HOKKAIDO UNIVERSITY

Title	COMPLEX ROLE OF d-ELECTRONS IN CATALYSIS BY TRANSITION METALS
Author(s)	JOHNSON, O.
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 28(3), 215-222
Issue Date	1981-06
Doc URL	https://hdl.handle.net/2115/25091
Type	departmental bulletin paper
File Information	28(3)_P215-222.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

J. Res. Inst. Catalysis, Hokkaido Univ., Vol. 28, No. 3, pp. 215 to 222 (1980)

COMPLEX ROLE OF *d*-ELECTRONS IN CATALYSIS BY TRANSITION METALS

By

O. JOHNSON*)

(Received July 21, 1980)

Abstract

The different behavior of localized *d*-electrons and mobile *s* and *p*-electrons in chemisorption is discussed in relation to the dominant role of *d*-electrons in the cohesion of transition metals. The important role of a category of itinerant *d*-electrons is also included in the model proposed for chemisorption and catalysis. Recent data from angle-resolved photoelectron spectroscopy support this participation of *d*-electrons. The similarity for catalysis of surface complexes on transition metals to the transition metal cluster compounds is consistent with this model.

Introduction

A large body of experimental work establishes the complexity of chemisorption on transition metal surfaces, and theoretical calculations for chemisorption are extremely difficult. In addition to the choice of a representative model and the approximations for the wave mechanical calculation, the theoretical treatment must take into account the changes at the metal surface compared to the bulk, possible reorganization in presence of adsorbate and the effect of adjacent adsorption sites. There is a multiplicity of surface sites, including attachment to a single metal atom, a bridged binding to two metal atoms and 3 or 4-center binding; there are also low coordination sites at steps and kinks of a single crystal surface. Adsorbents such as CO or hydrocarbons can also dissociate.

As a result of different theoretical approaches and assumptions, there is not a generally accepted conclusion as to the involvement of transition metal *d*-electrons in chemisorption and catalysis. Knor[1] has discussed the evidence for participation of both metal conduction electrons and localized *d*-electrons in chemisorption. The author has proposed a model for *d*-orbital participation in a "surface complex"[2] similar to that proposed by

*) Chemistry Department., University of Pittsburgh, Pittsburgh, Pennsylvania 15260; Present address, Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 OHE, England.

Bond.[3] Melius[4] has made a sophisticated calculation for chemisorption of H on Ni and concluded that localized *d*-electrons are not involved in this chemisorption except in reorientation of orbitals during surface catalysis. Messmer *et al.*[5] using an $x-\alpha$ method of calculation conclude that *d*-orbitals are involved in chemisorption of H on Pd or Pt but not for Ni. Gomer[6] and Muscat and Newns[7] have discussed the variety of methods of calculation of chemisorption and have demonstrated how the two main contributions emerge, the localized bonding *via* directional *d*-like orbitals and screening effects *via* nonlocalized *s*-electrons. Salem and Leforestier[8] and Minot, Kahn and Salem[9] have emphasized the chemical nature of *d*-electron waves in metals and use symmetry based descriptions of "surface (orbital) amplitude patterns" in chemisorption.

The above summary is intended to include only contributions which deal specifically with *d*-electrons. It should be added that it is now abundantly clear that the earlier concepts which related catalysis and chemisorption to "holes in the *d*-band" and changes in activity for certain alloys to "filling of the *d*-band" are not valid.[10]

In this short paper a discussion of metallic binding will be given to show the predominant importance of localized *d*-electrons in cohesion of transition metals and to show the need for a category of itinerant *d*-electrons.[11] Then a model for chemisorption will be suggested which takes into account in a qualitative way most of the complexities mentioned above. Finally, the experimental work supporting this model will be presented.

Aspects of Chemical Binding in Metals

The author has used an Interstitial-Electron Model (IEM) for metals[12] in previous discussions of Chemisorption[13] and Catalysis.[14] Since this model can be related to both band theory and valence bond treatments of metals it is appropriate for a chemical discussion of the metal surface and chemisorption. In the IEM the idealized metallic binding is considered to be the electrostatic attraction of freely moving conduction electrons and the positive ion cores. The conduction electrons have a relatively uniform electron density in the interstital regions compared to that in ionic or covalent binding. However, there are expected to be flat maxima in valence electron density at the center of octahedral or tetrahedral interstices in the metal lattice. Such a maximum in electron density had been observed experimentally for Be[15,16] and found by calculation of electron density for Mg and Al[17] and Nb.[18] This pattern of conduction electron distribution also follows the consideration that the moving conduction electron spends the least time in the vicinity of the positive ion core. The electron density in interstitial

regions can be determined by assigning electrons to oct and tet interstices just as electrons are assigned to bonds in covalent compounds or to the anion in ionic compounds. In assigning electrons to oct or tet interstices, it is assumed that electrons of the same spin occupy non-adjacent interstices; thus, the geometry of the lattice is an important factor in electron distribution.

