

THE CALCULATION OF SURFACE ORBITAL ENERGIES FOR SPECIFIC TYPES OF ACTIVE SITES ON DISPERSED METAL CATALYSTS.

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Abstract

An angular overlap calculation has been used to determine the s, p, and d orbital energy levels of the different types of surface sites present on dispersed metal catalysts. These data can permit a Frontier Molecular Orbital treatment of specific site activities as long as the surface orbital availability for overlap with adsorbed substrates is considered along with its energy value and symmetry.

1. Introduction

While dispersed metal catalysts have been used to promote a variety of reactions there are still a number of problems to be solved before new catalysts and processes can be developed from first principles. Among these are questions concerning both the nature of the active sites and a reasonable description of the surface electronic orbitals present on them. With these data Frontier Molecular Orbital (FMO) considerations which have been so useful in organic synthesis [1] could also be applied to reactions taking place on the catalyst surface. Among the recent approaches to this problem has been the calculation of the Density of States (DOS) for the 111 and 100 faces for a number of metals. These surface bands were found to be rather narrow indicating a reasonable degree of localization of the atomic orbitals on the metal surface.[2]

Data have also been obtained which show that reactions involving C-C bond cleavage or hydrocarbon isomerization occur on ensembles of atoms present on the metal particles. Most other reactions, particularly those involving C-H bond formation or breaking take place on single atom sites, the more highly coordinately unsaturated corner or defect atoms.[3, 4] The problem, then, is that while the DOS and related calculations have been successful in determining the adsorption characteristics of the 111 and 100 metal planes, extension of this approach to the determination of the adsorption and reaction characteristics of single atom active sites present as edge and corner atoms resulting from the intersection of these planes is not straightforward.

2. Nature of the Surface Active Site

With the catalytically active site for most synthetically useful reactions being a single surface atom [3, 4] and the Isoglobal Analogy [5] stating that such sites can be thought of as discrete entities, it would seem reasonable to consider the surface of a metal particle as being made up of a number of different types of "surface complexes" composed of a central metal atom surrounded by its nearest neighbor "ligands" with the surface orbitals of this active site localized and perturbed only by interaction with the nearest neighbor, "ligand" atoms. The degree of surface electron localization found by the DOS calculations lends support to this assumption.

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Most catalytically active metals have an fcc crystal orientation and, as such, have atoms in the bulk which are surrounded by twelve neighboring atoms as shown in Fig. 1. One can, then describe all of the different types of single atom surface sites by removing various atoms from this central, twelve coordinate, species. By doing this thirteen different types of sites can be identified and distinguished by their orientation and their number of nearest neighbors (Fig. 2). These range from atoms on the two low Miller index faces, the 111 (site A) and 100 (site B) to four edge sites made up by the intersection of these planes at 120° (wide) or 60° (narrow) to seven different types of corner atoms ranging from the cubooctahedral corner (site G) to the tetrahedral corner (adatom on a 111 face) (site M). For reaction purposes the 110 face is best described as a series of narrow 111-111 edges. Since in the fcc metal lattice the nearest neighbor atoms are bonded by t_{2g} d orbitals [6], the 90° intersection is not permitted so the cubic 100-100 edge does not exist.

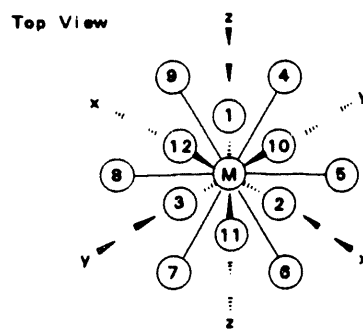


Fig. 1. Basic "twelve coordinate complex" from which surface sites are formed.

