species	Total Energy (eV)	Binding (eV)[†]	Binding/CO	ΔB
Ni + CO	-278.182	--	--	--
Ni(CO)	-279.996	1.814	1.814 eV	1.814
$Ni(CO)_2$	-459.651	3.287	1.644	1.473
$Ni(CO)_3$	-639.509	4.963	1.654	1.676
$Ni(CO)_4$	-819.105	6.377	1.594	1.414

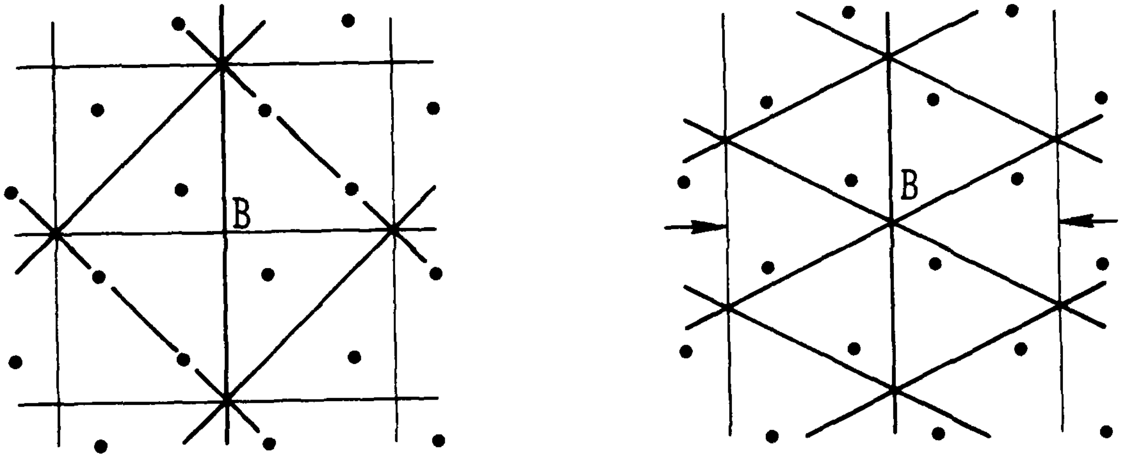
[†] relative to Ni + nCO

IV. CO ADSORPTION ON Ni(100) AT HIGH COVERAGE

A. Geometry Model

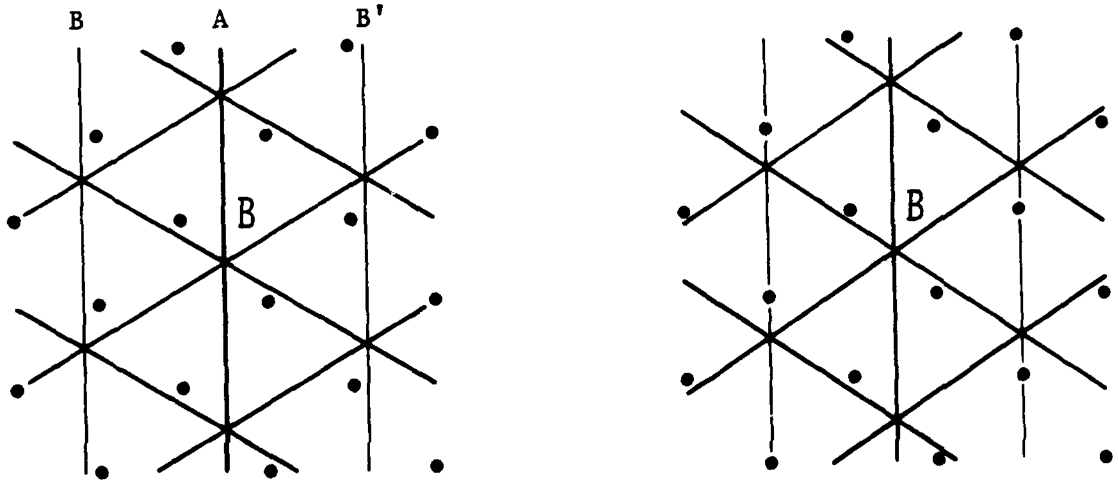
LEED studies of carbon monoxide adsorption on nickel (100)(21) have determined that for coverages (θ) up to 50% the adsorbing molecules form a simple C_{2x2} arrangement (Figure 3a). By $\theta = .61$ the adsorbed layer has shifted to a hexagonal pattern which is compressed by $\sim$ 3% (Figure 3c). The maximum compression observed corresponds to a coverage of 0.69 monolayers (which is equivalent to 1.10×10^{15} molecules/cm^2). For intermediate coverages (50-60%) some disorder was indicated.

