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CATALYSIS AND THE INTERSTITIAL-ELECTRON MODEL FOR METALS

V. Hydrogenation Catalysis

By

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Abstract

The Interstitial-Electron Model for the electronic structure of metals gives a detailed pattern of the d-orbitals and itinerant electrons above the surface of positive metal ion cores. With some simplification the metals of importance in hydrogenation catalysis can be divided into 3 classes depending on the orientation and occupancy of d-orbitals localized on the metal ion cores: Class I. Vacant d-orbitals perpendicular to the surface (Mo, W). Class II. Vacant d-orbitals at 36~45° angles to the surface (Rh, Ir, Ru, Os, Tc, Re, Cr). Class III. Partially occupied d-orbitals at 30~45° angles to the surface (Co, Fe, Ni, Pd, Pt). These classes are based on the 111 plane for CCP and HCP and the 110 plane for BCC metals. There are less important variations within each of these classes of metals due to differences in adjacent d-orbitals and in itinerant electron density of the metal. There can be added a 4th class of metals (Zn, Cd, Ga, In, Sn, Pb) which are characterized as d^{10} metals with asymmetrical structures and which are not important as gas phase hydrogenation catalysts.

Chemisorbed species are proposed which follow from the above description of orbitals on the metal surface along with known experimental observations and which are termed "surface complexes". Class I metals are expected to show compound formation (carbide from hydrocarbons) and considerable cracking activity, class II metals are expected to have a "surface complex" with delocalized electron bonding, while class III metals utilize the partially occupied d-orbitals to give a more localized σ-bonding. Class III metals give considerably more D_2-exchange and isomerization during hydrogenation than class I or II metals. This classification provides a theoretical background for many of the mechanistic discussions in the literature.

The Interstitial-Electron Model for metals provides a basis for showing that the different properties of metals, transition-metal complexes and metal oxides as hydrogenation catalysts are predominantly due to the different localization of electron density available for the chemical binding of hydrogen or hydrocarbons to these catalysts. Taking into account these differences in electron density localization makes it feasible to use some of the observations on the simpler homogeneous catalyst and metal oxide catalysts to suggest

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behavior of chemisorbed species on metals.

Metal work function (ϕ_M) has been previously shown by the interstitial-electron model to provide a useful measure of relative binding strength of itinerant electrons to the metal surface. Reactions of hydrogen atoms on a metal surface are described in terms of competitive attraction of metal electrons by chemisorbed hydrogen and positive ion cores of the metal, and there is a good correlation of such hydrogenation activity and ϕ_M. Since unsaturated hydrocarbons are more strongly chemisorbed than hydrogen atoms this greater, but more complex competition for electrons at the metal surface leads to an optimum ϕ_M for a given reaction. These correlations with ϕ_M are related to previous correlations with ΔH of chemisorption and with heats of formation of related metal compounds, and it is concluded that all are fundamentally correlations with strength of attachment of catalytically active species to the metal surface. ϕ_M is considered to be an important parameter for comparing catalysts, and one for which more data are available than ΔH. In general, metals with optimum ϕ_M also appear to be Class II metals, postulated to form "surface complexes" with delocalized binding.

It is emphasized that although "surface complexes" are involved in metal catalysis, because of a range of binding energies they have differences in catalytic properties from the usual chemical compound or organometallic complex. This range of binding energies results from changes in electron attachment to the metal ion cores with coverage due to *all* of the chemisorbed species whether they are involved in the reaction or not.

In addition to the σ-binding of adsorptives by Class III metals, there is a role of d-electrons in catalysis both in chemisorption at high coverage (where energies of d-electrons approach or become higher than those of itinerant electrons) and in the transfer of electrons to facilitate dissociation of hydrogen as well as hydrogenation and desorption of products. A very weak hydrogen chemisorption at high coverages of hydrocarbon which is highly dependent on d-orbital occupancy explains some of the hydrogenation properties of metal catalysts. It is considered that the concept of d-character is a parameter vaguely related to ΔH or ϕ_M, but one which cannot be useful for any detailed description of surface complexes. It is suggested that for alloy catalysts the use of the "holes in d-band" from simple band theory be limited to comparisons of activity with *experimentally* observed changes in paramagnetic susceptibility or with actual magnetic moments on ion cores (known for same alloys from neutron diffraction). It is likely that alloys based on Class II metals or Class II–III Combinations can give catalysts with significantly higher activity and selectivity than those with Cu, Ag or Au.

Differences in properties of hydrocarbons undergoing hydrogenation can also influence catalytic patterns of metals. Whereas ϕ_M was a decisive parameter in H atom reactions, the pattern of d-orbitals becomes highly important in olefins where there are multiple pathways for reaction, and in the case of acetylene which has acidic hydrogens, basic properties of metals appear to be important for activity.

I. Introduction

Band Theory of Metals and related descriptions of metals such as pseudopotential theory have been highly developed for interpretation of metal

properties. However, Band Theory concepts such as the Fermi level of electrons and density of states are difficult to relate to the chemistry of hydrogenation and have not been generally useful in interpretation of details of metal catalysis[1]. In the case of semiconductors as catalysts the picture of electrons in energy bands for interpretation of catalysis has been well developed[2,3]. In this paper the Interstitial-Electron Model[4] will be used for interpretation of hydrogenation catalysis by metals. The addition this model incorporates into Band Theory is the spatial location of itinerant electron density and the location and occupancy of *d*-orbitals, and this makes it possible to discuss chemisorption and reactions in much the same way as ordinary chemical reactions are discussed using molecular orbital theory. In addition the Band Theory concept of electron energies can still be used.

Catalysis by metal surfaces have been traditionally approached by searching for correlations of catalytic activity with some parameter of the metal surface. The partial success of many different parameters illustrates very well the great complexity of the catalytic process. Useful correlations have been developed between catalytic activity for certain reactions and intermetallic distance[5], initial heat of chemisorption of a reactant[6], *d*-character of metal[7], valency of metal[8] and heat of formation of compounds[9,10] of one of the reactants. The merits of these correlations have been discussed in terms of "geometric" factors and "electronic" factors[11]. The typical volcano curves[12] shown in the correlations of catalytic activity and heat of a related bulk compound[13] offer considerable insight into catalysis by introducing the concept of an optimum binding strength for active species on a metal surface.

Bond[14] and ANDREEV and SHOPOV[15] have used ligand field theory to show the relation of chemisorption and the direction of emergence of *d*-orbitals on the metal surface with some application to hydrogenation catalysis. It has also been pointed out that a property such as electron affinity of metals[16] (represented by the sum of its first three ionization potentials or metal work function, ϕ_M) or electron/atom ratio[17] can explain many of the gradations of chemisorption and catalytic activity of metals and metal complexes. The presence of trends in the periodic arrangement of metals has been used by ROONEY and WEBB[18] in comparing catalysis by metals with that by homogeneous catalysts.

There have been only limited comparisons of ϕ_M and activity. WANSBOROUGH-JONES and RIDEAL[19] attempted to show a relation of ϕ_M and activation energy for oxidation reactions. DOWDEN and REYNOLDS[20] predicted that the decomposition of H_2O_2 should decrease with increasing ϕ_M because transfer of an electron was required in the reaction. KEMBALL[21]

concluded that since ions are not often involved in chemisorption and catalysis, ϕ_M is not of importance. However, the general importance of electron transfer of itinerant electrons of the metal into binding regions for surface compounds does makes ϕ_M of importance. In this paper metal work function will be shown to be a parameter which can be of fundamental importance in comparing catalysts and which also includes the concept of an optimum binding strength in terms of an optimum work function for activity in a given reaction.

The major portion of this paper will be devoted to the formulation of "surface complexes"[22] using all of the experimental data available and using the Interstitial-Electron Model[4] as a guide. This can provide a microscopic analogue to the detailed discussion of reaction mechanism such as recently reviewed by HORIUTI and MIYAHARA[23] for the hydrogenation of C_2H_4.

