

Comments on the cluster approach to chemisorption

Citation for published version (APA):

Santen, van, R. A., & Zonneville, M. C. (1992). Comments on the cluster approach to chemisorption. In G. Pacchioni, P. S. Bagus, & F. Parmigiani (Eds.), *Cluster models for surface and bulk phenomena : proceedings of a NATO advanced research workshop, held in Erice, Italy, April 19-26, 1991* (pp. 293-303). (NATO ASI Series, Series B: Physics; Vol. 283). Plenum Press.

Document status and date:

Published: 01/01/1992

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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COMMENTS ON THE CLUSTER APPROACH TO CHEMISORPTION

R.A. van Santen^a and M.C. Zonneville^b

^a Schuit Institute of Catalysis
Faculty of Chemical Engineering
Eindhoven University of Technology
P.O. Box 513, 5600 MB-Eindhoven, The Netherlands

^b Kon/Shell Laboratory
Amsterdam (Shell Research BV)
Badhuisweg 3, 1031 CM Amsterdam, The Netherlands

Abstract

Cluster size and shape effects on the chemical bonding of adsorbed molecules and atoms are summarized. Highlighted are electronic structure features that control coordination preferences. Pauli-repulsion as well as orbital symmetry effects play an important role. Orbital symmetry effects are discussed in terms of symmetry adapted group orbitals. Examples are given for CO, NH₃ and H₂ adsorbed to group VIII and IB metal clusters.

Keywords: Chemisorption, clusters, coordination, electronic structure, orbital symmetry, group orbital.

Introduction

On a catalytically active transition-metal surface, molecules can adsorb and dissociate. The reaction products arise from subsequent recombination of these molecule-fragments and their desorption. The complete catalytic process thus encompasses four elementary reaction-steps: adsorption, dissociation, recombination and desorption. Chemical bonding aspects of the first, of adsorbed molecules and ad-atoms generated upon dissociation, are becoming relatively well understood¹⁻⁵. In addition, a few of the principles controlling surface dissociation or recombination reactions have been formulated, although this subject remains relatively underinvestigated.

Chemisorption of molecules and atoms has been extensively studied using a spectrum of theoretical methods. Initially, mainly formal theoretical physics approaches applicable to semi-infinite systems were used^{7,8,9}. Such approaches find a close link between the theories explaining chemisorption and those used to describe surface-state

phenomenon. It has been found that chemisorption is both a geometric and an energetically local phenomenon. The stronger the chemisorption bond, the broader the energy region of the substrate local density of states that is probed. This can be understood in a very simple view by considering the strength of the interaction to be proportional to an overlap term and inversely proportional to ΔE . Thus the stronger the overlap, the larger ΔE can be to give a non-negligible resulting interaction. The sensitivity of the chemisorption bond to the details of the surface-electronic structure, given by its local density of states, is found to decrease with the parameter μ , being the ratio of the adsorbate-surface interaction strength to the metal-metal interaction strength. From later work¹⁰, it has become clear that μ fluctuates around the value of one, which one may call the intermediate bonding limit.

Details of the surface electronic structure are only essential to the chemisorption bond on a relatively coarse scale, compared to the overall width of the surface local density of states. This is likely the reason for the success of more modern approaches in the analysis of the chemisorption phenomenon. In particular, it can explain the utility of cluster approaches, results of which will be dominated clearly by local electronic factors. More recently, less formal theoretical physics and more chemically based methods have been used. For example, the semi-empirical Extended-Hückel method has been expanded to enable application to two-dimensional infinite slabs as geometrically more accurate models of substrates¹. These studies have taught us the importance of orbital overlap population analysis to probe the electronic interactions. It enables an analysis of the chemical bond in terms of the occupation of bonding and antibonding orbital fragments, these fragments being conveniently defined as adsorbate and substrate separately.

Whereas occupation of bonding orbital fragments results in an attractive contribution to the chemical bond, occupation of antibonding orbital fragments results in a bond weakening or a repulsive interaction. The relative stability of molecules adsorbed in different adsorption sites depends strongly on the extent to which antibonding orbitals are occupied. Also a comparison of the adsorption strength of different molecular fragments to the same site reveals a strong dependence on the antibonding orbital occupation. Whereas the population of bonding orbital fragments tends to favour binding to high coordination sites, population of antibonding orbitals leads to repulsive interactions that tend to become minimized in low coordination sites^{10,11}. The final site preference is controlled by the balance of these two opposing forces¹².

