

Symmetry rules in chemisorption

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SYMMETRY RULES IN CHEMISORPTION

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SUMMARY

A molecular orbital theory of chemisorption is presented that relates the structure of the adsorption site to the group orbital local density of states at the Fermi level projected out from the surface molecular orbitals by the adsorbate orbitals.

Preferential adsorption of CO to "on-top" sites of the faces of noble metals such as Ni, Pt and Rh is ascribed to the subtle balance between on-top directing interactions with the metal valence d-electrons and bridge coordination directing interactions with the metal valence s-electrons. The work clarifies the difference in hydrogenolysis behaviour between Ni and Pt.

INTRODUCTION

Frontier Orbital theory has been developed into a fruitful Molecular Orbital theory to predict molecular geometries in organic and inorganic chemistry (ref. 1). It can also be used to predict coordination geometries of molecules or atoms chemisorbed to metal surfaces.

The bond energy E can be considered to be the sum of two terms:

$$\Delta E = E_{\text{rep.}} + E_{\text{attr.}}$$

According to the Frontier Orbital theory the attractive component can be calculated using the second-order perturbation theory expression:

$$\Delta E_{\text{attr.}} = -2 \left[\sum_{\substack{\epsilon_j \geq \epsilon_F \\ E_j \leq E_{\text{HOMO}}} \frac{\beta'_{ij}{}^2}{\epsilon_j - E_j} + \sum_{\substack{\epsilon_j \leq \epsilon_F \\ E_j \geq E_{\text{LUMO}}} \frac{\beta'_{ij}{}^2}{E_j - \epsilon_j} \right] \quad (1)$$

β'_{ij} is a non-diagonal coupling matrix element; ϵ_j and E_j are, respectively, the surface and adsorbate molecular orbital levels before interaction. The relative positions of levels ϵ_j and E_j are sketched in Figure 1. E_{HOMO} is the highest occupied orbital energy of the adsorbing molecule; E_{LUMO} is the energy of the lowest unoccupied molecular orbital of the adsorbing molecule. ϵ_F is the Fermi level of the metal surface. If the Lowest Unoccupied Molecular Orbital (LUMO) has an energy lower than the highest occupied orbital of the metal or if the

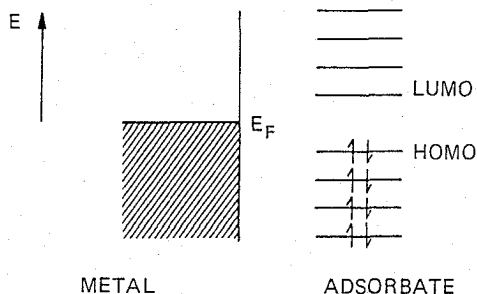


Fig. 1. Relative positions of surface and adsorbate molecular orbital levels

Highest Occupied Molecular Orbital (HOMO) has an energy higher than ϵ_F , charge transfer may occur and the ion of the adsorbate has to be taken as the reference state.

The repulsive term is due to overlap of the orbitals of the adsorbate and the metal surface. According to a crude approximation (ref. 2) it is proportional to $N^{\frac{1}{2}}$, with N being the coordination number of the adsorbate orbital to metal surface atomic orbitals:

$$\Delta E_{\text{rep.}} \sim N^{\frac{1}{2}} S \quad (2)$$

Since the levels ϵ_j forms a continuum, expression (1) can be partially integrated to give the surface interaction analogue of expression (1) (see Appendix A):

$$\Delta E_{\text{attr.}} = -2 \left[\sum_{\substack{E_j \leq E_{\text{HOMO}} \\ \alpha_j}} \rho_{\alpha_j}(\epsilon_F) |\beta'_{\alpha_j}|^2 \frac{\Delta_{\alpha_j}(1 - P_{\alpha_j})}{\epsilon_F - E_j + \Delta_{\alpha_j}(1 - P_{\alpha_j})} + \sum_{\substack{E_j \geq E_{\text{LUMO}} \\ \alpha_j}} \rho_{\alpha_j}(\epsilon_F) |\beta'_{\alpha_j}|^2 \frac{\Delta_{\alpha_j} \cdot P_j}{E_j - \epsilon_F + \Delta_{\alpha_j} P_{\alpha_j}} \right] \quad (3)$$