The descriptions of hydrogenation catalysis on metals will be in terms of fundamental interactions between positive ion cores, localized d-electrons, and itinerant electrons of the metal with the chemisorbed species, and will emphasize the degree and direction of electron transfer between metal surface and reactants. Related concepts are developed for transition metal complexes and metal oxides so that use can be made of data on all these systems, and it is anticipated that the concepts developed will extend to other catalysts and to catalytic reactions other than hydrogenation.

II. Relation of metal catalysis to transition metal complex catalysts and transition metal oxide catalysts.

Comprehensive discussions of metal catalysts refer to the similarities in activity patterns between homogeneous and heterogeneous catalysts[16,18]. The well established influence of d-electrons in the metal ion of oxide catalysts[24] has been compared to more complex influence of d-electrons in metals. However, there appear to have been no attempts to explore and utilize the fundamental *differences* between metals, metal oxides and transition metal complexes as catalysts. This will be attempted here on the basis of the interstitial-electron model, and use will be made of observation on the simpler metal oxide and transition metal complex sytems when they are applicable to metals.

In previous papers it was already indicated[4] that the chemical binding changed from almost complete delocalization of binding electrons in metals to partial delocalization in transition metal complexes. This will be illustrated for particular cases and compared to ionic binding in metal oxides where there has been electron transfer to form cation and anion. The usual M.

O. description of complexes will be extended here in a way which allows some estimate of electron localization. The new description is more general than the Dewar-Chatt Model, but it is also a delocalized description that includes metal cluster compounds.

Fig. 1 shows the structure found for $RhH(CO)(Ph_3P)_3$ by electron diffraction[25], and the molecular orbital electron energy diagram along with an electron distribution scheme given by the interstitial-electron model. The latter differs from the customary electron population analysis in suggesting the spatial location of electron density in binding regions[26]. The basis is exactly the same as for the M. O. diagrams which places 18 electrons in
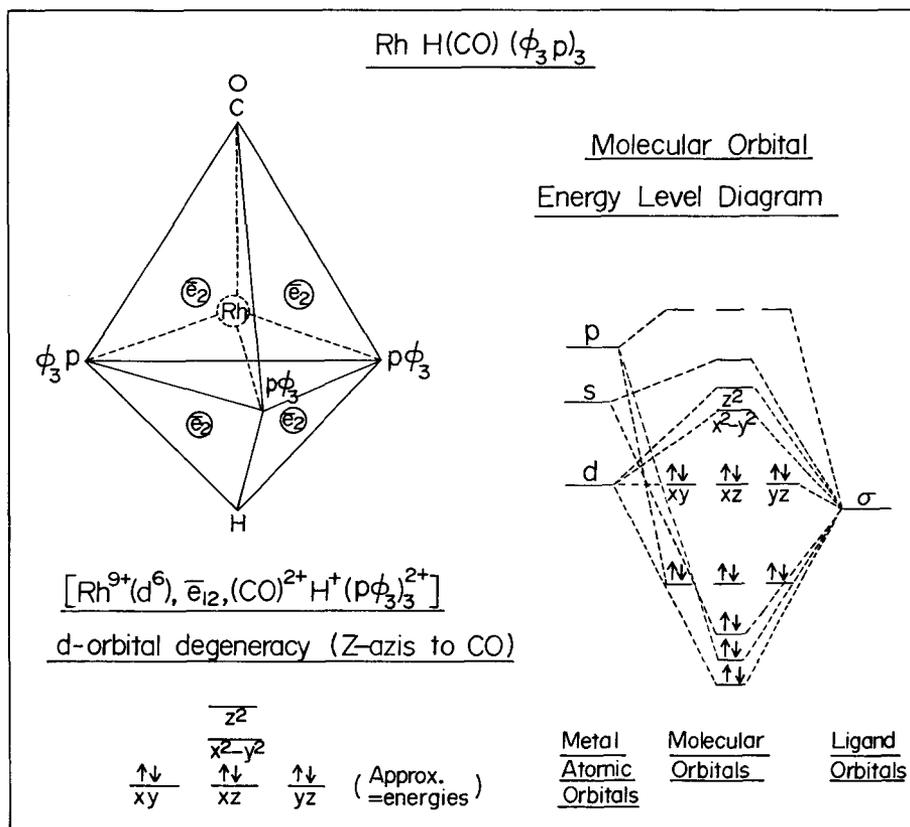

Fig. 1. Structure of $RhH(CO)(\phi P)_3$ with Interstitial-Electron Formulation and Molecular Orbital Energy Level Diagram. (Rh–H, 1.72 Å, Rh–CO, 1.18, Rh–P, 2.314, 2.317 and 2.337, Rh is 0.36 Å above plane of three P in the direction of CO. $\widehat{e_2}$ represents electron density localized near centers of triangular faces.)

molecular orbitals, a process which leaves $(CO)^{2+}$, $3(P\phi_3)^{2+}$ and H^+ ion cores along with the transition metal cation $Rh^{9+}(d^6)$. The ion cores are not usually explicitly stated in connection with M. O. electron energy diagrams. The stability of a transition-metal complex as well as its ability to "co-ordinate" an olefin or additional hydrogen is clearly a function of both ligands and metal cation. However, the chemical binding can be specified precisely and is the same for each molecule of metal complex.

The general principle for stability in these transition metal complexes appears to be that 1) positive ion cores form a polyhedron giving maximum separation (minimum repulsion of M^{n+}) 2) binding electrons ($\bar{e}_2$) are found in binding regions located in direction of unoccupied d-orbitals 3) occupied d-orbitals extend between positive ion cores, and these electrons fulfill the binding role usually termed back-binding. Within this framework
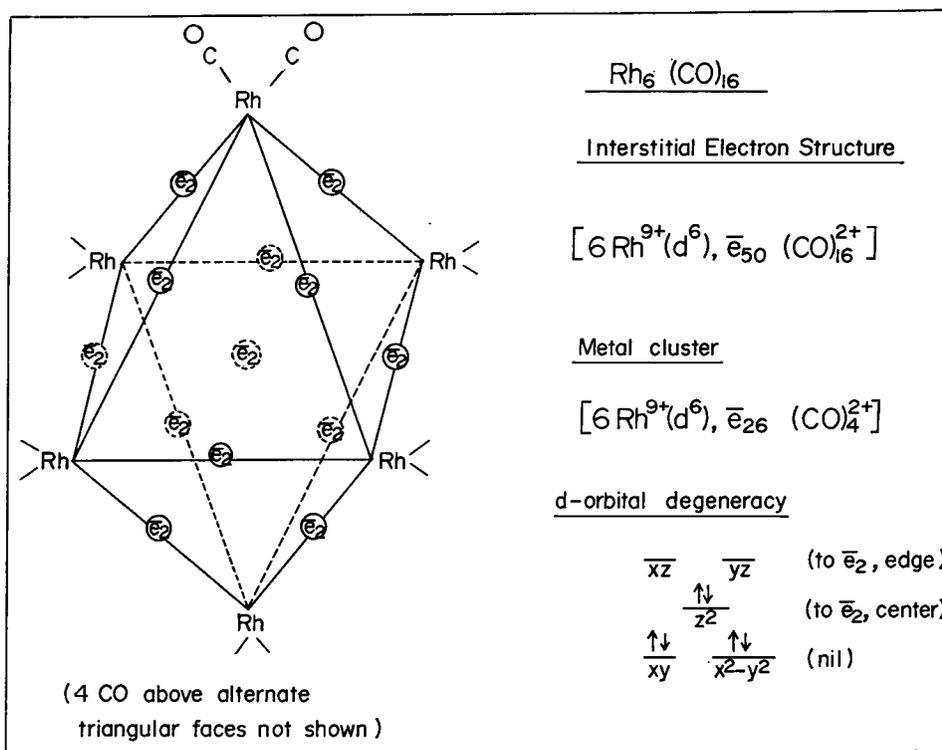

Fig. 2. Structure of $Rh_6(CO)_{16}$ with Interstitial-Electron Formulation. (The 12 $\bar{e}_2$ on edges represents regions of localized electron density. For determination of d-orbital degeneracy the x and y axes are placed along diagonals of the square of four Rh and the z-axis is perpendicular to the square.)

electron distribution depends on relative attraction of ion cores for electrons and mutual repulsion of electrons and of ion cores. The mutual accomodation of ion cores, localized $\bar{e}_2$ (electron density) and d electrons was illustrated for $Ni(CO)_4^{26)}$.