With these facts in mind, a model for high coverage was devised. Figure 3 illustrates the relation between the symmetries of the substrate and overlayer. The LEED studies do not determine whether the C_{2x2} overlayer structure (Figure 3a) should be registered over terminal, bridge (shown), or four-fold bonding sites. The intersections of the lines indicate CO molecules, and nickel atoms are indicated by dots. Our studies on Ni_9CO indicate that location at the four-fold sites is preferable. The elongated hexagonal pattern in Figure 3b is obtained by shifting the CO positions in every other column of 3a by ± 1.762 Å. If this pattern is then compressed horizontally (see arrows) by one nickel column in every six, the 60% coverage pattern in (c) results. This structure is compressed by about 5% from a regular hexagon. When the compression is one of every four columns of nickel atoms, the resultant coverage is 67%. These two coverage levels are close enough to the critical coverages found experimentally to suggest that the periodic registration which defines the models (despite their general misregistered character) is significant, and that the models are reasonable.



a) $B\text{-}C_{2x2}$ 50%

b) B hex 50%



c) B hex 60%

d) B hex 67%

Figure 3. Models of CO Adsorption at High Coverage.

B. Results

The most sophisticated clusters for the high (60%) coverage calculations consisted of a single layer of nine nickel atoms overlaid by three CO molecules in a nearly equilateral arrangement (see Figure 4). Due to periodicity, it was not necessary to vary the x-coordinates more than 1.175 Å in the course of seeking the optimum position of the CO's relative to the substrate. This was an important factor in minimizing edge effects. In most cases, energies from two calculations (labeled by left and right) were required to obtain an energy representative of the hexagonal pattern, since the environments of adsorbed molecules in columns A and B of Figure 3c are different and there are twice as many B columns as A columns. Arrangements were labeled by the site of the central hexagonal molecule, as indicated in Figure 3. Table 3 gives the adsorption energies obtained for the terminal-bridge-, and four-fold centered arrangements and the three intermediate arrangements. In these calculations, the height of the adsorbed molecules above the nickel surface was variable. Since it was not feasible to actually optimize each z-coordinate, each was approximately optimally predetermined by a model based on the low coverage optimized distances. The contours shown in Figure 5 indicate the values used. The arrangement of concentric square contours corresponds to a 3-D description in terms of square pyramidal peaks and holes at the terminal and four-fold sites, respectively. This flexibility in the cluster model was necessary because using a fixed distance would unfairly favor certain sites over others. The results of Table 3 show that the bridge-centered arrangement was the most stable, but that due to the forced misregistration, all of the energies were fairly similar.