According to this expression, chemisorption is governed by, amongst other factors, the surface group orbital density at the Fermi level:[®]

$$\rho_{\alpha_j}(\epsilon_F) = \sum_i |\langle \chi_{\alpha_j} | \psi_i \rangle|^2 \delta(\epsilon_i - \epsilon_F) \quad (4)$$

and

$$\beta'_{\alpha_j} = \langle \phi_j | H' | \chi_{\alpha_j} \rangle \quad (5)$$

with ϕ_j being the adsorbate molecular orbital and ψ_i the surface molecular orbital. χ_{α_j} is the linear combination of surface atomic orbitals that is projected out of the surface molecular orbitals by adsorbate orbital ϕ_j . Δ_{α_j} is the bandwidth of the metal valence electron band coupling with ϕ_j ; β_{α_j} is a measure of its fractional electron occupation. The symmetry of the adsorbate orbitals determines the symmetry of the surface group orbital χ_{α} to which it couples, since H' is fully symmetric.

We will first illustrate the use of expression (3) with a simple adsorption model. In subsequent sections the expression will be applied to adsorption and reactions on transition metal surfaces.

When chemisorption is modelled by interaction of a hydrogen type adsorbate with a tight binding s-valence electron metal surface, each metal atom contributes one atomic orbital and the hydrogen atom interacts with one surface atomic orbital. With the Bethe lattice approximation (ref. 3-5) for the local density of states, expression (3) reduces to:

$$\Delta E = - \frac{4Z_s^{\frac{1}{2}}\beta'^2}{Z_s\beta^2} \left[\frac{1}{\frac{\epsilon_F - E_0}{\sqrt{Z_s\beta}} + 2} + \frac{1}{\frac{E_0 + U - \epsilon_F}{\sqrt{Z_s\beta}} + 2} \right] \quad (6)$$

This expression applies if each metal atom contributes one electron. Two Bethe lattices are sketched in Figure 2. Z_s is the coordination number of the metal surface atom before adsorption, and $Z+1$ the effective coordination number in the bulk of the metal; $Z_s \leq Z$. β' and β are the adsorbate-metal and the metal-metal overlap potential, respectively. E_0 is the energy of the electron on hydrogen; U is the effective two-electron repulsion integral.

One observes that bonding increases with increasing $\frac{\beta'}{\beta}$, the ratio of hydrogen-metal to metal-metal interaction. If Z_s , the coordination number of the surface metal atom Z_s increases, the adsorbate bond strength decreases. Although the bond strength increases with decreasing Z_s when the surface metal valence electron band is half-filled, this is not the case at the edges of the band.

This follows from the expression for $\rho_1(E)$ (ref. 3)

$$\rho_1(E) = - \frac{1}{\pi} \text{Im} \frac{1}{\alpha - E - \frac{Z_s}{Z} \left\{ \frac{\alpha - E}{2} - i \frac{1}{2} \sqrt{4Z_s\beta^2 - (\alpha - E)^2} \right\}} \quad (7)$$

$$(\alpha - E)^2 \leq 4\beta^2$$

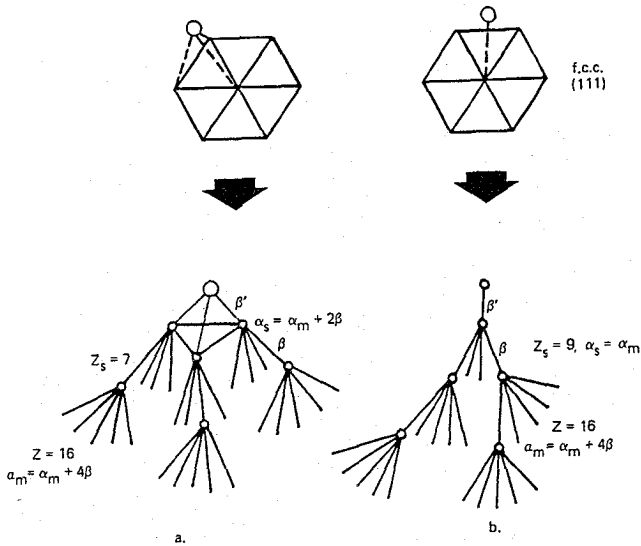


Fig. 2. Reduction of top and three coordination of hydrogen atom at (111)-face of f.c.c. s-band to Bethe lattice models

and normalization: $\int dE \rho_1(E) = 1$. α is the one-centre electron energy at a metal atom. As a result, one finds that if Z_s increases, the local density of states (LDOS) decreases in the centre of the valence electron band, but increases at the edges (see Figure 3).

THE GROUP ORBITAL LOCAL DENSITY OF STATES

Figure 4 presents $\rho_\alpha(E)$ for adsorbate orbitals of σ and π symmetry for a molecule adsorbing to the (111)-surface of a face-centred cubic (f.c.c.) crystal described by a tight binding s-electron valence band. E' gives the electron energy value for which the valence electron band has an occupation of one electron per atom.

