JOURNAL OF CATALYSIS 13, 123-127 (1969)

Quantum Chemical Estimation of Hydrogen Adsorption on Nickel Face-Centered Cubic Crystal

D. SHOPOV, A. ANDREEV, AND D. PETKOV

From the Institute of Organic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria

Received June 4, 1968; revised September 27, 1968

The quantitative estimation of the activity for hydrogen adsorption of different adsorption centers including metal *d* orbitals on different crystal faces of a face-centered cubic nickel crystal is given. The quantum chemical calculations are carried out by the molecular orbital method—the Wolfsberg-Helmholtz method. The results show the presence of adsorption centers with different binding force, depending on their structure, on different crystallographic faces of a face-centered cubic nickel crystal.

The exact quantum chemical description of surface compounds faces great difficulties. This is valid even for the simplest case, as for instance the adsorption of a hydrogen atom on a solid surface. Certain attempts to calculate heats of adsorption of hydrogen on transition metals (*1*, *2*, *3*) have been made and in some cases quantum chemical methods were used (*4*–*7*) not taking into account, however, the crystal geometry and particular model of the crystal structure. Recently, on the basis of the model of the nickel face-centered cubic crystal proposed by Goodenough (*8*), Bond (*9*) showed some of the possible interactions of the hydrogen atom with the *d* orbitals of the metal, without offering any quantitative assessment.

The aim of the present paper is to give a quantitative estimation of the activity of the different adsorption centers including metal *d* orbitals on different crystal faces of a face-centered cubic nickel crystal.

MODEL AND CALCULATION DESCRIPTION

The model of Goodenough (*8*) discusses in detail the state of the metal atom *d* orbitals under the influence of the crystal field. It is assumed that the atomic orbital functions retain their symmetry in the crystal orbital functions. The crystal lattice is formed by the overlapping of the t_{2g} orbitals, directed towards the nearest neighbors (octahedral environments) and the t_{2g} electrons occupy a collective band. The remaining *d* electrons directed (but not interacting) towards the next to the nearest neighbors, occupy two narrow e_g bands divided by interatomic exchange splitting ($E_{\text{ex}} \approx 0.84$ eV). Therefore these electrons are localized.

The participation of the *d* orbitals in the hydrogen–nickel bond was established by studying hydrogen adsorption by magnetic methods (*10*). Only the localized $e_g d$ electrons have been discussed, since they have a higher potential ability for bonding than delocalized t_{2g} electrons, but it is possible that free valences due to t_{2g} electrons may be present on the metal surface. In this way our study concerns the so-called local interaction which plays a very important role in adsorption and catalysis (*11*).

As has been already mentioned, e_g orbitals are directed towards the next-nearest neighbors which account for the negligible interaction with the other atoms of the lattice. This has been confirmed by overlap integrals calculations, which proved to be negligibly small. Thus the solution of the problem is reduced to consideration of the interaction between the 1*s* electron of the hydrogen atom and the e_g electrons of the nickel atoms at a definite structure of the adsorption complex.

Let us consider Model 1 (Fig. 1). In this

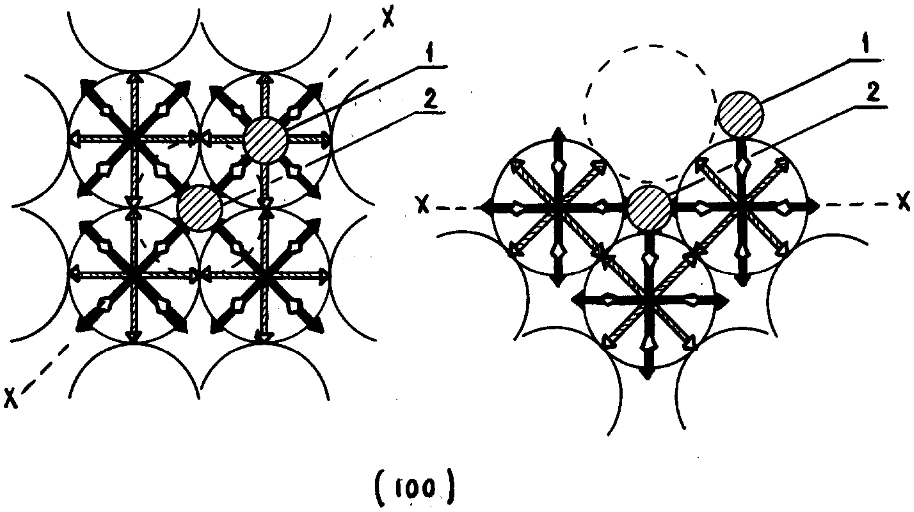

FIG. 1. Diagrammatic representation of *d*-orbitals on the 100 face according to Bond (*9*); filled arrows, e_g orbitals; open arrows, t_{2g} orbitals; 1, Model 1; 2, Model 2.