Whereas semi-empirical methods allow only a qualification of such effects, first principle calculations enable their quantification. However, the price to be paid is that a geometrically less precise model must serve to represent the adsorbate-substrate system. For chemical systems the reduction is usually to cluster models.

A potential exception is the LAPW-method, applied, for example, to CO adsorption on slabs of Ni^{13a}. In addition, recent developments of the Local Density Approximation^{13b} (LDA) for use in chemisorption studies on slabs are also of interest. The recent calculation of the adsorption energy of CO in different adsorption sites on a three atoms thick slab of Cu atoms representing the Cu(111) surface is also very promising¹⁴.

The cluster approach

Upon considering a number of different cluster calculations, using ab-initio methods^{3,4,5} as well as the local density method¹⁵, two important guidelines for the analysis of their results emerge. Firstly, of great importance is the balance of electrostatic and repulsive interactions between the orbitals of the two "pre-interacting" systems, i.e. the unperturbed adsorbate and surface independently. The balance between attractive and repulsive features will drive the site preference. The interaction between overlapping doubly occupied orbitals is repulsive.

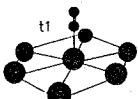

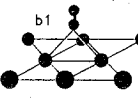
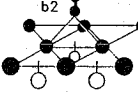
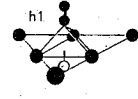
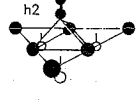
| | <u>E steric</u> | <u>E orbital</u> | <u>Binding E</u> |
|---|-----------------|------------------|------------------|
|  | 2.668 eV | -4.448 | -1.780 |
|  | 1.925 | -4.292 | -2.367 |
|  | 6.371 | -9.126 | -2.756 |
|  | 6.527 | -9.286 | -2.759 |
|  | 8.880 | -11.108 | -2.426 |
|  | 8.686 | -11.108 | -2.232 |

Figure 1. Binding energy contributions of CO adsorbed to Co clusters. Results of LDA calculations¹⁶, with $d(C - O) = 1.5\text{\AA}$; $d(C - Co) = 1.9\text{\AA}$.

Table 1. Geometric and energetic results of optimization of first the C-O distance in model clusters t2, b2 and h2 (as shown in Figure 1), followed by optimization of C-Co distance at this fixed C-O distance.

| Model | d(C-Co) | d(C-Co) | d(C-surface) | B.E |
|-------|---------|---------|--------------|-----------|
| t2 | 1.164 Å | 1.799 Å | 1.799 Å | -2.616 eV |
| b2 | 1.164 Å | 1.900 Å | 1.444 Å | -2.841 eV |
| h2 | 1.164 Å | 2.010 Å | 1.417 Å | -2.510 eV |

Calculation of this interaction, the Pauli-repulsion, using free-fragment-electron distributions show that it is significant. During formation of the chemical bond, electron density is removed from the region between the interacting fragments, so as to reduce Pauli-repulsion^{2,3}. Pauli-repulsion is always found to increase with coordination number and turns out to be atop directing^{2,11}. The attractive contribution to the chemical bond is due to electrostatic interactions as well as electron relaxation³ and/or electron polarization¹⁴. It usually favours high coordination sites.

The interaction of closed shell molecules such as H₂ with a surface is dominated by repulsive features. The interaction is weak and typically the preference is for atop adsorption¹⁵. LDA cluster calculations on H₂ adsorbed onto Ir₄ clusters show specifically that this is due to the strong increase in Pauli-repulsion at high coordination sites. The repulsion can be counteracted by removal of electron density from the bonding regime, for example by means of an electrostatic field as is present near cations in zeolites. Such a field can be mimiced by adding a Mg⁺ cation to the Ir₄ clusters. Indeed, the Pauli-repulsion is reduced with the result that the H₂ molecule can be adsorbed in high coordination sites.

Figure 1 shows recent results of LDA cluster calculations simulating CO chemisorption to the Co(001) surface¹⁷. Calculations have been done at fixed M-C and CO distances. E_{steric} is the sum of electrostatic and repulsive interactions of the non-electronically relaxed fragments. $E_{orbital}$ is the contribution to the bond energy from allowing the low electronic levels of the two systems to interact. Note the increase of E_{steric} as well as $E_{orbital}$ with increasing degree of CO coordination. The overall bond energy is the result of the balance of the two.