One observes that at low band filling σ orbital multicoordination is favoured, and at high band filling on-top coordination as well as π bridge coordination. Since β'_{α_j} is also a function χ_{α_j} , the binding energy ratio will be determined by $|\beta'_{\alpha_j}|^2 \rho_{\alpha_j}(E_F)$.

For an s-type valence electron band and an s-type adsorbate orbital we have:

$$|\beta'_{\alpha_j}|^2 \rho_{\alpha_j}(E_F) = Z_\alpha \rho_{\alpha_j}(E_F) \quad (8)$$

where Z_α is the number of metal atom neighbours of the adsorbate orbital j .

An orbital of π symmetry has of course no interaction with the on-top position.

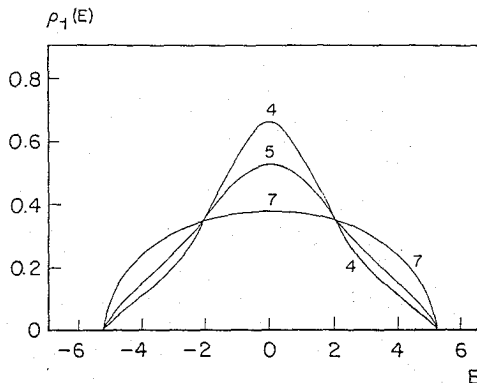


Fig. 3. LDOS at surface atom of a Bethe lattice. The numbers denote Z_S . $Z = 8$, $\alpha = 0$, $\beta = -1$

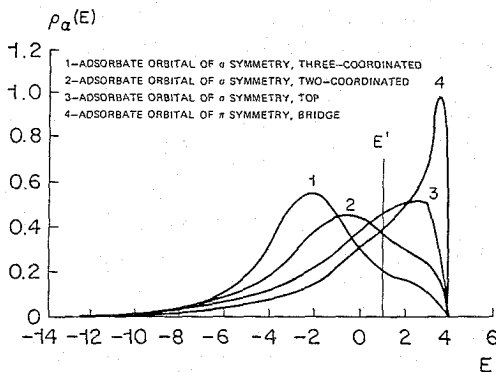


Fig. 4. Group orbital LDOS $\rho_\alpha(E)$ at the (111)-face of f.c.c. s-electron band metal. $\beta = -1$, $E_F = 1$ if electron density is equal to the 1 electron per atom

Interaction with d-band is considered to be only with the partially occupied d_{xy} , d_{yz} and d_{xz} subbands since these are partially occupied (ref. 4,18). At the (111) face each of the d_{xy} , d_{yz} and d_{xz} orbitals loses one of its four neighbours and for each orbital one lobe dangles from the surface towards the vacant positions. (Figure 5). The degeneracy at the surface is lifted by interaction between such lobes from different atoms. One finds one bonding and two antibonding combinations, as sketched in Figure 5b. Again one observes that σ

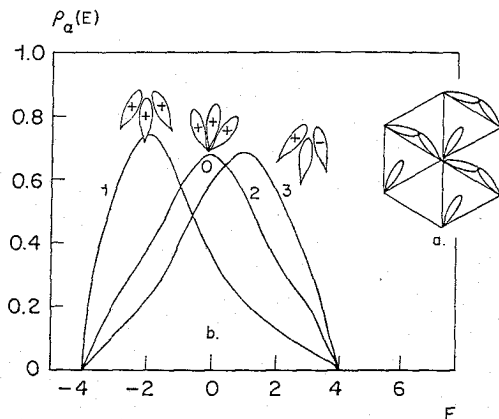


Fig. 5. a. Dangling orbital lobes of d_{xy} , d_{yx} and d_{xz} orbitals at (111)-face of f.c.c. crystal; b. LDOS of totally symmetric (1), non-bonding (2) and anti-bonding (3) combination of d_{xy} , d_{yz} and d_{xz} orbitals. $\alpha = 0$, $\beta = -1$

multicoordination is favoured at low band fill filling, and π multicoordination at high band filling. For Pt and Ni, which we will consider explicitly here, the d_{xy} , d_{yz} and d_{xz} subband occupation is 5/3 (ref. 4)

APPLICATIONS

CO chemisorption to Pt, Ni and Cu (111) faces

CO adsorbs on-top to the Pt (ref. 6) and Cu (111) (ref. 7) surfaces contradictory to chemical intuition, which predicts chemisorption to the surface Freundlich sites. We will discuss bonding to the metal surface according to the Blyholder model (ref. 8). The HOMO of CO is a doubly occupied 5σ orbital that donates charge to the metal. The LUMOs of CO are the two empty degenerate $2\pi^*$ orbitals, into which electrons can be backdonated from the metal surface orbitals.