case there is interaction between the 1*s* orbital of the hydrogen atom and the d_{z^2} orbital directed perpendicularly to the crystal face (100). An analogous Model 1′ can be realized on the crystal faces (010) and (001) but in this case a $d_{x^2-y^2}$ orbital of the metal atom is participating in the bond formation. Model 2 (Fig. 1) reveals another possibility of bonding on the crystal face (100). The orbital 1*s* of the hydrogen atom overlaps with five e_g orbitals—four $d_{x^2-y^2}$ and one d_{z^2} orbital. Model 3 concerns the (110) face where the 1*s* orbital overlaps four e_g orbitals belonging to four different nickel atoms (Fig. 2). On the (111) face Model 4 is realized (Fig. 3)—one 1*s* orbital overlaps three e_g orbitals in the hole between three nickel atoms. Model 5 includes the overlapping of the 1*s* electron with two e_g orbitals belonging to, two neighboring nickel atoms on the (110) face (Fig. 2).

In the present model the interaction between 1*s* orbital and e_g orbitals of the neighboring nickel atoms is neglected because this interaction is very small. For example, for Model 1 the overlap integral between the

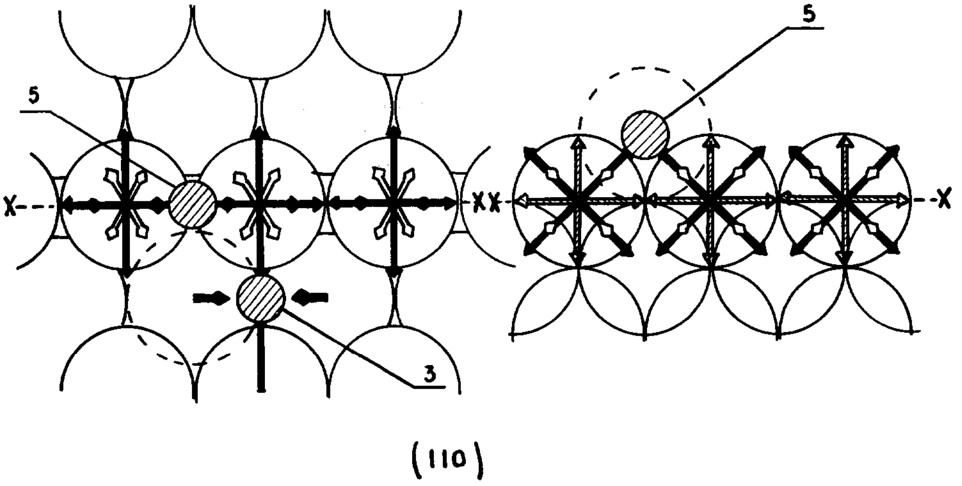

FIG. 2. Diagrammatic representation of *d* orbitals on the 110 face; 3, Model 3; 5, Model 5.

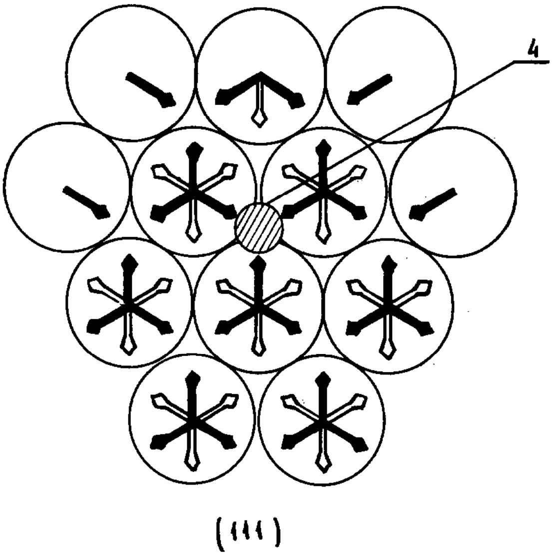

FIG. 3. Diagrammatic representation of d orbitals on the 111 face; 4, Model 4.

1s orbital and e_g orbitals of neighboring nickel atoms is 25 times smaller than that involving the e_g orbitals of the nickel atom included in the model.

The method of the molecular orbitals, the Wolfsberg-Helmholz method (*12*), was used for the calculation. Similar to Huckel's method the energies of the molecular orbitals, which are linear combinations of the basic atomic orbitals, are obtained by solving the secular equation

$$\text{Det}\ (H_{\mu\nu} - ES_{\mu\nu}) = 0 \qquad (1)$$

where $S_{\mu\nu}$ is the overlap matrix for the chosen basis. Diagonal matrix elements $H_{\mu\mu}$ in this method (*12*) are equal to the atomic ionization potential of the free atoms.