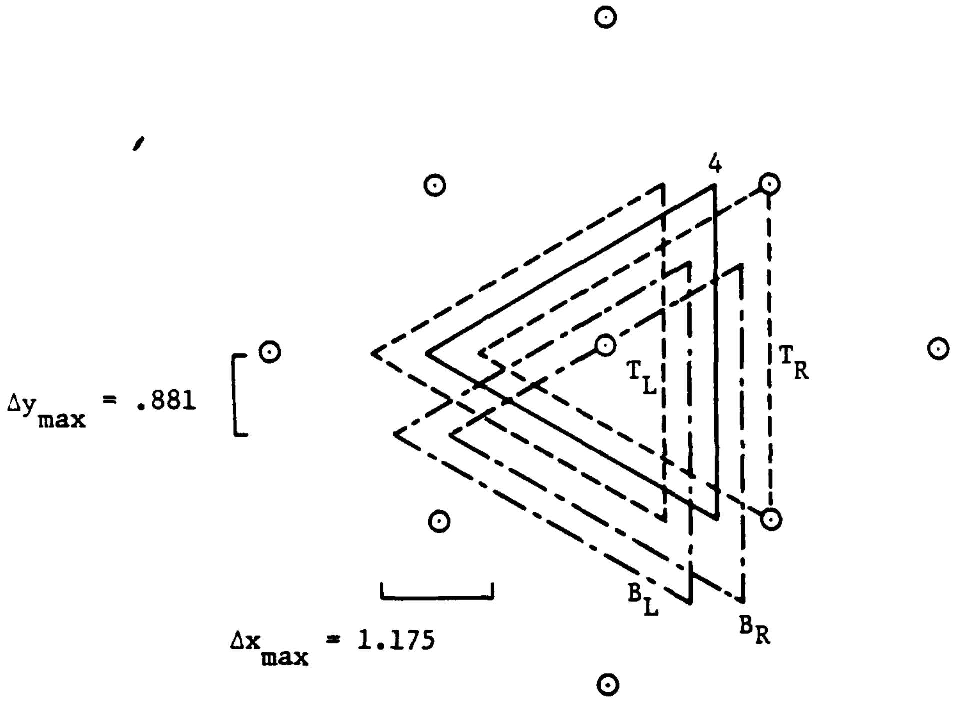


Figure 4. x- and y-Coordinates of High (60%) Coverage Model Calculations.

Table 3. Adsorption Energies of 60% Coverage Model Calculations

Location	Total Energy (eV)	Average Adsorption Energy (eV)/CO
B	-1439.783	2.82
B/4	-1439.099	2.59
4	-1438.896	2.53
4/T	-1439.474	2.72
T	-1438.959	2.55
T/B	-1439.181	2.62

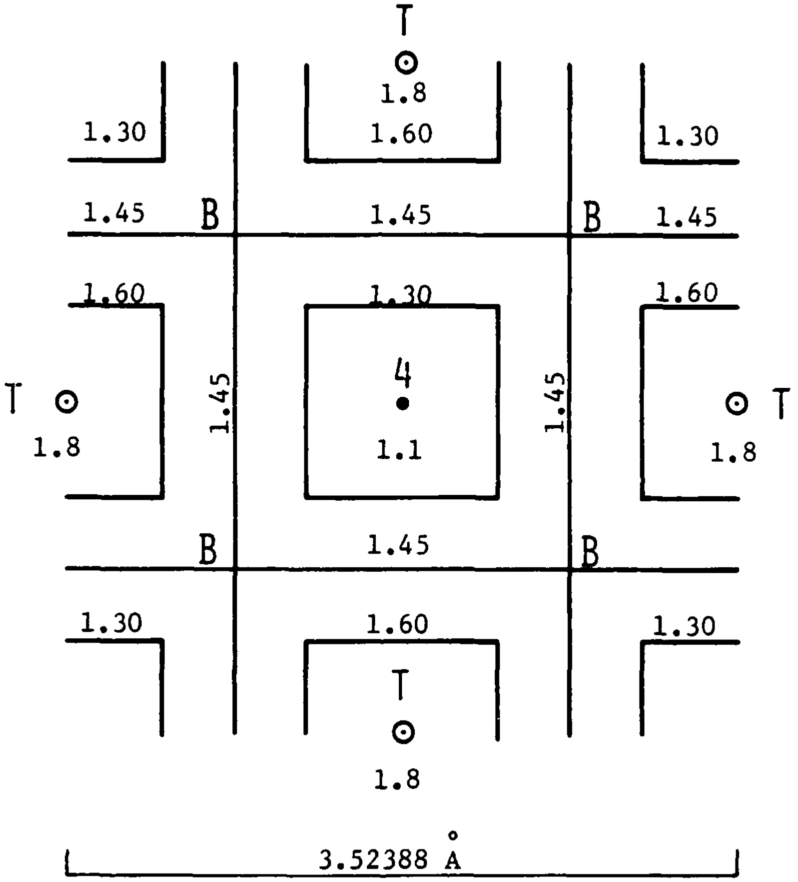


Figure 5. z-Coordinate Values for C Atom as a Function of x- and y-Coordinates Relative to Surface Nickel Sites.