The energy dependence of the corresponding group orbital local density of states with the s-valence electron band are sketched in Figure 4.

Since the adsorbate $2\pi^*$ orbitals do not interact in the on-top position, a strong interaction with the $2\pi^*$ levels favours bridging coordination, which is optimum at high valence electron band occupation.

In the bridging site interaction with the 5σ level is maximum at low band occupation and decreases if the valence band becomes occupied. At high band occupation 5σ on-top coordination becomes favoured.

Whereas the $2\pi^*$ orbitals do not interact with the metal s-valence electrons in the on-top position, they do interact with the metal d-valence electrons. The

dependence on electron band occupation is similar to that found for the s-band. $2\pi^*$ backdonation in bridging sites is favoured at high d-valence electron band filling, but 5σ donation is favoured in the on-top coordination site.

Table 1 summarizes the results of semi-empirical Hartree-Fock calculations for CO. Results ignoring overlap ($S=1$) of adsorbate and metal surface orbitals and including finite overlap ($S\neq 1$) of adsorbate and metal surface orbitals are presented. Details of the method can be found in ref. 5. The parameter values used are listed in Appendix B. If overlap is ignored ($S=1$), one predicts the bridge position to be most stable.

TABLE 1

Calculated bond strengths (eV) of CO adsorbed to the (111) faces of f.c.c. metals in the on-top and bridge positions. Parameters and details of the method can be found in ref. 3.

	S_{nondiag}	Top	Bridge	Exp.	Work function eV	d-Band halfwidth, eV
Pt				top	5.65	4.09
Lattice	=0	-1.501	-1.561			
	$\neq 0$	-1.296	-1.123			
Cluster	=0	-1.633	-2.531			
	$\neq 0$	-1.436	-2.124			
Ni				bridge	5.150	1.82
Lattice	=0	-1.001	-1.2005			
	$\neq 0$	-0.870	-0.888			
Cluster	=0	-1.092	-1.76			
	$\neq 0$	-0.967	-1.47			
Cu				top	5.05	1.82
Lattice	=0	-0.745	-0.920			
	$\neq 0$	-0.572	-0.550			
Cluster	=0	-0.729	-1.208			
	$\neq 0$	-0.569	-0.804			

Bonding is strongest to Pt, because of the large interaction with the d-valence electrons and weaker with Ni, because it has a much smaller d-bandwidth, it is still weaker with Cu, whose d-valence electron band is completely filled. Bridge coordination is found to become more favoured for Cu, because it has the lowest work function. The small difference in energy between the on-top and

bridge positions on Pt is due to the relatively large interaction of the 5σ orbital of CO with highly occupied metal d-valence electron band.

Agreement with experiment is found, if overlap of adsorbate and metal surface orbitals included ($S \neq 1$). The resulting Born repulsion is proportional to the square root of the number of neighbour atoms and is relatively independent of electron band occupation.

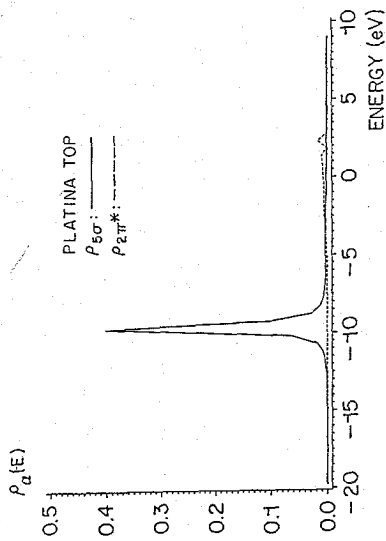
Table 1 also contains the results of cluster calculations, with parameters equal to those used for the semi-infinite lattices. The difference between the cluster and semi-infinite lattice calculations is that in the cluster only those metal atoms have been included, which are the nearest neighbour of the metal atom involved in chemisorption. As has also been observed by others (ref. 9), on small clusters a strong bias is found for chemisorption to the bridge position, because of the availability of occupied antibonding surface cluster orbitals of $2\pi^*$ symmetry.