Figure 2 summarizes computed Co-C orbital overlap populations which are split into the contributions from the interaction of the CO 5σ with the Co cluster orbitals of the proper symmetry, and the CO 5π with its cluster components. Whereas there is little change in 5σ orbital occupancy, the orbital overlap population changes from a bonding positive contribution (atop) to an antibonding negative contribution (three-fold), corresponding to the increased repulsion energy and larger electron occupation of antibonding orbital fragments in the latter case. As expected the 2π* occupation increases with the coordination number. It corresponds to increased metal surface-adsorbate backdonation. The 2π*-cluster orbital interaction is bonding and increases with the coordination number. This confirms that the 2π*-cluster orbital-fragments are only of a bonding nature and hence favour high coordination sites.

A second important feature emerging from cluster calculations in general is the need to optimize geometry. Bondlengths and angles in the adsorbate as well as cluster change when they interact. Table 1 shows the importance of geometry optimization of CO from the same cluster studies as mentioned above¹⁶.

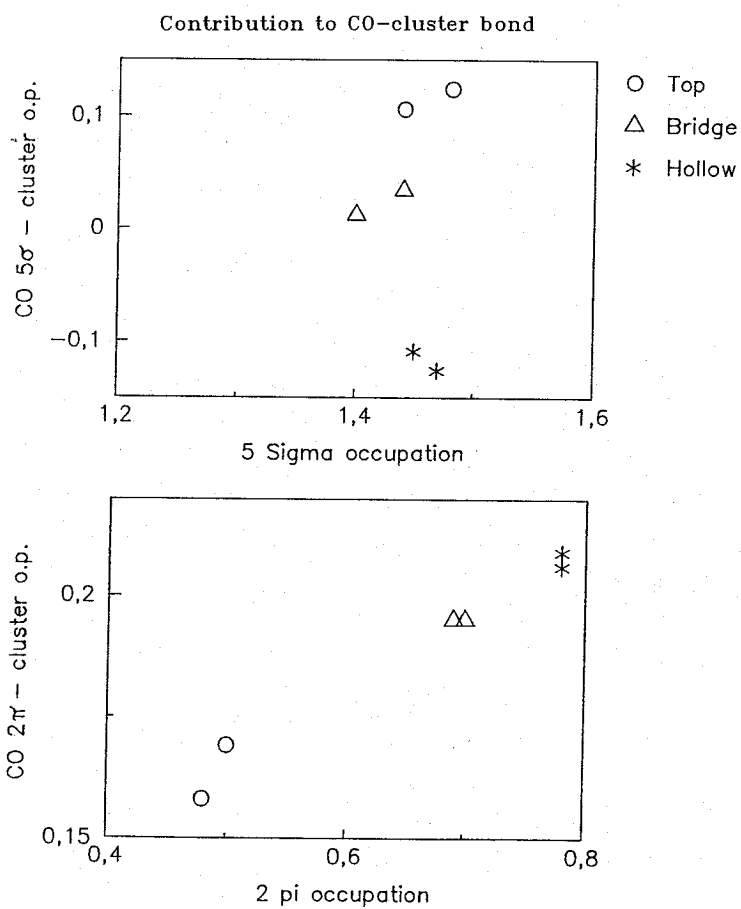


Figure 2. The total CO-Co cluster overlap population is split into the contribution from the CO 5σ-cluster interactions and the CO 2π*-cluster interaction¹⁶.

Bond formation between adsorbate and cluster tends to result in a weakening of the substrate metal-metal bonds between atoms to which the adsorbate coordinates. Especially when atoms, in comparison to molecules, adsorb onto the surface, large displacements may occur¹⁷.

Results may converge slowly with cluster size. Several contributing factors can be mentioned. Firstly, if one wishes to model a particular surface, the geometry of the surface-metal atoms interacting with the adsorbate has to be the same to at least the first coordination shell. For instance, at a (111) surface of a face centered cubic metal, surface atoms have nine metal-atom neighbours. Six of them are in the plane and three are located in the second layer. Clusters modelling chemisorption atop such a surface atom in a (111) surface should include at least these nine metal-atom neighbours. Often, because of cluster size restrictions, such conditions are not satisfied and only interaction between an adatom and nearest-neighbour surface-atoms is considered. Clearly this is only a satisfactory procedure when the metal-atom-adatom interaction strength is large compared to the interaction between the metal atoms.

Secondly, even when the first coordination shell of the surface-metal atom is fully included in the cluster model, a basic difficulty arises. On a real surface, the surface-metal atoms have a lower number of nearest neighbours than bulk atoms do. However, in the ten atoms metal cluster mentioned above, the central atom has nine neighbours, but these neighbour atoms share only four neighbour atoms amongst themselves. This reversal from the real surface situation leads to electron-distribution differences significantly deviating from that of a true surface atom.