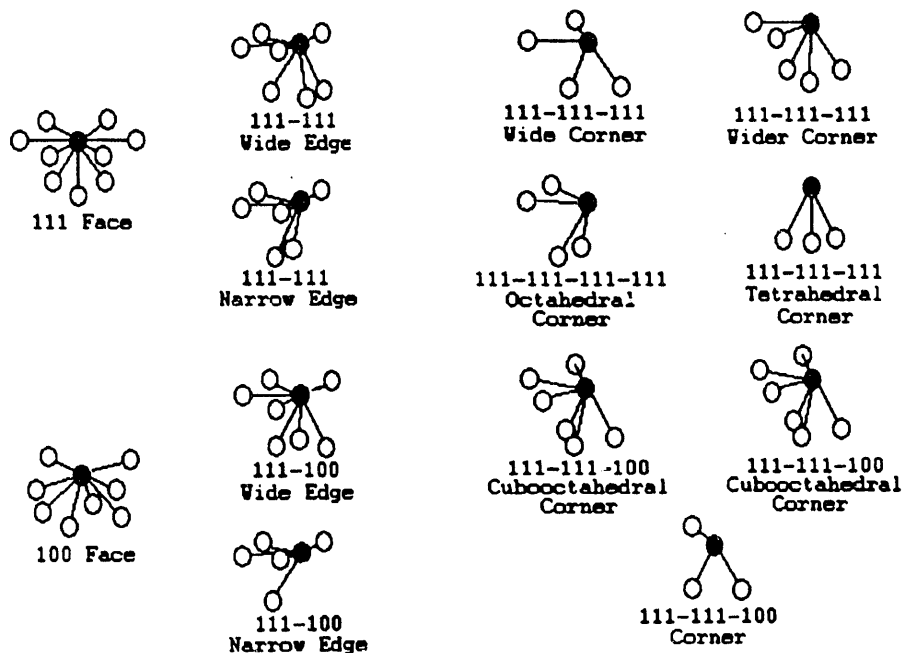


Fig. 2. Diagrams of the various types of atoms present on the surface of an fcc metal.

3. Angular Overlap Model

With the assumption being made that the catalytically active sites on a metal particle can be treated as "surface complexes" it should be possible to extend the analogy and calculate the orbital energy levels for each site using classical inorganic techniques. That approach considered to be the most useful in the present instance is the angular overlap model (AOM) [7] which is sufficiently general to be applicable to the wide range of sites

shown in Fig. 2. The AOM is a simple approximation of the full MO model which still contains all of the important characteristics of the metal-ligand (M-L) interactions in complexes. The primary difference between these two models is the simplifying assumption in the AOM that the energy values for the entire complex are considered as the sum of the energies of the individual M-L interactions. The energy of each M-L interaction is proportional to the square of the overlap integral between orbitals on the M and L atoms. This overlap can be broken down into two integrals, one composed of the radial components and the other comprised of the angular components of the overlapping atomic orbitals. AOM is used to determine the angular dependence of the overlap integral for each type of orbital. The spherical coordinates which are required for AOM calculations [7] were determined by placing the x, y, and z axes coincident with the direction of the e_g orbitals on the central atom as depicted in Fig. 1. These axes were thus fixed in a constant orientation for all of the "surface complexes".

To determine the orbital energy levels for a site the spherical coordinates for each ligand were inserted into the appropriate angular overlap matrix developed by Schäffer [8] to obtain the individual p and d orbital overlap integrals between the central atom and the ligand. These are then squared and summed to give the overlap energy for the specific ligand. This process is repeated for each ligand and the results added to give the energies of each p orbital in terms of $e_{p\sigma}$ and $e_{p\pi}$ and each d orbital in terms of $e_{d\sigma}$, $e_{d\pi}$ and $e_{d\delta}$, which are factors in the radial component of the M-L overlap integrals.[7] Since s orbitals are symmetrical there is no angular component associated with s orbital overlap so the s overlap integrals are expressed in terms of $e_{s\sigma}$ multiplied by the number of "ligands" associated with the "surface complex".

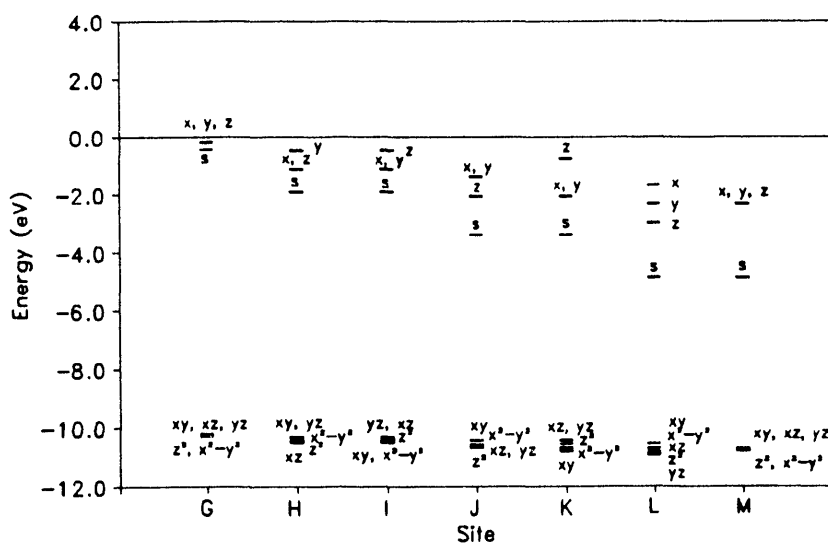


Fig. 3. Energy levels for the 6s, 6p and 5d orbitals on corner atoms on Platinum.

the metal. The various orbital energy levels for each type of surface site were then calculated with the results for Pt corners depicted graphically in Fig. 3.