Figures 6a,b and c present the calculated changes in the electron energy distribution which occur upon including finite overlap between adsorbate and metal surface orbitals. $\rho_{5\sigma}$, $\rho_{2\pi^*}$, ρ_S and ρ_D represent the local density of states of the adsorbate 5σ and $2\pi^*$ levels, and ρ_S and ρ_D that of the metal s- and d-electrons. The Fermi level of the metal is at position 0. Clearly, when overlap is included a shift of density is observed from bonding to antibonding orbitals.

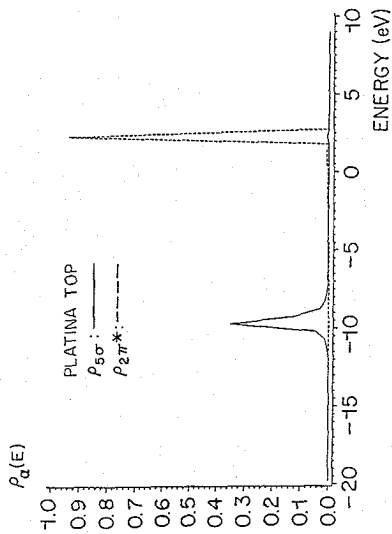
H₂ dissociation

A major advance in the theory of reactivity has been the development of the Woodward-Hoffmann rules, which relate the activation energy of a reaction to the symmetry of the orbitals of the reactants involved. Pearson (ref. 10) postulated that the symmetries of the HOMOs and LUMOs have to be the same for a reaction to proceed. As expression (3) illustrates, these rules are also applicable to chemisorption and surface reactions if one takes the surface group orbital local density of states at the Fermi level to represent the interacting HOMO and LUMO coefficients of the metal surface valence electron band. This can be illustrated by considering adsorption of H₂ to a string of Cu atoms, whose electron structure is described by one s atomic orbital per atom and electron occupation of one electron per atom.

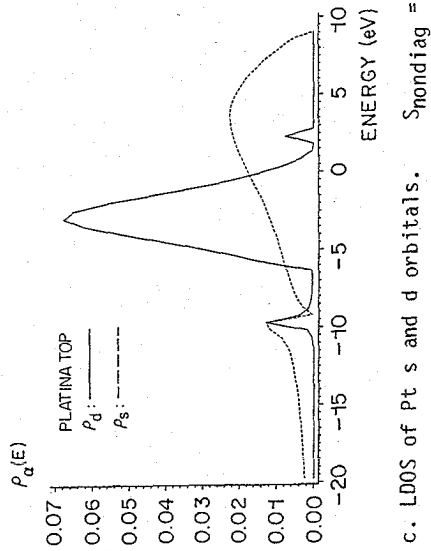
According to Pearson's rule the dissociation of H₂ by a Cu atom or Cu₂ is symmetry-forbidden, because the HOMOs and LUMOs have the same symmetry as the corresponding HOMO and LUMO of H₂. This changes if the Cu₂ molecule becomes embedded in the Cu surface lattice. As demonstrated by Figure 4, group orbitals with antisymmetric coefficients on neighbouring Cu atoms acquire a finite probability to become partially occupied at the Fermi level. The activation energy for H₂ dissociation decreases for two reasons:



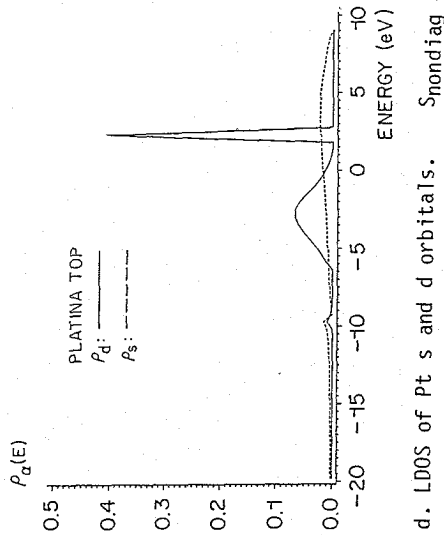
a. LDOS of CO 5σ and 2π* orbitals. Snondiag = 0



b. LDOS of CO 5σ and 2π* orbitals. Snondiag ≠ 0



c. LDOS of Pt s and d orbitals. Snondiag = 0



d. LDOS of Pt s and d orbitals. Snondiag ≠ 0

Fig. 6. Local density of states for Snondiag = 0 and Snondiag ≠ 0; CO chemisorbed on top to Pt

1. the hydrogen-hydrogen interaction is replaced by a metal-hydrogen interaction;
2. weakening of the H-H interaction by population of the antibonding σ^* orbital. Extended Hückel calculation by Baetzold (ref. 11), and by Saillard and Hoffmann (ref. 12) confirm the generality of this picture for the interaction of H_2 with transition-orbital surfaces.