One solution is to design special clusters, which do not contain this basic deficiency, as done by Goddard and Upton¹⁸. However, modelling of dense surfaces is necessarily excluded. Alternative approaches are to rearrange the electrons amongst the computed molecular orbitals, in such a way that the electron density on the atom modelling the surface becomes more similar to that of the true surface atom (17, 19).

Thirdly, whereas the large number of *d*-atomic levels in a cluster rapidly results in a *d*-molecular orbital valence electron band, with very small orbital energy differences resembling the continuum of the bulk *d*-valence electron density, this is not the case for the molecular orbitals of predominantly *s* - *p* character. As there are fewer *s* - *p* states, which additionally are more spread in energy the convergence to a continuous bulk valence band is slow.

The role of orbital symmetry

Orbital symmetry effects cannot be discussed without explicit consideration of the valence-electronic structure of the transition-metal surface. The group VIII and IB-metals of main interest to heterogeneous metal catalysis have a valence-electron structure that consists of a narrow *d*-valence electron band with electron occupations varying between six and ten electrons per atom. Overlapping this is a broad *s*-*p* valence-electron band containing approximately one electron per atom. The *s* - *p* valence-electron band can be considered mainly to be constructed from *s*-atomic orbitals. For didactic reasons we will use this simplifying assumption here. In actual calculations, it is found that it is incorrect to ignore the *p*-atomic orbitals, as they can contribute significantly to the surface-chemical bond²⁰.

The interaction with the *s*-valence electrons contributes significantly to the bond energy of adsorbed atoms or molecules, however, in a rather uniform way. Differences in bond energy, often chemically relevant, are more often mainly due to changes in the much smaller contribution derived from the interaction with the *d*-valence electrons. We can imagine the *d*-orbital interaction to serve as a "fine-tuning" of the bond character.

When adsorbed atop, an adsorbate orbital σ -symmetric with respect to the surface normal will interact with a surface metal s -atomic orbital; π -symmetric orbitals will not. At higher coordination sites, where an adsorbate has several surface metal-atom neighbours, orbitals π -symmetric with respect to the surface normal can interact with s -surface orbitals. However, this is restricted to specifically those of the proper symmetry, formed by linear combination of s -atomic orbitals. Symmetry adapted orbitals that are linear combinations of atomic orbitals on different atoms, are called group orbitals¹⁰. A pair of neighbouring atoms will have two types of s -group orbitals; $(s + s)$ bonding and $(s - s)$ antibonding.

Depending on the adsorption site and the critical adsorbate orbital, different surface group orbital local densities of states are probed upon chemisorption. Their energy distributions are generally quite different^{10,21} and consequently, so are the interactions with the adsorbate orbitals.

Because of the many d -atomic orbitals, symmetry constraints are less severe. σ , π as well as δ -symmetric interactions are possible also in the atop adsorbed mode. Again, in high coordination sites, different d -group orbitals will be able to interact depending on symmetry.

A general trend for σ -symmetric interactions is that high coordination sites are favoured as long as only bonding orbital fragments are occupied. This is usually the case when valence-electron bands are not more than half filled. Thus the interaction with s -valence electrons will favour high coordination sites, for σ -type interactions for the very reason mentioned above and for π -type interactions because they only occur in high coordination sites.

To understand the interaction with the substrate d -levels, recall that the group VIII or IB transition metals have nearly completely or completely filled d -valence electron bands and that adsorbates often have doubly occupied σ -orbitals but empty π -type orbitals. Because σ -symmetric antibonding combinations become filled, Pauli-repulsion now becomes important and preference drifts from high coordination to low coordination sites. Because bonding orbital fragments are usually occupied, these π -type interactions favour high coordination sites. The spatial extent of d -atomic orbitals increases moving downwards along a column of the periodic system, hence the interactions with the d -valence electrons tend to increase.

Thus whether atop or high coordination is preferred depends on the balance of the strength of the interaction with the s -valence electron interaction favouring high coordination sites and σ -type interaction with the d -valence electrons, tending to favour atop adsorption. Whereas on Ni, CO prefers high coordination sites, on Pt atop coordination is preferred. The 5σ orbital interaction with the d -valence electrons yields the atop directing force. Ammonia, predominantly interacting with a doubly occupied σ -symmetric orbital prefers atop adsorption on Cu. Its atop directing interaction with the doubly occupied Cu d -valence orbital tips the balance²². The methyl radical, with a very similar electronic orbital structure as NH_3 , prefers high coordination to a Ni(111) surface²³. Here the balance of σ -type interactions is dominated by the high coordination directing interaction with the metal s -valence electrons²⁰.