It is generally assumed that olefin complexes of transition metals have π-bonding of olefin, $M\leftarrow\|\begin{smallmatrix} C \\ C \end{smallmatrix}$ and that hydrogen is added to form alkyl species, $M-C_2H_5$. The other possibility is original formation of a *di-σ*-bonded olefin, $M\!\!<\!\!\begin{smallmatrix} C \\ | \\ C \end{smallmatrix}$. A recent *re*-examination[27)] of the Zeiss salt, $PtCl_3(C_2H_4)$, gives strong evidence for this type of bonding-rather than the relatively weak π-interaction assumed in previous studies.
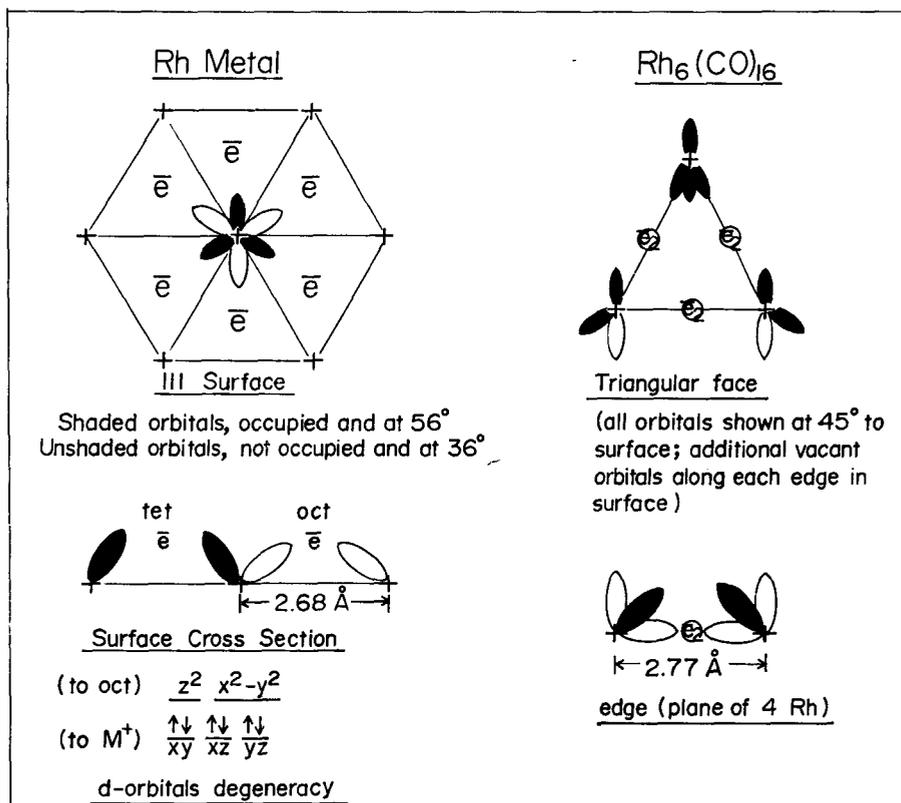

Fig. 3. Comparison of Interstitial-Electron Structures for $Rh_6(CO)_{16}$ and Rh metal. Projections of orbitals on the surface are shown in the top diagrams. The orbitals around each Rh in the $Rh_6(CO)_{16}$ are all the same even though those above the triangular face above are different.

Before making comparisons of metals to metal complexes it is of interest to consider "metal cluster" compounds, $e.g.$, $Rh_6(CO)_{14}$. The proposed electronic structure is shown in Fig. 2. The triangular faces shown in Fig. 3 are rather like small metallic elements. The Rh–Rh distance[28] in the complex is 2.776 ± 0.01 Å, which is close to the Rh–Rh distance in Rh metal of 2.68 Å. In formulating the electronic structure of the $Rh_6(CO)_{16}$ metal cluster, it appeared most reasonable to include the 4CO attached to alternate faces of the octahedron in the cluster unit $[6Rh^{9+}(d^6), 4(CO)^{2+}, \bar{e}_{26}]$ where $\bar{e}$ density can be distributed as 12 $\bar{e}_2$ on edges of the octahedron in a delocalized binding region. The remaining 2 electrons must be localized over the whole unit and as such came close to metallic electrons; the complex exhibits metal-like paramagnetism[28]. These 2 electrons are probably of lowest energy in the cluster system.

One can now compare these Rh complexes to the surface of Rh metal which has been characterized by the Interstitial-Electron Model[4] as having itinerant electron density and d-orbitals as also shown in Fig. 3. On the basis of the electronic structures given in Figures 1, 2 and 3, the degree of delocalization of electrons is seen to go from a delocalization in the region of a $\triangle$ face of 3 ion cores in metal complex to the delocalization into 4 or 6 ion-core-surrounded interstices in metals (tet or oct). The metal cluster compounds occupy an intermediate position in which the ligands away from the "metal cluster" have electron distributions as in ordinary transition metal complexes while the metal ion cores in the metal cluster with some ligands attached ($i.e.$ the Co attached to 3 Rh out from a face of the octahedron) have a greater delocalization of electrons which is closer to that in metals.

The hydrogen in metal complexes such as $H Co(CO)_4$ can be characterized by the range of proton nmr adsorptions which are high (5–18 ppm) and indicate high shielding of H. The hydrogen in $HCo(CO)_4$ is highly acidic, and acidity declines by substitution of CO by groups which increase $\bar{e}$ density on the metal, $e.g.$, $(P\phi_3)$ or $P(O\phi)_3$. The complex $H Co(PBu_3)_4$ is no longer acidic, and the hydrogen is regarded as H^- instead of H^+. For metals the chemisorbed hydrogen has been designated as $H^{\delta-}$, and this seems reasonable on comparison of metal electron density to that in complexes. Presence of $H^{\delta+}$ on metals is postulated[33] for certain lattice planes and on some at metals high coverage of H.

The chemical binding in metal oxides can be rather well described by the ionic binding of M^{n+} cations and O^{2-} anions. The M^{n+} ion core contains d-electrons for metals oxides beginning with V_2O_3, and activities are similar to the pattern of crystal field stabilization[29] by d-electrons $i.e.$ a

maximum activity at d^3, minimum at d^5, a second maximum at d^7 (instead of d^8) and minimum at d^{10}. An alternate explanation[31] suggests that high activity for TiO_2 and V_2O_3 are connected to the metal-insulator transition for these metallic type oxides. Possible chemisorption of the reactant on O^{2-}, as for ZnO (see below), indicates that crystal field stabilization around M^{n+} may not be the only factor in rate of catalysis on metal oxides.

The unique feature of catalysis by the metal oxides is the fixed character of the electronic structure of the transition metal ion. Unless the coordination of oxygen changes, the environment remains constant. Chemisorption on adjacent metal cation or oxide ion will usually have only a small indirect influence on electron distribution around M^{n+} through polarization effects.