If the hydrogen molecule is adsorbed on top of Cu parallel to the surface, no interaction between the σ^* level and the Cu-s orbital is possible, hence the perpendicular configuration becomes favoured. This is also found for the on-top position of Ni (refs. 11,12) because of the small interaction with its d-valence electron band. In the bridged coordination site parallel adsorption is clearly favoured because of the interaction with the σ^* level, leading to dissociation.

In metals with large d-orbitals the situation may change, because d-orbitals become occupied with a symmetry such that H_2 σ^* orbitals parallel to the surface in the on-top configuration can interact, and reductive elimination by combination of two hydrogen atoms coordinated to a single metal atom may occur because the σ^* interacts with unoccupied d-electrons, as has been proposed for organometallic complexes. Extended Hückel calculations on adsorption to the Ni (111) surface by Saillard and Hoffmann indeed indicate that H_2 adsorption is perpendicular in the on-top configuration, but parallel in bridging coordination.

No comparable calculations have been published for Pt. However, one expects that the interaction with the d-band will increase on going from Ni to Pt, because of the much broader d-band of Pt. This is also indicated by the increased bond strength of CO coordinated to Pt when compared to Ni. So on-top dissociation is more likely to occur on a Pt surface than on a Ni surface. This would explain an interesting catalytic effect, which so far has not been understood.

It appears that hydrogenolysis of alkanes proceeds in quite a different way when catalysed by Pt instead of Ni. On Ni mainly methane is found, whereas on Pt a more uniform cracking pattern is observed (ref. 15,16). Upon alloying with Cu, nickel behaves more like Pt (ref. 16). Methane production implies that dissociation of bonds between primary and secondary carbon atoms predominates. Minot et al. (ref. 17) have made an interesting analysis of the coordination of alkyl groups to a transition-metal surface, which is of interest in this context. They found that hybridization of the carbon atom attached to the metal surface significantly affects the coordination of the hydrocarbon fragment to the metal surface. A primary C atom, after losing its three hydrogen atoms, prefers coordination to three metal atoms. Secondary and tertiary C atoms prefer bridge or on-top coordination. Since the interaction with the d-electron of Ni is much less than that with the d-electrons of Pt (ref. 18), it is the interaction with the s-valence electrons that dominates with Ni. A strong preference for bridge or

threefold coordination will be found for Ni. On the other hand, Pt will also tend to favour on-top coordination. It is well documented (refs. 19,20) that alkane activation occurs by CH dissociation followed by C-C splitting. So it appears that the coordination of primary C atoms is favoured on Ni in three coordination, leading to CH₄ production whereas on Pt secondary and tertiary C atoms are also activated, leading to a more diverse hydrogenolysis product. According to the secondary ensemble effect (ref. 21), alloying with inert metal causes on-top coordination to become favoured, suppressing activation of primary carbon atoms on Ni and thus inducing the Pt atoms to behave more like Ni. It also explains the Pt-type behaviour of Ni in hydrogenolysis reactions upon alloying with Cu.

CONCLUSION

This paper discusses the importance of changes in electronic structure for the coordination of adsorbates on the basis of elementary solid-state quantum chemical considerations. We have shown how this may affect the selectivity of surface reactions. This is of significant importance to the theory of heterogeneous catalysis, which rejected the relevance of the classical electronic factor on the basis of studies in alloy catalysis (ref. 21) and demonstrated the inadequacy of relating the bulk Fermi level electronic density to surface phenomena. We have shown that changes in the surface group orbital local density of states at the Fermi level are relevant to changes of the chemisorptive bond strength.

APPENDIX A

Derivation of expression (3):

With $\rho(E) = \sum_i \delta(E - \epsilon_i)$, expression (1) of the text can be rewritten as:

$$\Delta E_{\text{attr.}} = -2 \left[\int_{E_F}^{\infty} dE \rho(E) \sum_{E_j \leq E_{\text{HOMO}}} \frac{|\beta'_{j,E}|^2}{E - E_j} + \int_{-\infty}^{E_F} d\rho(E) \sum_{E_j \geq E_{\text{LUMO}}} \frac{|\beta'_{j,E}|^2}{E_j - E} \right] \quad (\text{A1})$$