Association and dissociation reactions

In surface dissociation and association reactions, orbital symmetry considerations are also important. The effect of the metal surface is to lower the activation energy for dissociation or recombination. We will discuss the course which a dissociation reaction takes. The propensity for dissociation increases as the antibonding orbitals become populated. This is what happens on a metal surface during the formation of the chemisorptive bond. Since for the molecule parallel to the surface antibonding orbitals are π -symmetric will respect to the surface normal, occupied antisymmetric surface

group orbitals have to interact. This can occur with *s*-valence electrons in high coordination sites, as has been found for O₂ on the Ag(110) surface²⁴ or with *d_{xz}* or *d_{yz}* atomic orbitals in side-on atop adsorbed configurations⁶. For the (111) and (100) surfaces of Rh, Extended-Hückel calculations indicate that CO dissociation is activated in the latter geometry.

For the overall thermodynamics of the surface reaction, the difference in energy of the adsorbed molecule versus that of the adsorbed atoms generated upon dissociation is important. The chemisorptive bondstrength of a molecule varies much less between different metals than does that of adsorbed atoms. In a molecule the difference in energy between bonding and antibonding orbitals is directly related to the molecular bondstrength. In the atom the valence-atomic orbitals are usually partially occupied and have an energy inbetween the bonding and antibonding energy levels of a molecule, and in general have a better energy match with the substrate *d* levels. Figure 3 shows the computed LDOS of C-2*p* atomic orbitals of a C atom threefold coordinated to a nine-atom cluster modelling the Co(0001) surface²⁵. One distinguishes the bonding and antibonding orbital components around the Fermi level.

Clearly bonding to the metal surface is dominated by interaction with the carbon *p*-atomic orbitals. Analogous to CO, interaction with the surface results in a $\sigma - (p_z)$ and $\pi - (p_x, p_y)$ type interactions. In the case of an adsorbed atom, depletion of antibonding orbital fragments enhances the adatom interactions of σ as well as π -type symmetry.

Contrary to atomic adsorption, changes of the *d*-valence-electron band occupation to the chemisorptive bondstrength for molecules will be symmetry dependent.

For instance, a decrease in *d*-valence-electron-band occupation enhances the σ -type interaction (repulsion decreases) but decreases the π -type interaction (attraction decreases).

Figure 4 illustrates the effect of varying the *d*-valence-electron occupation on the dissociation energy and activation energy of CO dissociation, as computed for a 40 atom cluster with the ASED method²⁷, which is an extension of the Extended-Hückel method. Because atoms prefer high coordination sites, the clusters have to be chosen large enough that proper surface ensembles for the dissociating molecule are available.

Chemisorption to different surfaces

Finally, the difference in reactivity of metal surfaces of different degree of coordinative unsaturation is deserving of comment. It is known that heats of adsorption tend to increase and activation energies of dissociation tend to decrease on more open surfaces²⁸. The surface atom degree of coordination is largest on the most dense surfaces. The local density of states distribution of the valence electrons is broadened in approximate proportionality to the coordination number of the surface atom considered. Thus the electrons of a dense surface can be considered more delocalized. As a consequence, the interaction with adsorbing atoms or molecules decreases. The splitting between bonding and antibonding orbitals, or the ad-orbital bandwidth, is proportional to the effective interaction, and increases when surface atoms become coordinatively less saturated², i.e. on less dense surfaces. It implies that attractive orbital interactions increase as long as bonding orbital fragments are occupied. The repulsive interactions increase when antibonding orbital fragments are considered.

Since the interaction with the *s*-valence electrons usually dominates, the overall effect is an enhanced interaction energy. So one expects bonding to edge atoms to be stronger than to atoms in the center of a surface plane. Additional effects that have to be considered are changes in the coordination-site geometry when different surfaces are compared. Such effects may overrule the intrinsic changes in chemical reactivity of the surface atoms.