The close-packed metal lattices have 1 oct and 2 tet interstices per atom and 6 itinerant electrons would fill the interstices with paired electrons; thus, the model suggests that *d*-electrons become localized when the core charge of the transition metal reaches +6. Studies of *d*-electrons by polarized neutron diffraction[19] and by analysis of positron annihilation data[20] indicate that the number of localized *d*-electrons increases from Group VI to the end of the transition series. At the same time the number of itinerant *d*-electrons (*d*-electrons which exchange with conduction electrons), which has reached a maximum of 3.5 at Group VI declines to 3 at Group VI, to a fraction of an electron for Fe, Co and Ni and to zero for Cu.

This model for metals describes electrons in terms of their spatial location and can be used in a complementary fashion with band theory, *e.g.*, the itinerant *d*-electrons are at the top of the *d*-band of transition metals and have localized wave functions. The IEM treats a metal as an array of positive ion cores in an almost uniform valence electron density, and the concept of screening differs from that of the Wigner-Seitz model based on close-packed atomic spheres. In the IEM it is considered that the filled *d*-orbitals are directed toward nearest neighbor ion cores where the *d*-electrons act to screen the positive ion core repulsions and thus indirectly contribute to the chemical binding.

Gelatt *et al.*[21] analyzed the chemical binding for $3d$ and $4d$ metals using a "renormalized atom" approach. In an extensive set of SCF calculations using the local density approximation to electronic exchange and correlation effects, Moruzzi *et al.*[22] demonstrated that such calculations accurately described the lattice constant, cohesive energy and compressibility of the full range of metals given only the atomic number. In a treatment designed to present these results in terms of physically understandable concepts, Williams *et al.*[23] demonstrated the predominant role of localized *d*-electrons in the cohesion of transition metals.

The category of itinerant *d*-electrons (d_i) was discussed from the point of view of band theory by Stearns.[24] These d_i are at the top of the *d*-band and have parabolic bands. The d_i show up in spin density maps of Gd[19] in a diffuse region next to the positive ion core. They are antibinding electrons of the metal in that they add to the screening of the ion core-

conduction electron attraction. A partition into localized and itinerant d-electrons has also been proposed by Moldovan[25] to explain data on plasmon oscillations of transition metals. In terms of the IEM the d_i move between the interstitial region near the ion core and the localized d-orbitals on the ion core,

There have been a limited number of treatments of the electronic structure of the surface layer of transition metals. The author has given a qualitiative description of electron density[26] at the surface. Haydock and Kelly[27] have shown there to be a narrowing of d-bands at the surface in their band structure calculations. Desjonquéres and Cyrot-Lackmann[28] have used a tight binding scheme and shown an asphericity of charge density for Fe, Co and Ni. They give the orbital occupancy for d-orbitals of these metals. Arlinghaus *et al.*[29] have obtained self consistent densities of states and charge densities for thin films of Cu (100) and Ni (100) and N chemisorbed on Cu. There is a rapid change in density of states at the surface and a localization of the chemisorption bond. The surface studies of Salem *et al.*[8,9] have already been mentioned.

Models for Chemisorption at the Transition Metal Surface

Any generally useful model for the surface complex in chemisorption on transition metals must satisfy a large number of known properties of these systems, *e.g.*, the multiplicity of surface species (known from temperature programmed desorption). It must also account for the extremes in chemical binding, such as the nearly ionic attachment of alkali metal atoms which donate electrons to become positively charged adsorbents or the halogens which attract electrons to become anionic species on the surface.[30] The molecules of greater interest in catalysis are H_2, CO, N_2 and hydrocarbons. The first three attract electrons from the metal and attain a net negative charge as absorbents. This is shown by the increase in metal work function upon chemisorption[13] and by chemical shifts of core level binding energies to lower energies in x-ray photoelectron spectroscopy.[31] Hydrocarbons show the opposite effects and have a small net positive charge when adsorbed. The small electron transfer in chemisorption has been discussed in detail by Ugo.[32]

There is no reason to expect that the chemisorbed molecules just referred to will take positions of missing atoms of metal above the surface; rather they will prefer positions above the surface corresponding to interstitial regions of high electron density of the metal lattice. Thus, the d_i rather than localized d-electrons are of greatest importance in chemisorption.

The model generally used in discussions of chemisorption of molecules

like olefines or CO is the Dewar-Chatt model.[3] In the case of CO this model considers the chemical binding as due to electrons from CO forming a σ-bond with the e_g orbital of metal, and to electrons from metal t_{2g} orbitals donated to empty antibonding orbitals of CO forming a π-bond. Bond[3] has used this model to indicate attachments of CO and olefins using the scheme of metal orbitals suggested by Trost and Goodenough.