In our case $H^{\mathrm{H}}_{\mu\mu} = 13.595$ eV and $H^{\mathrm{Ni}}_{\mu\mu} = -11.985$ eV. The value for $H^{\mathrm{Ni}}_{\mu\mu}$ is evaluated from the ionization potential of the electron in a free nickel atom (*13*). The work function of the electron 4.50 eV (*14*) is added to the ionization potential value, and half of the energy of the exchange splitting, E_{ex} of the e_g orbital in the nickel lattice is subtracted. The atomic level gives an approximate idea of the energy of the d band of the metal, which is defined by shifting in accordance with ref. (*8*) as a result of the exchange splitting. The work function if taken into account in order to obtain an electron capable of interacting on the Fermi level.

The matrix element $H_{\mu\nu}$ is defined by the formula

$$\begin{aligned} H_{\mu\nu} &= \langle \chi_\mu | H^{\mathrm{eff}} | \chi_\nu \rangle \\ &= \tfrac{1}{2}(H_{\mu\mu} + H_{\nu\nu}) S_{\mu\nu} [\kappa + (1 - \kappa)\delta_{\mu\nu}] \qquad (2) \end{aligned}$$

where $\kappa \approx 2$ is the interaction parameter. In our case $\kappa = 1.93$ (calibrated by the experimental differential heat of adsorption). The overlap matrices $S_{\mu\nu}$ were calculated by means of Slater orbitals, and the effective charge $Z^* = 9.95$ a.u. was calculated by the improved rules of Slater-Eyring for d and f electrons given by Batcanov (*15*). The radius, giving a maximum value of the overlap integral, was used for Model 1. The distance $r = R/\sqrt{2} = 1.782$ Å, where R is the lattice parameter, was used for the rest of the models. In model 2 there is maximum overlapping with d_{z^2} orbital ($r = 0.804$ Å) and the overlap integral with $d_{x^2-y^2}$ is $<d_{x^2-y^2}|1s>$ cos 2φ, where the angle φ takes into account the deviation of bonding direction from the plane of the four nickel atoms in the model. The values of the overlap integrals are given in Table 1.

Let us assume that only the electron energy changes on chemisorption. Then the

TABLE 1
OVERLAP INTEGRALS VALUES

Type of matrix elements	Interatomic distance, r (Å)	Overlap integrals $S_{\mu\nu}$
$\langle 3d_{z^2} \mid 1s\rangle$	0.804	0.1599
$\langle 3d_{z^2} \mid 1s\rangle$	1.482	0.0565
$\langle 3d_{x^2-y^2} \mid 1s\rangle$	1.482	0.0489
$\langle 3d_{x^2-y^2} \mid 1s\rangle$ cos 2φ	1.482	0.0314

thermodynamic heat of adsorption ΔH may be given by the expression

$$\Delta H \approx \Delta E = 2E^{\circ}_{\mathrm{Ni}_n\mathrm{H}} - (E^{\circ}_{\mathrm{H}_2} - 2E_{\mathrm{Ni}_n}) \quad (3)$$

where $E^{\circ}_{\mathrm{Ni}_n\mathrm{H}}$ is the energy of the adsorption complex in ground state; $E^{\circ}_{\mathrm{H}_2} = 740.5$ kcal, the total electronic energy of the hydrogen molecule (*16*); $E_{\mathrm{Ni}} = H_{\mu\mu}$, and n is the number of nickel atoms taking part in the adsorption complex. The energy of interaction E of a hydrogen atom with the corresponding active center on the surface is equal to

$$E = E^{\circ}_{\mathrm{Ni}_n\mathrm{H}} - nE_{\mathrm{Ni}} - E_{\mathrm{H}} \quad (4)$$

RESULTS AND DISCUSSION

The results of the calculations for the energy of interaction (E) and heat of adsorption of a hydrogen with an active center with a certain structure are given in Table 2.

The calculations for the interaction of a free hydrogen atom with nickel atoms from different crystal faces (Table 2) show that this interaction is different and depends on the structure and geometry of the adsorption center. In our opinion these results may serve as a theoretical basis for the chemical heterogeneity of the adsorbing surfaces. It should be noted that these calculations do not take into account the defects of the surface and also the interaction between the atoms adsorbed. The strongest bonding of hydrogen with the metal surface is realized in Model 2.

To the different interaction energies correspond different adsorption heats. The data for the adsorption heats (Table 2) are in agreement with the experimental curves for the change of the adsorption heat with surface coverage for hydrogen adsorption on nickel (*17–21*). It is seen from Table 2, that the adsorption on the active center 3 takes place without heat evolution, while on centers 4 and 5, it is endothermic. Hydrogen atoms were also adsorbed on these centers because of migration of hydrogen atoms from places with stronger adsorption. The possibility for adsorption on these centers is supported by the fact that atomic hydrogen adsorbs on a surface previously covered with molecular hydrogen, and a change in the work function takes place (*22*).