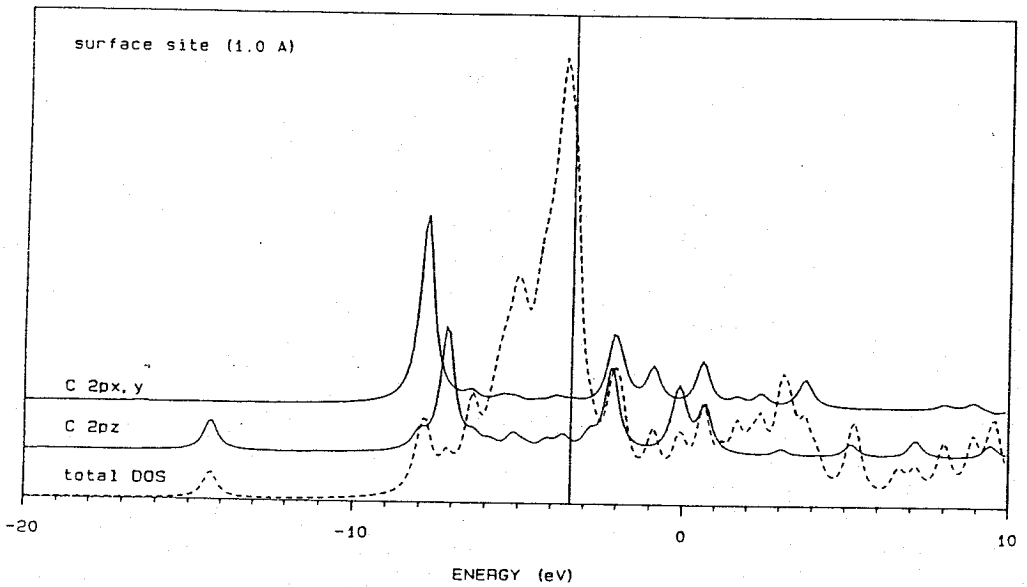


Figure 3. Projected Density of States (DOS) of C $2p_z$ (20x) and $2p_x, 2p_y$ (10x), and total (DOS) (dashed lines) for Co_3C clusters with C at $z=1.0 \text{ \AA}$. Results of LDA calculations²⁵.

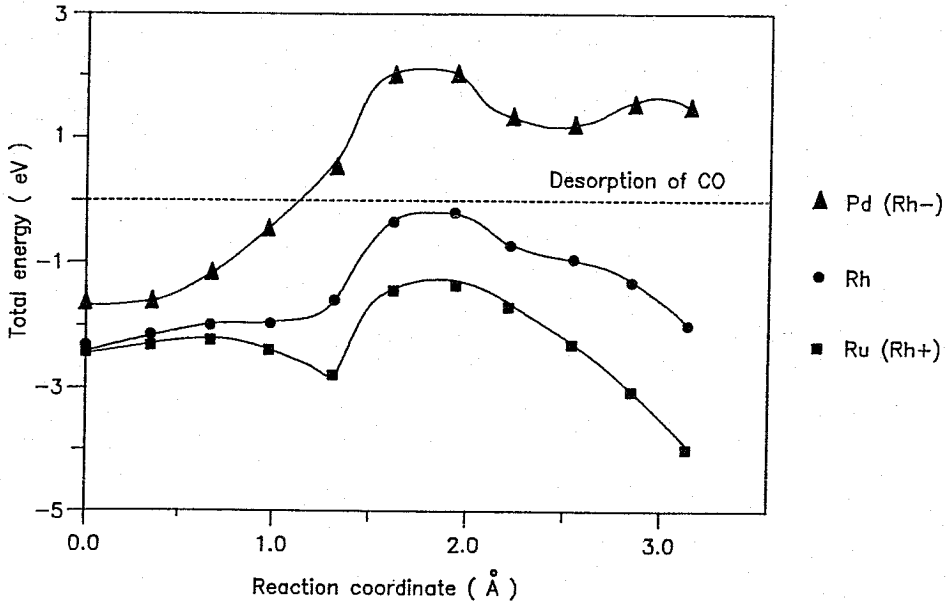


Figure 4. Changes in CO dissociation activation energy as a function of valence-electron occupation, on a fcc (111) surface of 40 metal atoms. Ru and Pd are created from Rh by respectively subtraction or adding 1 electron from the valence electrons²⁶.

Whereas low coordination atoms can easily be modelled using small clusters, care has to be taken to account properly for electrostatic surface potential effects.

The workfunction of metal surfaces decreases with decreasing surface-atom coordination. This is due to accumulation of positive charge on edge atoms and smearing out of the negative charge in surface valleys²⁹. Clearly clusters provide interesting systems to model this. The atoms bounding a cluster, simulating a dense surface, usually have low coordination and are edge like and first principle methods accounting properly for electrostatics are available to explore this.

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