During catalytic reactions such as hydrogenation of olefins the chemisorption of olefin on metal oxide is expected to be of the π-type, and in this case direct interaction with O^{2-} on the surface has been postulated by KOKES[30]. In addition there is probably weak chemisorption over Zn^{2+} with possible back binding interaction of adjacent O^{2-}. The heat of chemisorption of C_2H_4 on ZnO is 14 kcal/mol and has been characterized as a weak π-type complex. With propylene and ZnO, there is evidence for allyl complex formation over Zn^{2+} probably occuring via H abstraction from propylene, but this is not the case with Co_3O_4[57].

However, hydrogen chemisorption on oxides involves heterolytic splitting[16,30] of H_2 with formation of OH^- from O^{2-} and H^- over M^{n+}. This makes it possible for metal ions with no vacant d-orbitals to chemisorb hydrogen.

The probable electronic structures of catalytic sites of metal oxides and transition metal complexes need to be considered since it is important to be able to use data from the latter two systems to assist in the interpretation of the more complex catalytic process at the metal surface. For example, experiments[32] show little addition of H_2 to a $Rh(\phi_3P)\ Cl(C_2H_4)$ complex but rapid addition of C_2H_4 to $Rh(\phi_3P)\ Cl\ H$. It appears to be general that in metal complex catalysts a H attached to metal is required for olefin hydrogenation. It is reasonable to assume that the same requirement exists for metals, *i.e.*, that even though C_2H_4 is more strongly adsorbed than H, the desorption step involves reaction of chemisorbed H and C_2H_4.

The differences expected between surface complexes on metals and metal oxides and homogeneous metal complexes can be summarized as follows. There is attachment of olefin or hydrogen to a single metal in homogeneous complexes except metal cluster complexes[34] and to a single metal or oxygen in metal oxides; this makes d-orbital occupancy of critical impor-

tance for activity. As mentioned above an occupied d-orbital directed toward a potential site for chemisorption of H or olefin prevents or reduces catalytic activity. Metals, on the other hand, have many possible sites for surface complexes and the effect of d-orbital occupancy is more complex and less critical for activity (although as will be shown below, of considerable importance for selectivity in catalysis). In addition metals have the highly mobile itinerant electrons which participate in the binding of surface complexes and modify the metal surface complex to the extent that its binding electrons are delocalized. In general a wider range of stabilities is expected on the metal surface as compared to a homogeneous metal complex[17].

Another way of comparing metals with metal oxides is to consider the O^{2-} as the counterpart of interstitial-electrons in the metal but with considerably greater localization of electrons around the O^{6+} ion core. Thus, interaction with ethylene can occur on ZnO as $Zn^{2+}\underset{O^-}{[H_2C=CH_2]^{2+}}$ while on a metal the interaction of C_2H_4 with M^+ is more important than interaction of C_2H_4 with itinerant electrons.

III. Surface Model for Hydrogenation by Metals

The ion cores and itinerant electrons on metal surfaces were compared to the situation in metal oxides and metal complexes in Section II. Before discussing specific hydrogenation reactions on metal surfaces, some further details of the electron distribution need to be presented, and the effect of simultaneous chemisorption of two kinds of atoms must be considered. The previous papers[35] in this series have developed a detailed model for the metal surface in terms of location of itinerant electron density relative to the ion cores of the metal and of the surface location or sites for one adsorptive.

The model for hydrogen chemisorption will be discussed first. Aside from some special behaviour of certain lattce planes, hydrogen atoms are generally expected to adsorb in interstitial position[35], $i.\,e.$, above the center of 3 close-packed metal ion cores. Saturated hydrocarbons are expected to physically adsorb directly above ion cores. The influence of localized d-electrons, also discussed previously[33], is such that when occupied d-orbitals extend perpendicular to the metal surface, the tendency for hydrogen chemisorption above ion cores may be increased. When d-electrons extend into interstitial position above the surface, chemisorption in those positions may be enhanced. Because of the great variation of d-orbital occupancy in transition metals, as discussed below, catalytic behaviour due to d-electrons

is more complex than a parameter such as *d*-character[7,8] can indicate. There is an additional effect at high coverages which has been proposed to explain the desorption pattern and work function changes on single crystal planes of tungsten[33]. This is the adsorption of H as $H^{\delta+}$ due to strong attraction of metal ion cores for H, coupled with the possibility of electron transfer to *d*-orbitals. At high coverage the energies of *d*-electrons localized on ion cores approach those of itinerant electrons. This adsorption as $H^{\delta+}$ is expected to occur over sites with vacant *d*-orbitals. This may be similar to the weak "type C" chemisorption of H discussed by DOWDEN[29]. It is expected only at high coverages where ϕ_M has been increased by prior chemisorption of H as $H^{\delta-}$ (or by other molecules which attract metal electrons). It can also occur at very low temperatures under conditions where H_2 chemisorbs at the position it strikes the surface, some of which will be over vacant *d*-orbitals. At ordinary temperatures and low coverages these species would not be stable on the surface.

A more detailed picture of the *d*-orbitals above the the metal surface is needed to discuss olefin chemisorption. For olefins and other hydrocarbons, chemisorption as possible as σ-complexes with binding between metal and carbon, and as π-complexes or π-allyl complexes with delocalized electron binding. Magnetic measurements[36] show that ethylene chemisorption below 100°C lowers the magnetic moment of the Ni surface for each C_2H_4 by a factor of 1.4 times that of hydrogen (see further discussion below). In order to formulate surface complexes to explain this magnetic behavior and other experimental observation on surface complexes and also to discuss the complex selectivities in isomerization and D_2-exchange during hydrogenation of olefins and dienes, a complete picture of both occupied and vacant *d*-orbitals and itinerant electrons on the metal surface is needed. The previous surface models[33] emphasized the location of occupied *d*-orbitals, which was important in understanding work functions and chemisorptions of simple molecules.

The location and occupancy of *d*-orbitals on the metal surface and the interstitial location of itinerant electrons follow directly from the Interstitial-Electron Model. The *d*-orbital degeneracies are given in Table 1, and the spatial directions of *d*-orbitals relative to the plane of the surface are given in Table 2 for the 111 plane of CCP and HCP metals and for the 110 plane of BCC metals. These are the major planes expected in the surfaces of metals reduced at relatively high temperatures; the data for other planes follows from the model (see Appendix) and were presented in part in the previous paper IV on chemisorption[33]. Certain patterns of *d*-orbital occupancy emerge especially if some of the orbitals of high energy (antibinding

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TABLE 1 Degeneracy of d-orbitals in metals

(Ion cores with localized d-electrons listed)

BCC Metals (orbital axes at 45° to unit cell axes)

$Cr^{6+}(d^2)$

$\overline{xz}$	$\overline{yz}$	(to M⁺)	$\overline{xz}\;\uparrow$	$\overline{yz}\;\uparrow$	
$\overline{xy}$	$\overline{z^2}$	(to tet, edges)	$\overline{xy}$	$\overline{z^2}$	$Fe^{8+}(d^4)$
$\overline{^2x-y^2}\;\uparrow\downarrow$		(to tet, faces)	$\overline{x^2-y^2}\;\uparrow\downarrow$		

$Mo^{6+}(d^4)$ and $W^{6+}(d^4)$

$\overline{z^2}$	$\overline{xy}$	(to tet, edge)
$\overline{x^2-y^2}$		(to tet, face)
$\overline{xz}\;\uparrow\downarrow$	$\overline{yz}\;\uparrow\downarrow$	(to M⁺)

CCP Metals

$Ni^{10+}(d^{7.3})*$
(axes, 45°)

$\overline{x^2-y^2}$		(to M⁺)
$\overline{xz}\;\uparrow\downarrow$	$\overline{yz}\;\uparrow\downarrow$ (0.3)	(to tet)
$\overline{xy}\;\uparrow\downarrow$	$\overline{z^2}\;\uparrow\downarrow$	(to oct)

*(probably 70% d^7 and 30% d^8)

$Pd^{10+}(d^7)*$ or
$Pt^{10+}(d^7)*$
(axes, 90°)