The question remains as to how the coverage switches from 4-fold (centered) C_{2x2} to bridge-centered hexagonal. Suppose that Figure 3a had been drawn 4-fold centered. Then the shifting process (to obtain a hexagonal pattern) shown in (b) would have resulted in half of the adsorbed molecules being in terminal sites (which are the least favorable at low coverage). Thus rearrangement in this fashion is unlikely for energetic reasons. Of course, without compression a shift to the bridge-centered hexagonal would not occur either. The compression occurs because the stability gained by the increased number of absorptive bonds more than makes up for the decrease in binding per bond when a less optimal site is used. After the 4-fold site, the bridge site is the next best, so the result is a combination of 4-fold and bridge sites. The hexagonal pattern minimizes the intermolecular repulsions between adsorbed molecules.

C. Theoretical Coverage Limit

In principle, it should be possible to estimate the absolute coverage ratio theoretically. Some complications do arise from the use of a finite cluster model, however. Consider that for an infinite number of CO molecules in a two-dimensional hexagonal arrangement, the number of nearest neighbor interactions per molecule is three. However, our three-molecule model has only one per molecule. A seven-molecule cluster would still have less than two. Thus, the proper amount of repulsion for the infinite (macroscopic or experimental) case is not closely modeled by small clusters. This would lead to an overestimate of stability.

When the nickel substrate is truncated, the cluster is left with "dangling bonds", i.e., the nickels are coordinated by fewer nearest neighbors than usual. This applies to truncation in all three dimensions (±x, ±y, and -z, excepting, of course, the intended surface). This might also enhance the coverage calculation by overestimating the binding energy per CO molecule. Thus, unless adjustments are made, the theoretical coverage value will probably be an upper limit. However, since the interpretation of LEED data is often subject to discrepancies of a factor of two, a theoretical bound, even an approximate one, would be of interest.

Since the favored geometry at 60% coverage was the "bridge centered" one we start from that point. The study consisted of (arbitrarily) further compressing the lateral dimension (separation) of the CO's, starting from a sheet of nine nickel atoms and three CO molecules. The energies for coverages of 50%, 60%, 67%, and 100% were computed. The 67% geometry was included because it was a *symmetric point and* it was near the experimental absolute coverage value. The stability is calculated by determining the binding energy per CO molecule and multiplying it by the coverage (shown in column 3 of Table 4). Its units are therefore eV per nickel atom, and the predicted absolute coverage corresponds to the maximum in the stability. These calculations found the 100% case to be the most stable! Further examination revealed that the intermolecular repulsions between neighboring CO's were entirely too small, so that even trying to compensate for the missing nearest neighbor repulsions would be fruitless.

Therefore a correction procedure was devised. The original binding energies are given in the first column of Table 4. For the distorted hexagonal structure at the 60% coverage geometry, there are two nearest neighbors (nn) plus one almost as near. At 100% the structure will be C_{2x2} with two nn and two next nn (nnn) interactions per CO. The (nnn) analogs

Table 4. Calculated and Adjusted Stabilities as a Function of Coverage

Coverage	Binding Energy/ CO	Stability eV/Ni	Adjusted Stability eV/Ni
B-hex 50%	2.988	1.494	1.480
B-hex 60%	2.820	1.692	1.649
B-hex 67%	2.562	1.708	1.609
B-C_{2x2} 100%	2.963	2.963	0.557

in the hexagonal structure are the almost nn and a single nnn. At 50% hexagonal coverage, the pair of nn distances are actually larger than the single ("almost") nn and the nnn distance is > 7 Å. The repulsive part of the interaction potential between CO molecules (fit to experiment)(22)

$$\phi_{\text{repulsive}} = \frac{6.7829 \times 10^4 \text{ eV}}{r^{12}}$$

can be used to correct the stabilities. (The entire potential, including the attractive term,

$$\phi_{\text{attractive}} = \frac{-68.6 \text{ eV}}{r^6}$$

could be used.) The correction per CO molecule according to the appropriate neighbors described above has been calculated and weighted by the coverage to give the adjusted stability values shown in Table 4. These crude corrections indicate the absolute coverage level for the bridged models examined to be closer to 60% than 100%.

