CNDO MO Calculations for Hydrogen Atoms Adsorbed on Clusters of Nickel Atoms

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Summary CNDO MO calculations for the interaction of a hydrogen atom with a cluster of nickel atoms indicates that the bonding involves mainly the nickel *s* and *p* orbitals, and that the most stable position for a hydrogen atom is over a surface hole.

FULL quantum-mechanical treatments of metallic crystal surfaces are difficult, because the presence of metallic character strongly suggests that all atoms in the crystal should be included in any calculation. Such calculations do not appear to be feasible at present but the great strength of some chemisorption bonds and the variation in behaviour of different crystal faces suggest that calculations for a relatively small cluster of metal atoms plus an adsorbate will give a useful model of chemisorption. For hydrogen chemisorption, a general LCAO approach has been presented by Toya and Horiuti[1,2] in which the hydrogen atom is partially incorporated into the metal lattice.

As one of the primary aims of these calculations involved the determination of the most stable geometry, a CNDO procedure was chosen for this work, since this method has been reasonably successful in the prediction of equilibrium bond distances.[3]

TABLE 1

Nickel atom parameters for an initial configuration of 3d^8, 4s^2, 4p^0; β—*resonance integral,* ξ—*orbital exponential coefficient,* I—*ionization potential, and* A—*electron affinity*

β_s	-6
β_d	-10
ξ_s	1·8
ξ_d	2·5
$(I_s + A_s)/2$	4·3
$(I_p + A_p)/2$	1·3
$(I_d + A_d)/2$	10·0

The CNDO procedure used was basically a modification of that described by Pople *et al.*,[3] in which all molecular orbitals are doubly occupied except for the highest occupied MO which contains one electron. The modifications consist mainly in the recognition that *d* orbitals differ so significantly from *s* and *p* orbitals as to require separate treatment. Thus, the diagonal *F*-matrix elements, like those of Baetzold,[4] involve the assignment of different orbital exponents to *d*-orbitals from those of the *s* and *p* orbitals, and in the off-diagonal *F*-matrix elements, as in the work of Clack *et al.*,[5] a different parameter β_d was used to represent the resonance integrals for *d* electrons from that β_s used for *s* and *p* electrons. Slater type orbitals[6] were used; and all-valence shell electrons in the 3*d*, 4*s*, and 4*p* orbitals of nickel were included, while all inner shell electrons were treated as usual as part of a non-polarizable core.

The input parameters used for nickel atoms are listed in Table 1. These gave reasonable values of equilibrium bond length, *d* orbital occupancy, binding energy, Fermi level, and of *d* band width for a cluster of nickel atoms.[7] The hydrogen atom parameters are those given by Pople *et al.*[3]

The calculations reported here are for the interaction of a hydrogen atom with a (111) surface of a cluster of 10 nickel atoms arranged with six nickel atoms in a planar hexagonal pattern about a central nickel atom and three nickel atoms that are nearest neighbours to the central atom in a plane below the other seven atoms. The hydrogen atom was located (i) at 1·6 Å above the central nickel atom to represent adsorption directly over a surface atom and (ii) at 1·0 Å below the centre of the lower three nickel atoms to represent adsorption over a triangular hole on the (111) face. These values are the calculated equilibrium distances for the interaction of hydrogen atoms with smaller nickel clusters of a similar configuration, and in the calculations with smaller clusters, the equilibrium distances were found to be independent of the cluster size. In all cases the nickel–nickel distance is 2·5 Å as in bulk nickel.

The results of the calculations are given in Table 2, and show a much greater binding energy for a hydrogen atom over a hole than directly over a surface atom. The calculated binding energy of 73 kcal per mole over a hole is in good agreement with the experimental value[8] of 67 kcal per mole. These results contradict those of Fassaert *et al.*[9] who, using an extended Hückel molecular orbital (EHMO) calculation, found that adsorption over a surface atom was preferred. However, in the EHMO calculation, the H atom is much closer to the plane of the three Ni atoms forming the hole than it is in the CNDO calculation reported here. The location of the H atom for an EHMO calculation in the equilibrium position as indicated by these CNDO

Table 2

CNDO *calculation for* H *adsorbed on* (111) Ni

	Binding energy (kcal)	H atom charge (e)	Bond order			
			s	*p*	*d*	Total
H over Ni atom	26	−0·23	0·158	0·282	0·095	0·535
H over hole	73	−0·03	0·334	0·510	0·082	0·926

calculations could possibly result in better agreement for the two methods.

The H atom carries a negative charge for both positions, and implies a negative surface potential in agreement with experimental measurements.[8] In agreement with the EHMO calculation a H atom when located directly over a surface atom is more negative than one situated over a hole, but the CNDO H-atom charges are much lower and thus appear more reasonable than those calculated by the EHMO method.

The bond orders indicate that the nickel *s* and *p* orbitals are largely responsible for the bonding, and that the *d* orbitals play a relatively minor role. Although previous theoretical considerations[10,11] have emphasised the role of *d* orbitals in chemisorption, the results reported here are not in agreement with that view for hydrogen adsorption on nickel, and the EHMO calculations also indicated a minor role for *d* orbitals. That hydrogen adsorption mainly involves the nickel *sp* band electrons is supported by theoretical calculations of conductivity changes upon hydrogen adsorption.[12]

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[1] T. Toya, *J. Res. Inst. Catalysis, Hokkaido Univ.*, 1960, **8**, 209.
[2] J. Horiuti and T. Toya, 'Solid State Surface Science,' vol. 1, ed. M. Green, Marcel Dekker, New York, 1969.
[3] J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.
[4] R. C. Baetzold, *J. Chem. Phys.*, 1971, **55**, 4335.
[5] D. W. Clack, N. S. Hush, and J. R. Yandle, *J. Chem. Phys.*, 1972, **57**, 3503.
[6] J. C. Slater, *Phys. Rev.*, 1930, **36**, 51.
[7] G. Blyholder, submitted to *J. Res. Inst. Catalysis, Hokkaido Univ.*
[8] G. C. Bond, 'Catalysis by Metals,' Academic Press, New York, 1962.
[9] D. J. M. Fassaert, H. Verbeek, and A. Van der Avoird, *Surf. Sci.*, 1972, **24**, 501.
[10] G. C. Bond, *Discuss. Faraday Soc.*, 1966, **41**, 200.
[11] D. M. Newns, *Phys. Rev.*, 1969, **178**, 1123.
[12] M. Watanabe, *Surf. Sci.*, 1973, **34**, 759.