$\overline{z^2}\;\uparrow$	$\overline{x^2-y^2}$		(to oct)
$\overline{xy}\;\uparrow\downarrow$	$\overline{xz}\;\uparrow\downarrow$	$\overline{yz}\;\downarrow\uparrow$	(to M⁺)

$Rh^{9+}(d^6)$ or
$Ir^{9+}(d^6)$
(axes, 90°)

$\overline{z^2}$	$\overline{x^2-y^2}$		(to oct)
$\overline{xy}\;\uparrow\downarrow$	$\overline{xz}\;\uparrow\downarrow$	$\overline{yz}\;\uparrow\downarrow$	(to M⁺)

HCP Metals

$\overline{x^2-y^2}$ (to M⁺) $\overline{z^2}$ (to tet) $\overline{z^2}$

$Co^{9+}(d^{6.2})$

$\overline{z^2}\;\uparrow$	$\overline{xz}\;\uparrow\downarrow$ (0.2)	(to tet, near oct)
$\overline{yz}\;\uparrow\downarrow$	$\overline{xy}\;\uparrow\downarrow$	(Nil)

$Tc^{7+}(d^4)$ or $Re^{7+}(d^4)$

$\overline{xz}$	(near M⁺, oct)
$\overline{x^2-y^2}\;\uparrow\downarrow$	(to M⁺)
$\overline{yz}\;\uparrow\downarrow$ $\overline{xy}\;\uparrow\downarrow$	(Nil)

$Ru^{8+}(d^4)$ or $Os^{8+}(d^6)$

$\overline{xz}\;\uparrow\downarrow$
$\overline{x^2-y^2}\;\uparrow\downarrow$
$\overline{yz}\;\uparrow\downarrow$
$\overline{xy}$

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* Any d^6 configuration will lead to fractional number of unpaired electrons

orbitals) are eliminated. These are shown in Table 2 and also in Fig. 4 in terms of where orbitals are perpendicular to the metal surface or at an angle and whether vacant, filled or partially occupied by electrons.

In Table 2 the orbitals are divided into those which are vacant, occupied or partially occupied for each catalytic metal. Those with vacant orbitals can be subdivided into Mo and W with vacant d-orbitals perpendicular to

TABLE 2 Orientation and occupancy of d-orbitals
above metal surface[a]

Metal		Occupancy of d-orbital and Angle to Surface		
		Vacant	Partially-occupied	Occupied
I	(Mo, W)	90°		45°
		45° (tet)[b]		
II	(Rh, Ir)	36° (oct)		56° (M+/tet)[b]
	(Ru, Os, Tc, Re)[c]	45° (oct or M+)		45°
IIa	(Cr)	45° (tet)		90°
		45°		
III	(Co)		45° (1ē, M+/tet)	45°
	(Fe)	45°	45° (1ē, tet)	
	(Pd, Pt)		36° (<1ē, oct)	45° (M+/tet)
	Ni	56° (M+/tet)	36° (>1ē, tet)	45° (oct)
IIIa	Cu		30° (>1ē, tet)[d]	36° (oct)
	Ag, Au		36° (>1ē, oct)[d]	45° (M+/tet)

a) for plane of CCP and HCP metals and 110 plane of BCC metals
b) Oct or tet indicates an orbital directed into an interstitial position, M+/tet
   indicates an orbital directed toward a M+ in the next layer above a tet position.
c) The z^2 orbital 90° to surface is vacant. This is a high energy orbital directed
   toward tet, and these metals are not considered to be Class I.
d) Fully occupied unless d-electron promoted to conduction band.

the surface (called Class I) and those with vacant d-orbitals at angles of 36
or 45° to the surface which include Rh, Ir, Ru, Os, Tc, Re, Ni and Cr
(called Class II). A third group have partially occupied d-orbitals at 30,
36 or 45° to the metal surface and include Fe, Co, Ni, Pd and Pt (called
Class III).

There are additional occupied d-orbitals in various orientations, but,
except perhaps for Cr, these are not considered to be important for catalytic
properties as the vacant or partially occupied d-orbitals. Chromium is
designated in Table 2 as Class IIa became it differs from other Class II
metal in having an occupied d-orbital at 90° to the surface. Nickel can be
included in Class II or III, but it is concluded that the partially occupied
d-orbital is of greater importance than the vacant d-orbital at a high angle
(56°), and Ni is considered a Class III metal. Cu, Ag and Au are considered
Class IIIa metals since it is likely that during catalysis, promotion of d-
electrons occurs, and then a vacant d-orbital is present at 30 or 36° to the
surface. Table 2 also indicates whether the d-orbital of importance is
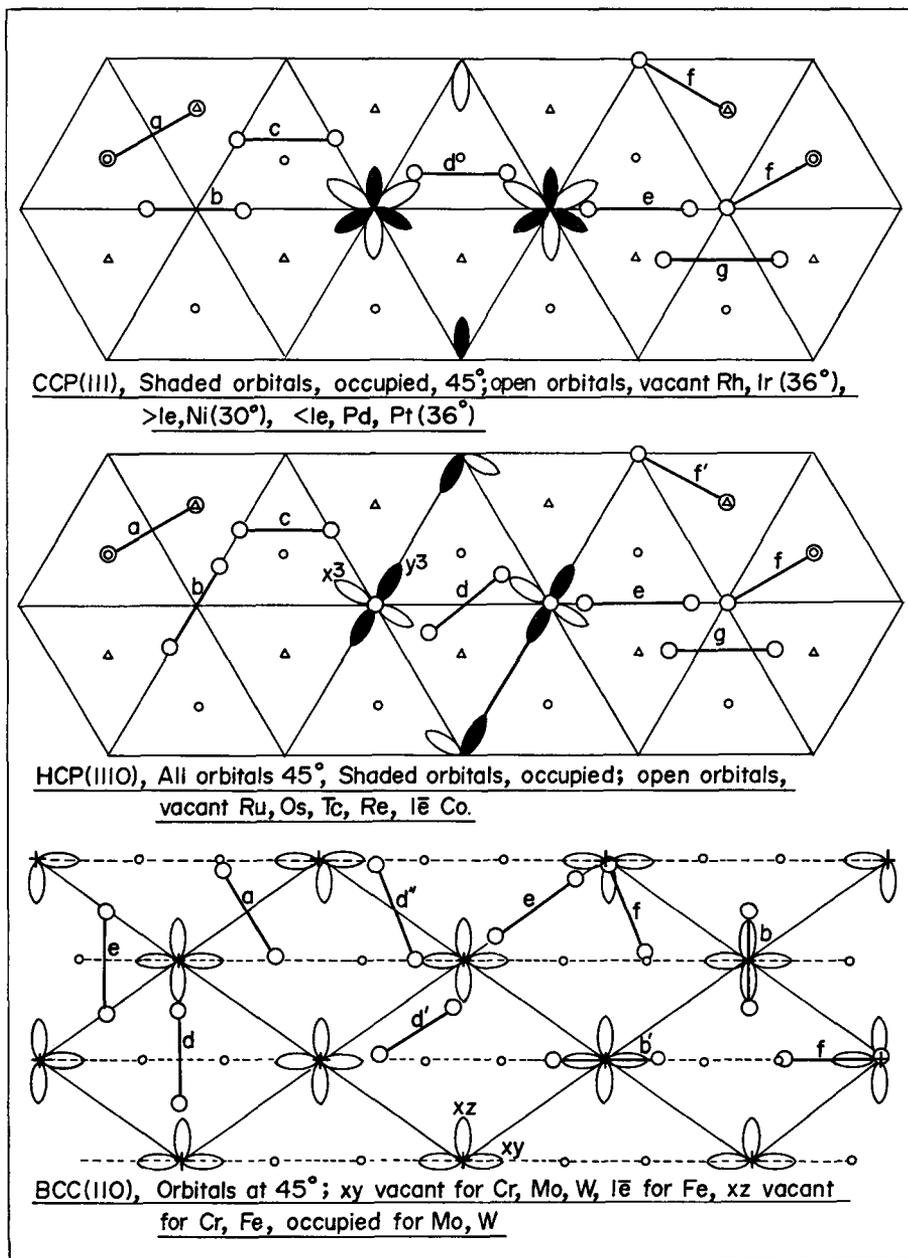
O. Johnson