In the future, ab-initio calculations of the CO-CO interaction should be carried out to be sure that the potential above is not the result of an erroneous assumption of the coverage level. Subsequently, the CO parameters (orbital exponents) used in the semi-empirical calculations should be modified to reproduce this interaction more reliably. This reparameterization would be expected to decrease the adsorption energies, bringing them closer to agreement with experiment. It is possible that the ordering of site preference would also change.

D. Energy Analyses

It is possible to analyze certain aspects of the formation of nickel carbonyl from an energetics viewpoint. Consider a nickel surface with a given amount of CO already adsorbed upon it and an influx of additional CO

$$Ni_n(CO)_{m(\theta)} + 4\ CO \quad . \qquad (4)$$

What products are likely? Since we have calculated the average adsorption energy (per CO) at several coverages and total energies of the various nickel carbonyl species we can examine the relative energetics of several processes. Suppose we use the adjusted adsorption energies (as a function of coverage) given in Table 5. We assume that n and m are large enough that removal of one nickel or addition of carbonyl does not affect the coverage significantly. Figure 6 shows the relative energetics of some of the competing processes, as a function of coverage. To make the curves basically horizontal we do not include the energy due to addition adsorption of CO as $m(\theta)$ increases, since it involves a large quantity which all of the processes have in common. In Figure 6 we see that at low coverage, the most favorable process is further adsorption. Moreover, in contrast to nickel carbonyl formation, we expect no activation energy for this process. However, as the absolute coverage limit is approached, the energetic advantage of this product channel decreases. Eventually the limit is reached so that for every CO that adsorbs another desorbs. At this point, the most favorable product is $Ni(CO)_4$.

Unfortunately, this graph does not tell us which nickel species first desorbs. We cannot tell from it the magnitude of the probable barriers to reaction. From our calculations we can conclude that even at higher coverages there is probably not a significant barrier to additional adsorption

Table 5. Adjusted Adsorption Energies as a Function of Coverage for Bridge-Centered Model Sites

θ	ΔE(eV)
0.0	-3.12
0.5	-2.96
0.6	-2.75
0.67	-2.41
0.7	-2.0
0.75	-1.5
0.8	-0.5
>0.8	-0.0

