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Classification of Metal Catalysts Based on Surface *d*-Electrons

A detailed description of the metal surface (*1*) in terms of positive ion cores, localized *d*-electrons on ion cores and interstitial localization of itinerant electron density has been given by the interstitial-electron model for metals (*2*). On the basis of this model, catalytic metals have been divided into 4 classes according to the orientation and occupancy of *d*-orbitals extending above the metal surface (*3*). Class I metals (Mo, W) have a vacant *d*-orbital perpendicular to the metal surface. Class II metals (Rh, Ir, Ru, Os, Tc, Re) have a vacant *d*-orbital at 36–45° to the surface. Class III metals (Fe, Co, Ni, Pd, Pt) have a partially occupied *d*-orbital at 30–36° to the surface. Class IV metals (Zn, Ga, Cd, In, Ge, Sn, Pb) have been shown by Kita (*4*) to differ from other metals with completed *d*-shells and have been characterized (*5*) as having an asymmetry in their *d*-shells. Promotion of a *d*-electron places Cu, Ag and Au with Class III metals. The above classification is based on the 111 surface for CCP and HCP metals and for the 110 surface for BCC metals. Orbital patterns which indicate more complex behavior for Ni, Pt and Rh as well as the minor changes in orbital orientation on other crystal planes are described in detail in a paper (*3*) discussing hydrogenation catalysis. The metal structures used to obtain *d*-orbital orientation and occupancy differ from those used by Goodenough (*6*), Bond (*7*) or Shopov and Andreev (*8*) in that the localization of itinerant electron density in metal interstices is taken to determine *d*-orbital degeneracy (*2*). The electronic structures for metals, so derived, are compatible with known magnetic properties, electronic heat capacity, Hall Coefficients and electrical conductivity of metals (*2*).

Surface complexes of olefins on metals are proposed (*3*) for Class III metals which utilize electrons in the partially filled *d*-orbitals to form σ-bonds and for Class II metals which utilize metal itinerant electrons in a delocalized electron bond. The expected greater ease of forming bonds with Class III metals (and thus, ease of alkyl reversal) is considered to be the basis for the greater exchange and isomerization observed over Class III metals compared to Class II metals. Classification of metals into 4 classes provides a plausible theoretical basis for many of the mechanistic discussions of hydrogenation reactions (*3*). In addition the interstitial-electron model provides a description of the metal surface which facilitates descriptions of surface complexes of hydrocarbons in familiar terms of ion cores and electrons and clearly relates them to transition metal complexes.

This description of the metal surface supplements metal band theory descriptions, but offers a more chemical approach for discussions of catalytic reactions than many current treatments based on concepts such as "*d*-character" or "holes in the *d*-band." Its emphasis on localized electron environment around metal ion cores has much in common with recent discussions of catalysis by Sachtler and Van der Plank (*9*), Knor (*10*) and also recent formulations by Dowden (*11*). A wave mechanical calculation of hydrogen surface states on several metals by Horiuti and Toya (*12*) has been compared to the present model (*1*). Other mathematical approaches to localized surface binding of adsorbates on metals are those pursued by Jansen (*13*), Grimley (*14*), Van der Avoird (*15*) and Gomer and Schreifer (*16*). Approaches which use recent advances in band theory of metals (*17*) including the use of pseudopotentials are apt to be extremely difficult to apply to catalysis.

The classification of metals according to *d*-orbital pattern offers a new approach to catalysis, but since "*d*-character" along with the companion concept of "holes-in-the-*d*-band" are featured in most text books on catalysis and widely used in correlations and discussions of catalysis, it appears worth while to point out their unsatisfactory theoretical basis to clear the way for all of the alternate approaches just mentioned.

First of all, a property like *d*-character would be expected to have a greater effect on selectivity in catalysis than on activity which has been shown (*18*) to be related to a parameter like ΔH of adsorption (or heat of formation of a related bulk compound) or metal work function (*1*). The definition of *d*-character by Pauling (*19*) comes from his valence bond model of metals and has no clear physical significance. Also, the valence bond model has been considerably changed in the extensions by Trost (*20*), Goodenough (*6*) and Engle–Brewer (*21*). At the very least a critical reevaluation of the concept of *d*-character should be made in terms of these new developments before it is used as a parameter to compare catalysts. The concept of *d*-character has already come under considerable general criticism (*22*, *23*).

Many textbooks and reviews on catalysis give a prominent place to the experiments on "filling of *d*-bands" in metal alloys to show the importance for chemisorption and catalysis of empty *d*-orbitals in hydrogenation by transition metal catalysts. The impression is given that for Ni and Pd, the addition of 60 atomic % Au (or Ag or Cu) fills the 0.6 hole in the *d*-band of Ni or Pd and reduces catalytic activity to zero. Actually, only 37.5 atomic % Au would suffice to fill the *d*-band if the conduction electron of each added Au occupied a hole in the Ni or Pd *d*-band. The experimental papers do point out that the basis for the 60% value is the experimentally observed diminution in magnetic susceptibility of Pd to zero at 60 atomic % Au in the Pd–Au alloy. Experiments designed to confirm this effect for catalytic reactions other than simple hydrogen reactions (*24*) often showed lack of correlation (*25*, *26*).

The more complex behavior observed than expected from a simple filling of holes in the *d*-band has been recently discussed by Dowden (*27*) who proposed a modified approach utilizing the ensemble theory of Kobozev and a modified *d*-band theory for alloys. Recent de Haas-Van Alphen experiments (*28*) have shown there to be 0.36 holes in the *d*-band for Pd. The magnetic moment on Ni may be associated with itinerant electrons (*1*, *29*), and a recent neutron diffraction study (*30*) of Ni–Cu alloys shows a decline in negative spin diffuse moment upon Cu addition, but retention of the localized Ni moment. Recent data on magnetic susceptibility of Pd–Au also indicate that zero susceptibility may be reached at values lower than 60 atomic % Au. Moss and Whaley (*31*) have recently discussed many of these problems related to catalysis by metal alloys. Current theoretical work on alloys (*32*, *33*) certainly strongly indicates that account must be taken of effects such as energies of itinerant electrons and screening by ion cores. The detailed studies by Sachtler and Van der Plank (*9*) have also demonstrated that surface species may differ from bulk composition of an alloy and strongly support a localized approach to binding of adatoms on alloys.

Thus, there seems to be a real need for a modified *d*-band description of metals or of alternate approaches as mentioned above and offered in this paper. The insufficient development of the theory of metals and metal alloys for detailed treatment of "surface complexes" of hydrocarbons is the major difficulty. One advantage of the above detailed description of surface *d*-orbitals (*3*) is that experimental observations on alloy catalysis can then be useful in extending similar metal classifications to alloy systems. The importance of combinations of Class II and Class III metals for systematic variation in catalyst selectivities has already been discussed (*3*).

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