Fig. 4. Possible sites for surface complexes of ethylene on metal surfaces.

directed to another M^{n+} or to an oct or tet interstitial position. This classification of metals seems qualitatively in agreement with known differences in catalytic behavior of matals. It also places Pd, Pt and Cu, Ag and Au with the ferro-magnetic metals (Fe, Co and Ni). This is commonly done with Pd and the Kita classification[40] places Cu, Ag and Au with transition metals in catalytic behavior. It should be added here that with the present classification the Kita classification of Group IIb–IVb metals (*e.g.* Zn, Ga, Ge) as distinctly different from the transition metal group would add Class IV for these metals. The characteristic *d*-orbital pattern for this Class IV (*e.g.* Zn, Ga, Ge, Sn, Pb) is probably fully occupied *d*-orbitals at 30~45° to the metal surface. This classification of metals into 4 Classes will be discussed further in connection with individual catalytic reactions.

The present formulation differs from that of BOND[14] or ANDREEV and SHOPOV[15] is that itinerant electron density is considered to determine degeneracy of *d*-orbitals instead of *d*-orbitals on other positive ion cores. This changes the splitting of *d*-orbital energy to a more complex pattern than the usual $e_g - t_{3g}$ splitting, but the new formulation has the advantage of showing a distinct difference in *d*-orbital orientation between the first transition series and that in the second and third transition series for most metals.

The above description along with the known interstitial location of itinerant electron density provides a clear picture of electrons available on the metal surface for binding of hydrocarbons. In order to propose sites for binding of "surface complexes" some criteria are needed as to what kind of binding is most likely. The following postulates have been made for this purpose and are largely based on analogy to transition metal complexes.

(1) "Surface complexes" on a metal surface have a high degree of delocalization of binding electrons.

(2) Since the closest analogy to "surface complexes" is the metal cluster compound, attachment to metal atoms in similar terminal positions or positions bridging edges and faces is expected.

(3) Since in most cases the adsorptive (A) gives up electrons to molecular orbitals (binding regions), as an A^+ species its repulsion by the metal ion cores must be considered. (The resultant polarity may be $A^{\delta-}$ due to location of electron density, however.)

(4) As in transition metal complexes the binding electrons in a surface complex will be in regions of vacant *d*-orbitals and not in regions near positive ion cores or filled *d*-orbitals.

(5) Since occupied *d*-orbitals are directed toward interstitial electron positions in 1st row transition metals and toward other positive ion cores
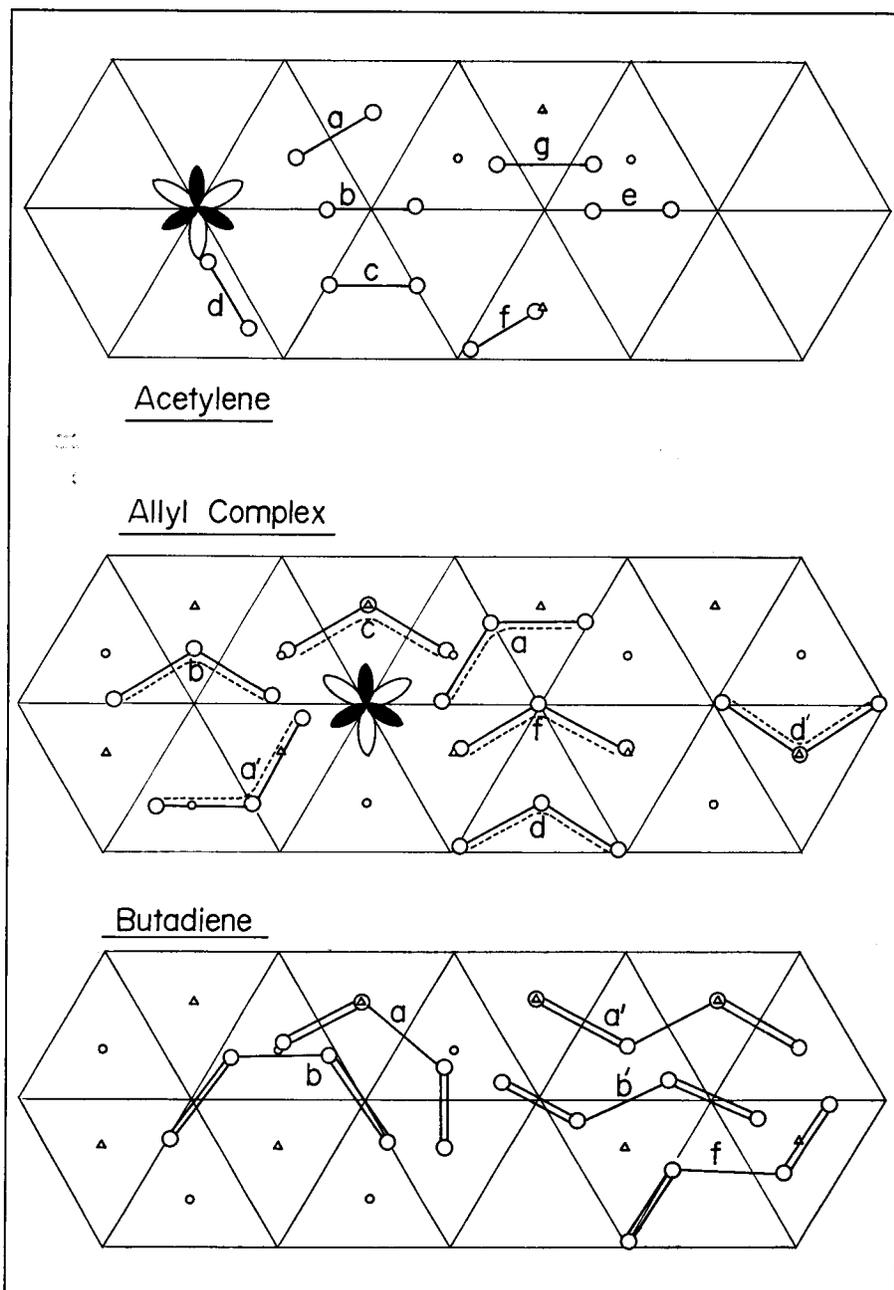
Acetylene

Allyl Complex

Butadiene

Fig. 5. Possible surface sites for allyl complexes and surface complexes of acetylene and butadiene.

in second and third row transition metals, differences in type and property of surface complexes are expected for the respective metals.

(6) The rule-of-18 for stability of transition metal complexes may hold in a modified form for surface complexes.

(7) Lability of "surface complexes" will be least when delocalization of the binding electrons is greatest.

(8) Partially occupied *d*-orbitals can be important for binding surface complexes and will have greater localization of ē than when only metal itinerant electrons are the binding electrons.

(9) Interactions possible between *d*-electrons localized on an ion core and itinerant electrons in Cr, Mn, Fe, Co, Ni and Pd (?) enable these metals to provide electrons for binding more easily than other metals.