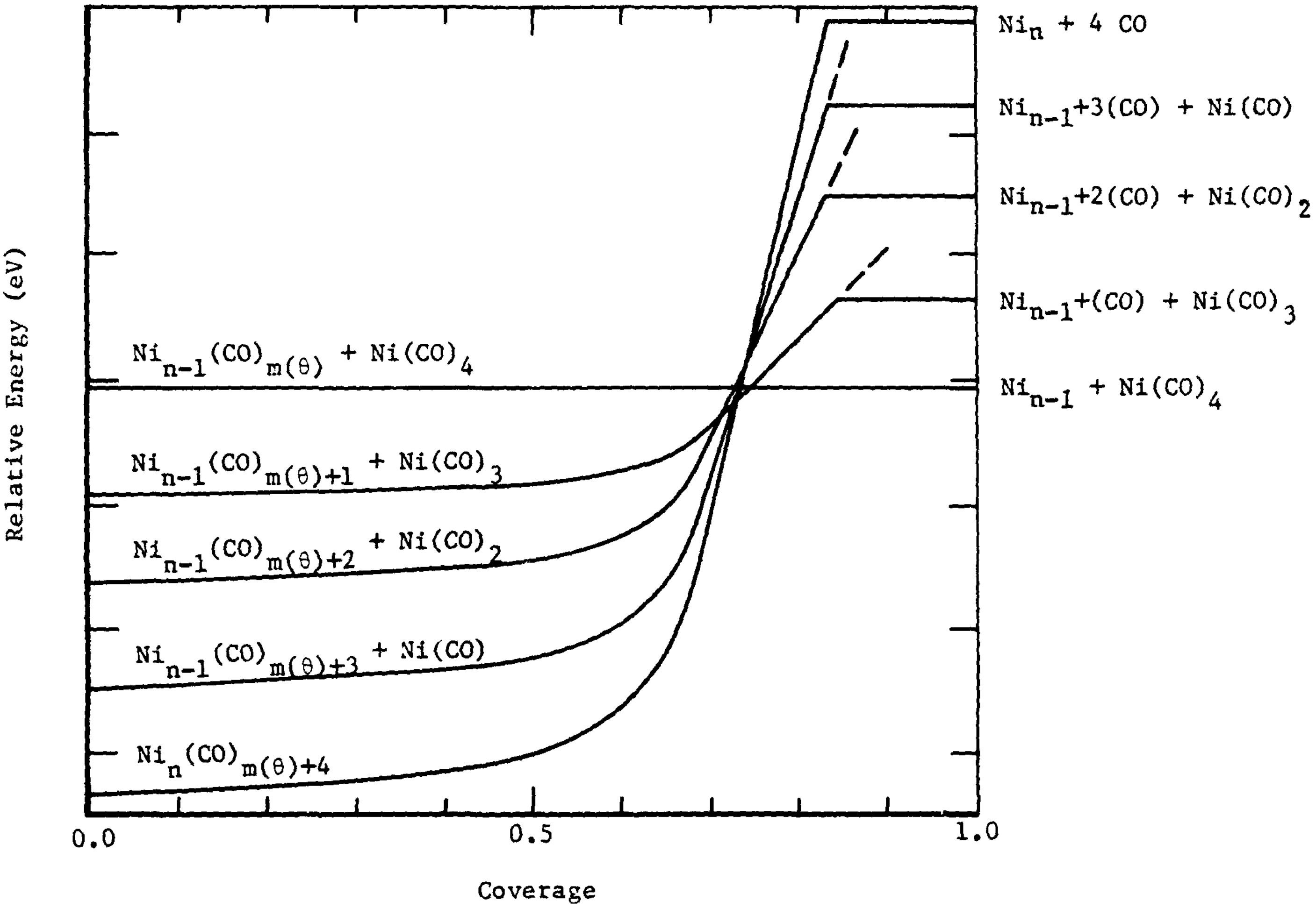


Figure 6. Relative Energetics of Competing Processes as a Function of Coverage.

because of the flatness of the potential energy surface due to misregistration. We may also examine the optimal geometry for clues.

Let us assume that at 67% coverage that the bridge centered arrangement is still the most favored. Consider the situation of an additional CO molecule approaching the surface. Actually, it first nears the layer of already-adsorbed carbonyls. The most favorable landing sites on the nickel substrate will presumably be determined by the holes in the overlayer, rather than by direct interaction of the incoming carbonyl with the nickel surface. We thus superimpose a "landing pattern" of probable interaction sites on Figure 3d, shown by dotted lines in Figure 7. We now indicate the adsorbed carbonyls by open circles.

This pattern is another hexagonal pattern, but it is rotated ∿ 30° from the carbonyl lattice. We note that for most of the more probable landing positions (particularly at the hexagonal corners), the incoming carbonyl will land near a nickel atom which is interacting with a nearby (already-adsorbed) carbonyl. This suggests the possibility that $Ni(CO)_2$ might be the candidate desorbing species. These molecules have been indicated by drawing in stick bonds. There are only two unique corner sites. One has one nickel dicarbonyl possibility and the other has two. In these high coverage calculations we have not allowed the surface nickels to move. It is possible that the adsorption of carbonyl would lengthen the surface-nickel-atom-to-bulk bond lengths, which would presumably enhance the possibility of reactions.