The results of the calculations for the charge distribution are in good agreement with the results from the measurements of the surface potential. In all cases studied by us a negative charge on the hydrogen atom is obtained. The "net atomic population" on the hydrogen atom (*23*) for all models is given in Table 2. The experimental measurements of the work function change when hydrogen adsorbed on nickel (*24*) shows

TABLE 2
RESULTS OF INTERACTION CALCULATIONS

Model	Crystal face	Type of the adsorption complex $\mathrm{Ni}_n\mathrm{H}$	Electronic energy of the adsorption complex $2E^{\circ}_{\mathrm{Ni}_n\mathrm{H}}$ (eV)	Heat of adsorption ΔH (kcal/mole)	Interaction energy of a free hydrogen atom with the surface E (eV)	Net atomic population on hydrogen atom[a] q_{H}
1	(100)	NiH	−57.47	32.00	3.15	1.32
1′	(010) or (001)	NiH	−56.90	18.92	2.87	1.40
2	(100)	$\mathrm{Ni_5H}$	−153.74	39.10	3.38	1.30
3	(110)	$\mathrm{Ni_4H}$	−128.00	0.22	2.46	1.53
4	(111)	$\mathrm{Ni_3H}$	−103.63	−8.94	2.26	1.60
5	(110)	$\mathrm{Ni_2H}$	−79.33	−16.64	2.10	1.68

[a] Reference (*23*).

negative values (the negative part of the dipole is on the hydrogen atom).

The quantum chemical calculations of hydrogen adsorption on nickel show the presence of adsorption centers with different binding force on different crystallographic faces of an ideal face-centered cubic nickel crystal. These results are in agreement with contemporary ideas for surface heterogeneity.

It must be remembered that the present calculations do not take into account the defects of the surface and the interaction between the atoms adsorbed, and there are various simplifications of the model for calculations.

In spite of certain simplifications of the model related to difficulties in similar calculations, the relative results of this works have a definite physical meaning.

REFERENCES

1. ELEY, D., *Discussions Faraday Soc.* **8,** 34 (1950).
2. STEVENSON, D. P., *J. Chem. Phys.* **23,** 203 (1955).
3. HIGUCHI, I., REE, T., AND EYRING, H., *J. Am. Chem. Soc.* **79,** 1330 (1957).
4. MOLINA, J., CARBO, R., *Afinidad* **22,** 101 (1965).
5. TOMIJUKI, T., *J. Res. Inst. Catalysis, Hokkaido Univ.* **8,** 209 (1960).
6. DUNKEN, H., AND DUNKEN, H. H., *Z. Chem.* **6,** 233 (1966).
7. GRIMLEY, T. B., *Proc. Phys. Soc.* **90,** 751 (1967).
8. GOODENOUGH, J. B., *Phys. Rev.* **120,** 67 (1960).
9. BOND, G., C., *Platinum Metals Rev.* **10,** 8790 (1966).
10. SELWOOD, P. W., "Adsorption and Collective Paramagnetism." Academic Press, New York and London, 1962.
11. DOWDEN, D. A., *Coloquio Sobre Qimica Fisica del Procesos en Superficies Solidas, Madrid, 1964,* p. 178 (1965).
12. WOLFSBERG, M., AND HELMHOLTZ, L., *J. Chem. Phys.* **20,** 837 (1952).
13. ZEVNEV, M., GOUTERMAN, M., *Teoret. Chem. Acta (Berlin)* **4,** 44 (1966).
14. BOND, G. C., "Catalysis by Metals," p. 498. Academic Press, London and New York, 1962.
15. BATZANOV, S., *Zh. Struk. Khim.* **5,** 293 (1964).
16. COULSON, C. A., "Valence," p. 20. Oxford Univ. Press, London, 1961.
17. BEECK, O., COLE, W. A., AND WHEELER, A., *Discussions Faraday Soc.* **8,** 314 (1950).
18. WAHBA, M., AND KEMBALL, C., *Trans. Faraday Soc.* **49,** 1351 (1953).
19. RIDEAL, E., AND SWEETT, F., *Proc. Roy. Soc. (London)* **A257,** 291 (1960).
20. EUCKEN, A., AND HUNSMAN, W., *Z. Phys. Chem.* **B44,** 291 (1960).
21. BENSON, J. E., AND KWAN, T., *J. Phys. Chem.* **60,** 1601 (1965).
22. PONEC, V., KNOR, Z., AND CERNY, S., *Discussions Faraday Soc.* **41,** 155 (1966); *J. Catalysis* **4,** 485 (1965).
23. MULLIKEN, R. S., *J. Chem. Phys.* **23,** 1833 (1955).
24. CULVER, R., AND TOMPKINS, F., *Advan. Catalysis* **11,** 67 (1959).