The expression $\beta'_{j,E}$ is given by:

$$\beta'_{j,E} = \langle \varphi_j | H' | \psi_E \rangle \quad (\text{A2})$$

where $\varphi_j(r)$ is the adsorbate molecular orbital and $\psi_E(r)$ a metal surface orbital of energy E . H' is the interaction Hamiltonian of adsorbate and metal

surface. We will study expressions (A1) and (A2) in the tight-binding approximation, so:

$$\psi_k(\epsilon_k) = \sum_l d_l^k \chi_l^m(r) \quad (A3a)$$

and

$$\varphi_j = \sum_n c_n^j \chi_n^a(r) \quad (A3b)$$

The functions $\chi_l^m(r)$ and $\chi_n^a(r)$ are atomic orbitals on the metal and adsorbate, respectively. Substitution of (A3) into (A2) gives:

$$\beta'_{j, \epsilon_k} = \sum_{l, n} c_n^{j*} d_l^k(E) \langle \chi_n^a | H' | \chi_l^m \rangle \quad (A4)$$

Suppose H' is of finite range, then not only index n , but also index l is of finite range. With (A4) one finds:

$$\begin{aligned} \sum_k \delta(E - \epsilon_k) |\beta'_{j, \epsilon_k}|^2 &= \sum_k \langle \varphi_j | H' | \psi_k \rangle \delta(E - \epsilon_k) \langle \psi_k | H' | \varphi_j \rangle \\ &= \sum_k \sum_{l, l'} \langle \varphi_j | H' | \chi_l^m \rangle d_l^k d_{l'}^{k*} \delta(E - \epsilon_k) \langle \chi_{l'}^m | H' | \varphi_j \rangle \end{aligned} \quad (A5)$$

The symmetry of adsorbate orbital determines the linear combination of metal surface atomic orbitals that are projected out by overlap with the adsorbate orbital φ_j . This defines the metal surface group orbital $\chi_{\alpha j}$:

$$\chi_{\alpha j} = \sum_l A_{l, \alpha j} \chi_l^m \quad (A6)$$

Using (A6), (A5) then reduces to:

$$\begin{aligned} \sum_k \delta(E - \epsilon_k) |\beta'_{j, \epsilon_k}|^2 &= \sum_{\alpha} |\langle \varphi_j | H' | \chi_{\alpha} \rangle|^2 \langle \chi_{\alpha} | \delta(E - H_{\text{surf}}) | \chi_{\alpha} \rangle \\ &= \sum_{\alpha} p_{\alpha}(E) \beta_{j\alpha}^2 \end{aligned} \quad (A7)$$

$\rho_\alpha(E)$ is the group orbital surface density of states defined in expression (4). With (A7) expression (A1) can be rewritten as:

$$\Delta E_{\text{attr.}} = -2 \left[\int_{E_F}^{\infty} dE \left\{ \sum_{\alpha} \rho_\alpha(E) \frac{|\beta_{j,\alpha}|^2}{E-E_j} \right\} + \int_{-\infty}^{E_F} dE \left\{ \sum_{\alpha} \rho_\alpha(E) \frac{|\beta_{j,\alpha}|^2}{E_j-E} \right\} \right] \quad (\text{A8})$$

$E_j \leq E_{\text{HOMO}} \qquad E_j \geq E_{\text{LUMO}}$

Expression (A8) will be evaluated using partial integration. Let us consider the term:

$$\int_{E_F}^{E_{\text{max}}} dE \rho_\alpha(E) \frac{|\beta'_{i,\alpha}|^2}{E-E_i} = N_\alpha(E_{\text{max}}) \frac{|\beta'_{i,\alpha}|^2}{E_{\text{max}}-E_i} - N_\alpha(E_F) \frac{|\beta'_{i,\alpha}|^2}{E_F-E_i} - \int_{E_F}^{E_{\text{max}}} dE N_\alpha(E) \cdot \frac{d|\beta'_{i,\alpha}|^2}{dE} \frac{1}{E-E_i} \quad (\text{A9})$$

$N_\alpha(E)$ is the number of electrons accommodated in the valence electron band α , if the band is filled up to energy E , E_{max} is the maximum energy of the valence band electrons. Since we are dealing with weak interactions, the last term in expression (A9) may be ignored. We will expand $N_\alpha(E_{\text{max}})$ around $N_\alpha(E_F)$:

$$N_\alpha(E_{\text{max}}) = N_\alpha(E_F) + \rho_\alpha(E_F)(E_{\text{max}}-E_F) \quad (\text{A10})$$

Substitution of (A10) into (A9) gives for the first two terms of (A9):

$$N_\alpha(E_F) |\beta'_{i,\alpha}|^2 \left[\frac{1}{E_{\text{max}}-E_i} - \frac{1}{E_F-E_i} \right] + \rho_\alpha(E_F) |\beta'_{i,\alpha}|^2 \frac{E_{\text{max}}-E_F}{E_F-E_i+(E_{\text{max}}-E_F)} \quad (\text{A11})$$