Examination of high coverage on other surfaces is of interest because of recent experimental findings which reveal that due to some unknown selectivity, etching of (100) and (110) surfaces leads exclusively to (111)

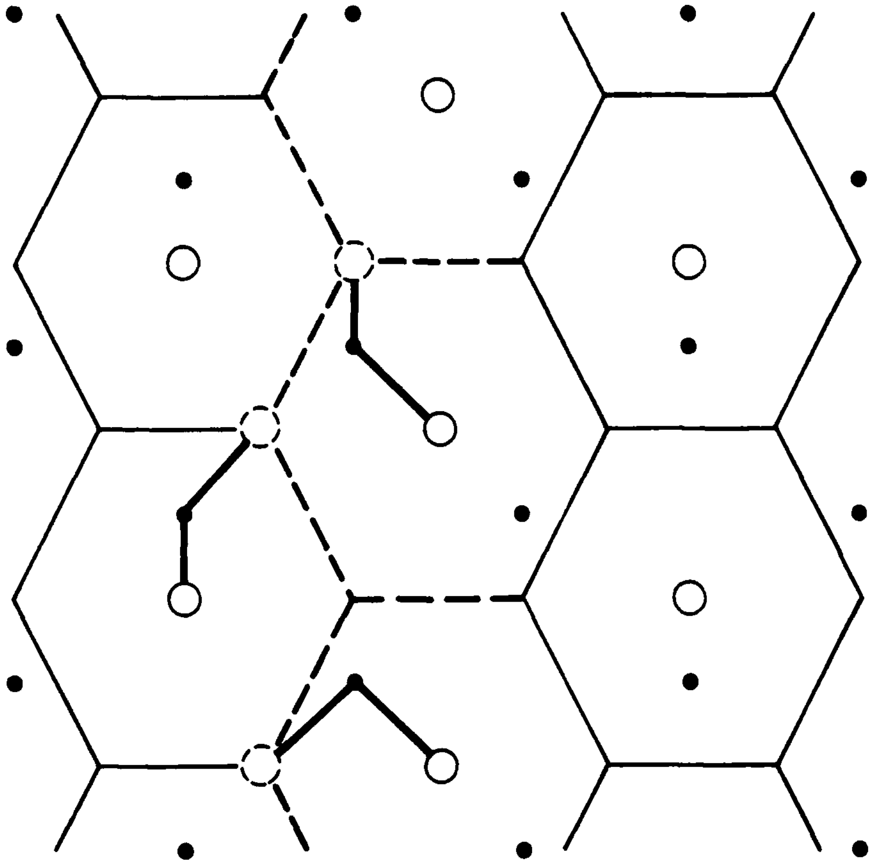


Figure 7. Lattice of Probable Interaction Sites for CO on Ni(100) at High (67%) Coverage.

facets.(23) Thus, the steady state nickel carbonyl formation rates observed starting with various surface orientations have actually been only the rate on (111). Further experimental investigations to measure the rates on non-(111) faces will be difficult because they will presumably be concerned with the early stages of reaction, when the well-known problems of surface cleanliness and preparation are particularly troublesome. On the other hand, the difficulty of theoretical studies is not affected by the choice of crystal orientation. Thus, theory may be able to aid in the determination of the relative ordering of rates for the various surfaces and, thereby, the cause of facetting. It is possible that examination of "landing sites" will lead to such explanations.

V. PRELIMINARY CALCULATIONS ON THE (110) AND (111) FACES OF NICKEL

In light of the preceding discussion, some preliminary calculations of CO adsorption on the (110) and (111) nickel surfaces were performed. The previous nickel s-orbital exponent [optimized for the (100) surface] was used for preliminary calculations on the (111) and (110) surfaces. Surface atoms in these orientations have different numbers of neighbors than the (100) face. The (111) surface atoms have nine rather than eight nearest neighbors, six in the surface plane and three in the next layer.† The (110) surface is furrowed in comparison to the (100) and (111) faces. It is composed of alternating upper and lower rows of atoms, such that those in the upper row have 7 nearest neighbors, while those in the lower (almost internal) row have 11.