The author has proposed a similar model[2] for the "surface complex" which sets out the d-orbital requirements for chemisorption while also including the participation of conduction electrons of the transition metal. The following will include some modification and addition to the model as previously described.[2] The degeneracy and occupancy of the d-orbitals of the surface transition metal atoms follow from the geometry of the lattice and the core configurations[34], which specify numbers of localized and itinerant d-electrons; the d-orbitals directed toward nearest neighbor metal atoms are at the lowest energy level (band) and those toward oct interstices are at the next highest energy while those directed toward tet interstices are at the highest energy level. The following main points of the model extend the earlier description of the "surface complex":

(1) An adsorbate will be chemisorbed on a transition metal surface in the direction of empty or partially filled d-orbitals. There will be no chemisorption in the direction of filled d-orbitals.

(2) An adsorbate may have either a net positive or negative charge compared to the metal surface, and this is accompanied by an appropriate shift of the bonding electron density as expected for a metallic substrate. The chemical binding of an adsorbate to the transition metal surface is similar to that in transition metal cluster complexes but with greater delocalization of the bonding electrons.

(3) Itinerant d-electrons can initiate chemisorption by their facile movement into the above described binding region of the surface complex. There can also be shifts of d_i to give optimum core configuration for chemisorption; *i. e.*, localization of some d_i or shifting of d_i to the conduction band (renormalization.[21])

An example will be given to show how the IEM is used to characterize a surface complex. The core configurations of the metal which are central to the scheme have been derived from positron annihilation data.[20] These core configurations agree well with those available from band structure calculations, but due to lack of complete data on positron annihilation for $4\,d$ and $5\,d$ metals, core configurations for some of these metals are tentative. A more complete discussion of transition metal surface complexes will

be deferred to a subsequent paper.

The electronic configuration determined for Re metal is

$$\left|\mathrm{Re}^{7+}(d_l)^4(d_i)^2,\ 1\bar{e}\right|_{\mathrm{HCP}}$$

a configuration which shows 4 localized and 2 itinerant d-electrons and 1 conduction electron per metal atom. The d-orbital degeneracy, based on the interaction of d-electrons with both nearest neighbor ion cores and the electron density in interstital regions, is as follows;

$$\begin{array}{ccl} & & z^2 \\ \underline{d_i} & \underline{d_i} & xz, yz \\ \underline{d^2} & \underline{d^2} & xy, x^2-y^2 \end{array}$$

This is the same degeneracy as used by Desjonquéres and Cyrot-Lackmann[28] for HCP cobalt, and the IEM places 4 localized d-electrons in the xy and x^2-y^2 orbitals and 2 itinerant d-electrons in the xz and yz orbitals. Each of the above levels represent overlapping bands with the d_i in a very broad band. For Re (0001) the fully occupied d-orbitals are in the surface layer and the vacant z^2 orbital is perpendicular to the surface; the xz and yz orbitals emerge at 45° to the surface. Upon chemisorption of CO a core configuration of $|\mathrm{Re}^{7+}(d_1)^4|$ is expected with a shift of d_i to a binding region; there will be shifts of electron energies and possible further splitting.[35] In a bridging attachment of CO to Re (0001) the CO will be in the direction of xz and yz orbitals. In using the model, experimental properties such as work function and resistivity indicate direction of electron transfer and the effect of additives or other surface species.

The surface complex described in this section offers a very general description of chemical binding in chemisorption. It is consistent with M. O. descriptions of valence electrons and with band theory calculations; it adds a spatial characterization of the valence electron density to the alternate treatments.

Experimental Support for the Model

There is direct evidence for the involvement of d-electrons in chemisorption in the study of CO on the (0001) plane of Re by Braun *et al.*[35] They find from their angle-resolved photoemission study that there is an attenuation of density of states of the d_{xz} and d_{yz} orbitals. The attenuation extends over a rather broad region of energy as is expected from the above discussion of d_i which have the broad band of itinerant electrons. The d-orbital

degeneracy developed by Braun *et al.*[35] differs in detail from that given in the previous section.

Demuth[36] concluded from photoemission studies of H chemisorption on Pd and Pt that there was domination by the *d*-orbitals in the chemisorption. Another example of the shift in states of the *d*-band is in the study of the chemisorption of oxygen on Ni(100) by Ertl and coworkers.[37] In this case there was no appreciable shift in the metal *d*-band until there was NiO formation with the appearance of the d^8 configuration of Ni^{2+}. Since Ni metal has a large number of localized *d*-electrons and only a fraction of an itinerant *d*-electron, changes in the *d*-band on chemisorption are expected to be small.