From this rather lengthy background one can conclude that surface complexes can be of two types, one involving primarily itinerant electrons

TABLE 3 Types of surface complexes and
relation to metal properties

Type (from Fig. 4)	Characterization of Binding	Metal Preference
a	Delocalized, 3-center binding over adjacent oct and tet interstices (also H adsorption site)	Large numbers of interstitial electrons destabilize these orbitals. Mo, W, Ni, Co, Ru, Os preferred. Binding Strength α $1/\phi_M$
b	π-type complex	>Preference Mo, W. Some preference for Ru, Os, Tc, Re due to a vacant *d*-orbital to surface.
c	Delocalized, 2-center binding (bridging 2 M$^+$)	>Preference in CCP Metals (HCP has occupied *d*-orbitals which interfere)
d	Complex attached via vacant or partially occupied *d*-orbitals (σ-bonds)	>Preference Ni, Co, Fe, Pd, Pt. Next for Rh, Ir, Ru, Os, Tc, Re
e	M–C binding not via *d*-orbital positions (σ-bonds)	Preference high ϕ_M metals *e.g.* Pt, Pd, Ir
f	Combination of (a) and (e)	Preference for Ni
g	Like (a) but via non-adjacent interstices (probably great strain in binding olefins)	

(delocalized binding) and the other involving *d*-orbitals which are partially occupied (σ-bonds). To the extent that the binding is via carbons of the surface complex which have positive ion cores, these carbons will tend to be in bridging or interstitial positions. Vacant orbitals perpendicular to the ion core in the surface can lead to a 3rd type of chemisorption sites above positive ion cores (π-type binding).

Figures 4 and 5 shows a wide variety of possible adsorption sites for olefins, allyl complexes, butadiene and acetylene. The probable surface complexes are described as a, b, c, d, e, f and g complexes in table 3 and so indicated on the figure. Some of the reasons for this choice of surface complex can be given in general terms, others will depend on the specific properties of each metal.

First of all, π-olefin complexes are undoubtedly present on the surface and are expected to be most important for Mo and W which have vacant *d*-orbitals perpendicular to the surface, as well as occupied *d*-orbitals at 45° to the surface available for donation of electron to carbons. This fits the usual DEWAR-CHATT model for π-complexed olefins which, however, may be less applicable to the metal surface than to complexes in solution because of the greater variety of electrons and electron-positions on the metal surface. Also, as mentioned above, recent work[27] indicates that the binding in the Zeiss salt, K PtCl$_3$(C$_2$H$_4$) is probably of the sigma type formulated as $\begin{bmatrix} C\text{---}C \\ \diagdown Pt \diagup \end{bmatrix}^-$. This work is based on a careful study of vibration spectra and Cl$_3$

analyzes the contradictions in previous formulations as a π-complex $\left(Pt \leftarrow \begin{matrix} C \\ \| \\ C \end{matrix} \right)$.

The possible wide variety of olefin surface complexes is also shown by the variation of heat of adsorption of ethylene on ZnO (14 kcal/mol) to tungsten (140 kcal/mol). Even on ZnO there has been observed by temperature programmed desorption[65] both a strong and weakly bound ethylene, and it is the more weakly adsorbed C$_2$H$_4$ which reacts with hydrogen.

Although not directly applicable to metal surface complexes, NMR data[37] on the magnetic shielding of protons in ethylene in transition metal complexes is of interest in showing variable behavior of different metal ions. The value for proton shielding is 4.6 ppm for ethylene. It decreases to 4.3 ppm for Ag-olefin complexes which is less shielding and has been interpreted[37] as demonstrating a shift of electrons from olefin to Ag$^+$. Other transition metals (Mn, Re, Rh, Pt) show shifts in the range 5.3~8.5 ppm, and the increased shielding is interpreted as a shift of electrons to the olefin. Similar

measurements on surface complexes of ethylene on metals would be of great importance. Surface potential data for C_2H_4 on Cu and Ni is discussed in Section VI. 1 and indicates presence of $(C_2H_4)^{i+}$ species which would mean electron transfer from olefin to metal, just opposite to that in corresponding transition metal complexes.

Some recently reported data for infra-red adsorption on Ni reported by SHEPPARD *et al.*[40a] have given evidence of σ-bonded species on Pt, Pd and Ni. These investigators postulate a σ-type adsorption equivalent to that of type "e" and "d" surface complexes in Fig. 4. They include both dissociative and associative complexes of σ-type.

It appears reasonable to assume also on metals that there are various degrees of adsorption, that the initial surface complex is σ-bonded and that at high coverages where $\bar{e}$ in the metal surface are readily available (ϕ_M has increased due to chemisorption), there may be π-bonding which represents a much weaker attachment of C_2H_4 to the metal surface.

Magnetic masurements by SELWOOD and coworkers[36] offer some of the few experimental data available that directly relate to chemisorption sites on metals. For H_2 on Ni and Co it was found[33] that chemisorption of H produced a decline of 0.6 and 0.5 μ_β/adsorbed H, respectively, for Ni and Co.

This is compatible with a surface complex of H involving interaction with itinerant electrons which according to the Interstitial-Electron Model lowers the moments by 0.7 and 0.8 in Ni and Co, respectively. The model thus gives the first explanation of the low value for cobalt. If the chemisorption had involved d-orbitals on the metals there would have been a decline of $1\mu_\beta$/H for both metals. For ethylene chemisorption below 100°C on Ni the magnetic data show a decline in μ_β of 1.4 times that of hydrogen. The preferred surface complex for ethylene on Ni is probably type "d". This would preferentially give electron pairing for those d-orbitals on Ni with one electron and lead to a decrease in moment of $2\mu_\beta$/C_2H_4 adsorbed. Since this is higher than the observed decrease in magnetic moment due to ethylene adsorption (and also dissociative adsorption gives higher values), there must be chemisorbed species present which give smaller or no magnetic effects. Type "a" complex would give a decrease in moment of 0.6 μ_β/C_2H_4 and type "c" or "e" complex would not affect the moment. The greater declines in μ_β on chemisorption of C_2H_4 at temperatures above 100°C are due to dissociation and thus combined effects of H and acetylenic fragments.

The above gives a rather broad picture of "surface complexes" on a metal surface during catalysis. BURWELL[31] has suggested use of such multiply bonded species. It is quite likely that such a variety of complexes are

present, but that only one is primarily important in the catalytic pathway. However, it should be emphasized that any chemisorption profoundly affects the whole metal surface through the change it causes in ϕ_M. Since olefins are more strongly adsorbed than hydrogen, there is chemisorption of hydrogen only on a surface highly occupied by olefin, i.e., a surface with considerably higher ϕ_M but fewer vacant sites than that of the bare metal. Dissociation of H_2 would be expected to more difficult on the olefin rich surface than on bare metal.

These changes in the metal surface will be discussed in more detail for C_2H_4 and other individual reactions. Besides the differences in adsorption sites there is a lowering of the average energy level of metal itinerant electrons (Fermi level) due to chemisorption, and thus a change in the energies of itinerant electrons relative to energies of d-electrons. Since there probably is a small energy difference between states of electrons in d-bands (itinerant electrons) and d electrons localized on an ion core, changes in d-orbital pattern for some metals can be expected with temperature increase, with kind of molecule adsorbed and with coverage (see Section VI–3). The model thus gives a description of chemisorption in terms of surface compounds, but the binding electrons of these surface compounds exist in a dynamic equilibrium with the itinerant electrons of the whole metal structure. Since the electron energies change with coverage the binding energy of the surface compound changes with coverage.

It is proposed to discuss hydrogenation reactions starting with single reactions involving hydrogen atoms and proceeding to more complex olefin hydrogenations. The way in which the previous material on surface complexes will be used in this discussion can be summarized as follows:

1) Catalytic Activity will be compared to ϕ_M values to see if general availability of metal itinerant electrons may be the most important factor.

2) Trends in activity or selectivity with d-orbital direction and occupancy will be examined. This will involve possible relationships to the classification into metals of class I, II, III or IV mentioned in Section II.

3) Trends in the periodic table, which also give a measure of M^+ ion core fields and d-electron energies (and spatial extension), will also be examined.

4) Catalytic Activities will be examined on the basis of lability of surface complexes which follows from the comparisons in 2). Comparisons to "structure insensitive" and "structure demanding" reactions can be made.