As long as $\rho_\alpha(E_F) \gg \frac{N_\alpha(E_F)}{E_F-E_i}$ the first term of (A11) and the last term of (A9)

can be ignored. Substitution of the second term of (A11) and a similar term derived for the second term of (A8) into (A2) results in the desired expression (3) of the text, with $\rho_{\alpha j}$ defined as:

$$\rho_{\alpha j} = \frac{E_F - E_{\text{min},\alpha j}}{E_{\text{max},\alpha j} - E_{\text{min},\alpha j}} \quad (\text{A12})$$

APPENDIX B

The parameters used to derive the table of calculated bond strengths

Ref. 5 gives the full expressions of the self-consistent equations, yielding the figures tabulated. Only the adsorbate levels 5σ and $2\pi^*$, are included in the calculations. $\alpha_{5\sigma}$ and $\alpha_{2\pi^*}$ represent the attractive part of the electron energies, whereas $U_{5\sigma,5\sigma}$ and $U_{2\pi^*,2\pi^*}$ are effective repulsion integrals. The two-centre electron-electron repulsion integrals are zero in the calculations. $\beta_{5\sigma,d}$ or $\beta_{5\sigma,s}$ are the overlap energy integrals of adsorbate orbitals 5σ and metal lattice orbitals s and d . Overlap energy integrals have also been included for the two $2\pi^*$ orbitals. β is the overlap energy integral between metal atom orbitals i,j . The overlap integrals $S_{5\sigma,d}$, etc., between adsorbate orbitals and metal surface orbitals are also listed. The Green functions on the lattices are calculated within the Bethe lattice approximation, as explained in ref. 5.

TABLE 2

Chemisorption parameters (unit eV)

a. Pt:

	s	d
5σ	-2	-1.2
$2\pi^*$	0	-1,1
β' , top		

	s	d
5σ	-2	-1.2
$2\pi^*$	-1.7	-1.2
β' , bridge		

	s	d
5σ	0.01	0.01
$2\pi^*$	0.0	0.02
S ,top		

	s	d
5σ	0.01	0.01
$2\pi^*$	0.005	0.02
S ,bridge		

$$U_{5\sigma,5\sigma} = 10$$

$$U_{2\pi^*,2\pi^*} = 8$$

$$\beta_s = -3$$

$$\beta_d = -1$$

$$E_F = 0.0$$

$$\alpha_{5\sigma} = -19$$

$$\alpha_{2\pi^*} = 1$$

$$\alpha_s = -3$$

$$\alpha_d = -2.3$$

b. Ni:

	s	d
5 σ	-1.6	-0.8
2 π^*	0	-0.7

 β' , top

	s	d
5 σ	0.01	0.01
2 π^*	0.0	0.02

S, top

$$\begin{aligned}
 U_{5\sigma,5\sigma} &= 10 \\
 U_{2\pi^*,2\pi^*} &= 8 \\
 \beta_S &= -1.5 \\
 \beta_D &= -0.5 \\
 E_F &= 0.0
 \end{aligned}$$

c. Cu:

	s	d
5 σ	-1.6	-0.8
2 π	0	-0.7

 β' , top

	s	d
5 σ	0.01	0.01
2 π^*	0.0	0.02

S, top

$$\begin{aligned}
 U_{5\sigma,5\sigma} &= 10 \\
 U_{2\pi^*,2\pi^*} &= 8 \\
 \beta_S &= -1.5 \\
 \beta_D &= -0.5 \\
 E_F &= 0.0
 \end{aligned}$$

	s	d
5 σ	-1.6	-0.8
2 π^*	-0.42	-0.7

 β' , bridge

	s	d
5 σ	0.01	0.01
2 π^*	0.005	0.01

S, bridge

$$\begin{aligned}
 \alpha_{5\sigma} &= -19.4 \\
 \alpha_{2\pi^*} &= 0.6 \\
 \alpha_S &= -1.5 \\
 \alpha_D &= -1.15
 \end{aligned}$$

	s	d
5 σ	-1.6	-0.8
2 π	-0.42	-0.7

 β' , bridge

	s	d
5 σ	0.01	0.01
2 π^*	0.005	0.02

S, bridge

$$\begin{aligned}
 \alpha_{5\sigma} &= -19.5 \\
 \alpha_{2\pi^*} &= 0.5 \\
 \alpha_S &= -1.5 \\
 \alpha_D &= -3
 \end{aligned}$$

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