Binding (adsorption) of CO at various sites on small nickel clusters modeling the (100), (110) and (111) faces is illustrated (as a function of Ni-CO bond length in Figure 2. The curves have been shifted so that CO adsorbed at each bridge site is the zero of energy. CO on Ni(111) has basically three types of bonding sites: terminal (T), bridged (B), and three-fold (3) sites with either a hole or an atom underneath (in the second layer). The Ni-C bond lengths were optimized at these sites (only the 3-fold-atom site was used since the 3-fold-hole site was assumed to be similar because second layer location is ∿ 3.4 Å away). As for the (100) face, the highest coordination (3-fold) site was found to be preferred. Again the terminal

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† The additional repulsion which results indicates that (ideally) the exponent might need to be increased for nickel atoms on this surface. However, a small difference here may not be significant at this point.

site was the least favored, and the Ni-C bond length was similar to that for the Ni(100) terminal site.

On Ni(110) there are narrow (B) and wide (W) bridge sites, a terminal site (T), and a rectangular (R) site. Here also, terminal bonding near 1.8 Å was less ideal than the other sites. The most favorable site was the wide bridge site. The rectangular site was intermediate (between the two bridge sites) energetically.

These sites should be examined more closely. The rectangular site is actually a 5-fold site since it has terminal bonding to the Ni atom in the trough row. The bond distances to the four corner nickels are 2.27 Å, and the terminal bond is 1.95 Å. The wide bridge site has Ni-C bond lengths of 1.96 Å to the peak row nickel atoms and 2.44 to the trough row nickel atoms, and could thus be considered to have 4-fold coordination. The C-(peak/trough) Ni bonds for the short bridge site vary more (1.91/3.22) and do not indicate 4-fold coordination. For comparison the second layer nickel atom for the (100) 4-fold site are 2.86 Å from the CO, and the two for the (100) bridge site are > 3.4 Å away, mostly because the distance between layers is 0.5 Å larger for (100). The five-fold site is probably not the most favorable site because it has mainly terminal bond character (less favorable) and the bond distances to the rectangular corner nickels are stretched in comparison to the (100) 4-fold case. Moreover, the wide bridge site bears some similarity to the (favored) 4-fold site on (100): the 4-fold site can be considered as a "double wide-bridge site" because of its diagonal Ni-Ni distance. Subsequent calculations will use readjusted nickel and carbonyl parameters to determine these single carbonyl adsorption geometries, and the character of the bonding at each site will be analyzed in detail.

VI. EMPIRICAL MODEL

This last section describes an empirical modeling program which has been assembled for the purpose of locating reaction pathways and transition states for the various processes relevant to nickel carbonyl formation. The economical advantages of this model include being able to treat much larger clusters and to calculate many more points on the potential energy surface. Within this model, CO is treated as an atom. Its parameters are adjusted to reproduce the adsorption energy, frequency, and equilibrium geometry of CO on nickel.

In our first application of this model, a 5 layer cluster of 46 atoms represented the nickel surface. When the top layer was allowed to relax, the surface equilibrium position (inter-layer distance) was found to be 3% larger than the bulk separation. This result implies that the use of nickel exponents (in the semi-empirical calculations) which correspond to longer surface nickel bonds lengths may actually be more realistic than that of those which reproduce the bulk characteristics.

A second preliminary calculation modeled the desorption of NiCO from the nickel (100) surface. The system was treated in a three-body LEPS (London-Eyring-Polanyi-Sato) formulation, in which the components were a single Ni atom, the (n-1)-atom nickel cluster, and the CO molecule. The interaction parameters (in this case) were fit to experimental values for nickel and adsorbed CO, and *ab initio* values for NiCO. The model predicted an intrinsic barrier of 0.7 kcal/mol resulting in an activation energy (relative to adsorbed CO) of 127.6 kcal/mole. This quantity is the total of the binding energy of a nickel atom to the surface plus the adsorption energy of

CO on the nickel surface minus the molecular binding energy of NiCO [relative to Ni(g) + CO(g)] plus the intrinsic barrier height. These results correspond, of course, to the low coverage case. As a first guess, one would expect that the activation energy (relative to free CO) under high coverage conditions would be primarily unchanged, and that the barrier relative to adsorbed would approach this value as the binding per additional CO tended to zero. Thus, these preliminary calculations indicate a rather substantial activation energy requirement for nickel carbonyl formation via the monocarbonyl intermediate.

This model will be used in future studies to further examine the dicarbonyl and other arrangements suggested by landing site arguments and for subsequent transition state investigations.

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