These data can be used for a Frontier Molecular Orbital (FMO) development of specific site reactivity. For this to be effective, though, it must be kept in mind that these surface sites are rigid and have definite geometric and steric relationships between the active sites and the nearby surface atoms, be they "ligands" or not. Thus, some of the surface orbitals may be oriented in such a way that they are sterically not available for chemisorption even if the energy and symmetry are correct. It is essential, then, that these

To this point the solution is generic and can be applied to any metal with an fcc crystal orientation.

The differences between these metals lie in the values of the s, p, and d overlap integrals for each metal. The values of $e_{s\sigma}$, $e_{p\sigma}$, $e_{p\pi}$, $e_{d\sigma}$, $e_{d\pi}$ and $e_{d\delta}$ were determined for each metal by an EHMO calculation on the diatomic M - M with the overlap integrals calculated from Slater type orbitals using published Huckel parameters [2] for the surface metal atoms and the bulk interatomic distance of

steric constraints to maximum substrate interaction be determined before using this FMO approach.

The single atom active site responsible for the hydrogenation of double bonds must have sufficient coordinative unsaturation to chemisorb both a H₂ molecule and an alkene on the same atom. Such a site could be the tetrahedral corner (Site M, Fig. 2). As shown in Fig. 4 H₂ chemisorption can take place on this site by σ donation from the H-H bond to the LUMO 6s orbital. Backbonding to the σ^* orbitals can occur using the HOMO d_{xz} orbital lobes. Double bond adsorption on the resulting M-H₂ species can take place through alkene π donation to the now LUMO p_y orbital along with back bonding to the π^* orbitals using the HOMO d_{xy} orbital lobes. The catalytic cycle is then completed by hydrogen insertion to give a hydrido metalalkyl which then undergoes reductive elimination to produce the alkane and regenerate the active site.

It appears, then, that AOM calculations on single atom active site "surface complexes" on a metal catalyst can provide data concerning the localized surface electron energy levels which are useful in understanding the adsorption and reaction characteristics of the various types of sites present on dispersed metal catalysts. The primary factor in the use of these data is that the availability of the orbitals for overlap with adsorbing substrates must be considered along with their energy and symmetry. Extension of this approach to the calculation of electron energy values for sites on which H is adsorbed has been somewhat successful. Preliminary data indicate that H adsorbed on a tetrahedral Au atom results in bond energies higher than those of the H-H bond. With other metals the energy is lowered. Such data could explain why Au is inactive for catalytic hydrogenations.

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References

1. R. B. Woodward and R. Hoffmann, Conservation of Orbital Symmetry, Academic Press, NY, 1970.
2. S. -S. Sung and R. Hoffmann, *J. Am. Chem. Soc.*, **107**, 578 (1985); M. C. Zonneville and R. Hoffmann, *Langmuir*, **3**, 452 (1987) and references cited therein.
3. J. H. Sinfelt, J. L. Carter and D. J. C. Yates, *J. Catal.*, **24**, 283 (1972); P. S. Kirilin and B. C. Gates, *Nature*, **325**, 38 (1987).
4. R. L. Augustine and M. M. Thompson, *J. Org. Chem.*, **52**, 1911 (1987); R. K. Herz, W. D. Gillespie, E. E. Petersen and G. A. Somorjai, *J. Catal.*, **67**, 371 (1981).
5. R. Hoffmann, *Angew. Chem.*, **21**, 711 (1982).
6. J. B. Goodenough, Magnetism and the Chemical Bond, Interscience, NY, 1963.
7. J. K. Burdett, *Adv. Inorg. and Radiochem.*, **21**, 113 (1978); R. S. Drago, Physical Methods in Inorganic Chemistry, Saunders, 1977, pp 396-406.
8. C. E. Schäffer, *Pure and Applied Chem.*, **24**, 361 (1970).

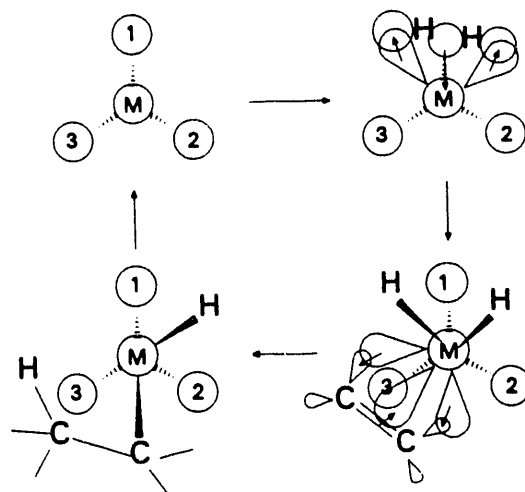


Fig. 4. Alkene hydrogenation sequence on a tetrahedral corner atom of Pt.

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