Conclusions

The model of a "surface complex" on a transition metal surface described in this paper is characterized by a chemical binding which has aspects of a localized bond but one in which previously itinerant *d*-electrons participate. The model thus allows for an indirect effect of metal conduction electrons as well as "renormalization" of the ion core configuration. The model is compatible with similar descriptions of transition metal cluster complexes by Ugo[32] and Moskowitz[38].

References

1) Z. Knor, Ch. 3 in "Surface and Defect Properties of Solids", Vol. 6, Spec. Periodicals Series, Chem. Soc., London, 1977.
2) O. Johnson, J. Res. Inst. Catalysis, Hokkaido Univ., **22**, 157 (1974).
3) G. C. Bond, Disc. Farad. Soc., **41**, 200 (1966).
4) C. F. Melius, Chem. Phys. Lett., **39**, 287 (9976).
5) R. P. Messmer, D. R. Salahub, K. H. Johnson and C. Y. Yang, Chem. Phys. Lett., **51**, 84 (1977).
6) R. Gomer, Accounts of Chem. Res., **8**, 420 (1975).
7) J. P. Muscat and D. M. Newns, Prog. in Surf. Sci., **7**, 1 (1978).
8) L. Salem and C. Leforestier, Surf. Sci., **82**, 390 (1979).
9) C. Minot, O. Kahn and L. Salem, Surf. Sci., **94**, 515 (1980).
10) F. C. Tompkins, 6th Int. Congress on Catalysis, Vol. 1, p. 32. Chem. Soc., London, 1977.
11) O. Johnson, "Transition Metals, 1977", Conf. Series No. 39, Inst. of Physics, London (1978).
12) O. Johnson, Bull. Chem. Soc. Japan, **45**, 1599, 1609 (1972); **46**, 1919, 1923, 1935 (1973).
13) O. Johnson, J. Res. Inst. Catalysis, Hokkaido Univ., **20**, 125 (1922).
14) O. Johnson, J. Res. Inst. Catalysis, Hokkaido Univ., **21**, 50 (1973).
15) R. F. Stewart, Acta Crtst., **A 33**, 33 (1977).

16) Y. W. Yang and P. Coppens, Acta Cryst., **A 34**, 2113 (1978).
17) J. Hafner, Solid State Comm., **27**, 263 (1978).
18) M. L. Cohen, Phys. Rev. Lett., **41**, 580 (1978); Phys. Lett., **44 A**, 375 (1973).
19) R. M. Moon, W. V. Koehler, J. W. Cable and H. R. Child, Phys. Rev., **B 5**, 997 (1972).
20) O. Johnson, Phys. Stat. Solidi, **b 99**, 745 (1980).
21) C. D. Gelatt, H. Ehrenreich and R. E. Watson, Phys. Rev., **B15**, 1613 (1977); A. R. Williams, J. Kübler and C. D. Gelatt, Phys. Rev., **B 19**, 6099 (1979).
22) V. L. Moruzzi, A. R. Williams and J. F. Janak, Phys. Rev., **B 15**, 2854 (1977); V. L. Moruzzi, J. F. Janak and A. R. Williams, *Calculation of Electronic Properties of Metals*, Pergammon, New York, (1978).
23) A. R. Williams, C. D. Gelatt and J. F. Janak, to be published.
24) M. B. Stearns, Phys, Rev., **B 13**, 1183 (1976); *ibid.*, **B 9**, 2311 (1974).
25) A. Moldovan, unpublished studies, Univ. of Pittsburgh, (1978).
26) O. Johnson, J. Res. Inst. Catalysis, Hokkaido Univ., **20**, 95 (1972).
27) R. Haydock and M. J. Kelley, J. Phys. C (solid State), 8, L 290 (1975).
28) M. C. Desjonquéres and F. Cyrot-Lackmann, J. Chem. Physics, **64**, 3707 (1976).
29) F. J. Arlinghaus, J. G. Gay and J. R. Smith, Phys. Rev., **B 21**, 2055 (1980).
30) A. Clark, *Theory of Adsorption and Catalysis*, Acad. Press., New York, (1970).
31) O. Johnson, Chemica Scripta, **8**, 166 (1975).
32) R. Ugo, Catalysis Reviews-Science and Engineering, **11**, 225 (1975).
33) See F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, N. Y., (1966).
34) O. Johnson, J. Chem. Phys. Solids, **42**, 65 (1981). See also ref. 20.
35) W. Braun, G. Meyer-Ehmsen, M. Neumannand E. Schwarz, Surf Sci., **89**, 354 (1979).
36) J. E. Demuth, referred to in ref. 5.
37) G. Ertl, Angew. Chem. (Int. Ed.), **15**, 391 (1976).
38) M. Moskowitz, Accts. Chem. Research, **12**, 222 (1979).