IV. Reaction of Hydrogen Atoms on Metal Catalysis

IV-1 The Hydrogen-Electrode Reaction

This reaction was the subject of Part I of this series[39]. It has been shown by KITA[40] that there was a good correlation between activity and either ΔH of chemisorption of H_2 or metal work function for transition metals and Group IB metals. This was connected to a mechanism involving H atom recombination as the rate-determining step. Lack of activity dependence for "d-metals" of groups IIB–IVB on either ϕ_M or ΔH was explained by a different mechanism involving an H_2^+ intermediate on these metals. This example of a dependence of H atom recombination on ϕ_M of the metal electrode was the first instance in which a clear connection between catalytic activity and metal ϕ values was established. CONWAY and BOCKRIS[41] have called attention to the inverse relation between heats of adsorption of hydrogen on metals and work function and also shown a relation between ϕ_M and d-character.

IV-2 Hydrogen Atom Recombination

BOND[42] has discussed this reaction and pointed out that the activity of metal catalysts increases slightly from group IV to Group VIIIc and then declines to Group IIB. In addition, activity is high from metals with ΔH of adsorption of 30 kcal/mol and less and declines for metals with higher ΔH. The dependence on heat of adsorption is as expected, *i.e.* a high heat of adsorption accompanies a strong attachment of hydrogen to the metal surface which makes H atom recombination more difficult. For this reaction the expected dependence of activity on work function (ϕ) of metal is shown in Fig. 6.

The accepted mechanism for the hydrogen recombination reaction is

$$M + H \rightleftharpoons M\text{-}H_{ads}$$

$$M\text{-}H_{ads} + H \rightleftharpoons M + H_2$$
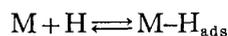
As such the strength of attachment of H to metal is expected to be the factor determining catalyst activity.

The work functions used for the correlations in this paper are the values suggested by BOUWMANN and SACHTLER[43]. These values, which are higher than the usually accepted ϕ_M values, are those for sintered metals where low index planes and defects (which tend to give low ϕ_M valuse) have been removed or diminished by the heat treatment (393°C, usually). These values are chosen since most of the catalysts have had a heat treatment comparable
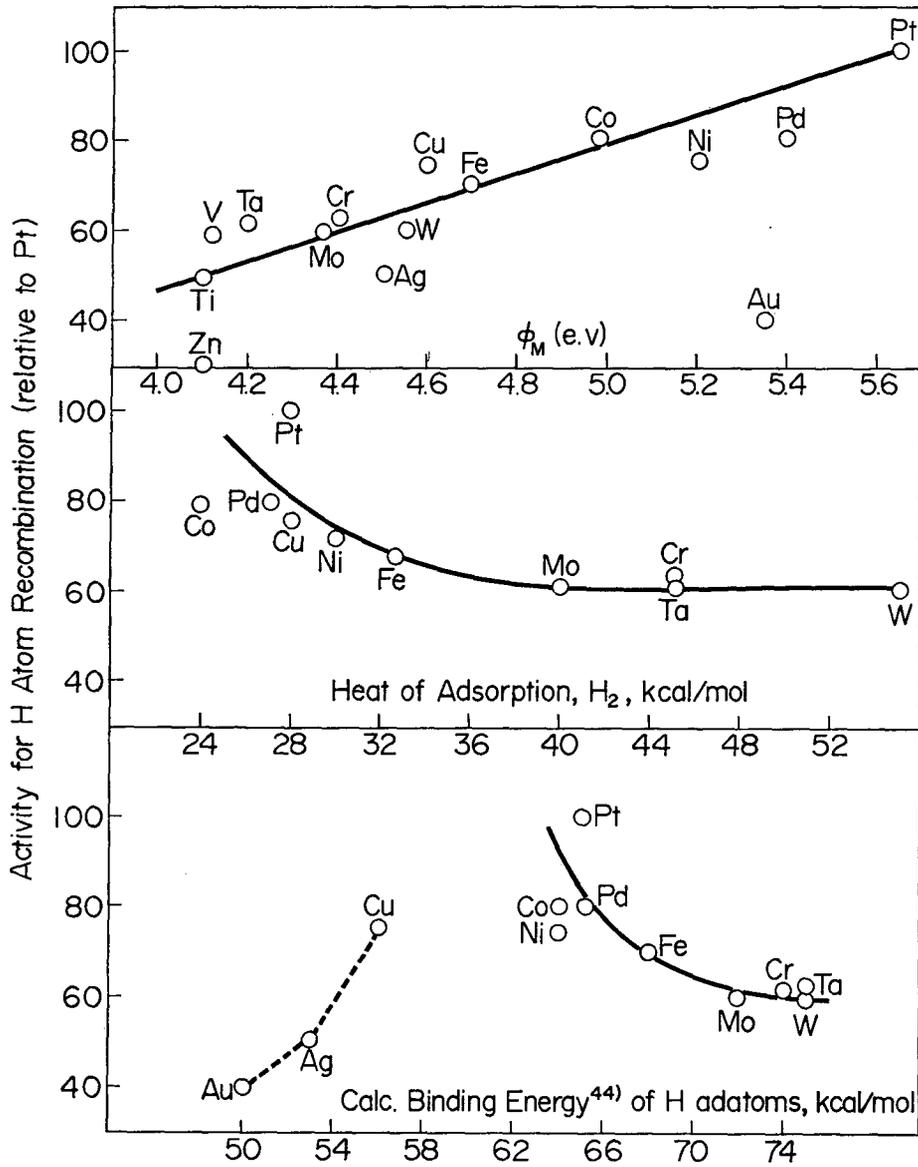
O. JOHNSON

Fig. 6. Dependence of activity of metals for H atom recombination on ϕ_M and heat of adsorption of hydrogen.

to that corresponding to the ϕ_M values of BOUWMANN and SACHTLER[43]. The values of ϕ_M used in the previous paper on chemisorption[33] were the lower values for metal films deposited at low temperatures since these represent the substrates most often used for measurement of $\Delta\phi$ on chemisorption.

There is generally an increase in activity with increasing ϕ_M in Fig. 6, again as expected for weaker chemisorption of H by high work function metals. In contrast to the dependence on ΔH, also shown in Fig. 6 b, the ϕ_M vs. activity curve shows an approximately linear dependence. For Figure 6 c, strength of adsorption for hydrogen atoms are used as suggested by EHRLICH[44] who gives calculated binding energies for H atoms. The curve of activity vs. ΔH of chemisorption indicates a very small change in activity after ΔH reaches a value of 36 kcal/mol for H_2. This is a region of strongest chemisorption of H_2 on metals, and shows that ϕ_M may give a better indication of catalytic behavior than ΔH. Plots of ϕ_M vs. ΔH shows that a constant ΔH of chemisorption in is reached for H at $\phi_M = 4.7$, for CO at $\phi_M = 5$ and for O_2 at $\phi_M = 4.5$ ev. (See Paper IV)[33]

The metals Cu, Ag, and Au occupy an unusual position in Figure 6 c. These metals all have completed d-shells with d-electrons extending into interstitial positions above the metal surface. These metals do not dissociate H_2, and the complete occupancy of d-orbitals may also interfere in H atom recombination activity. The very low position for Au in Fig. 6 a may indicate some different type of binding of hydrogen[18,45] on this high work function metal.

The small amount of data for H atom recombination on single crystal planes offers additional support for the use of ϕ_M as a correlating parameter. For Cu and Ag the activity is higher on the 111 plane than the 100 plane[46]. The ϕ_M values for Cu are $\phi_{111} = 5.54$ and $\phi_{100} = 5.15$ ev. For Ni the 110 plane is reported to have highest activity; the method of polishing single crystals may have affected these results as shown by the data of NAKADA[47]. However, according to the interstitial-electron model Ni_{110} has vacant d-orbitals at bridging sites which may chemisorb hydrogen as $H^{\delta+}$ at high coverages. This type of adsorption has been pointed out by SACHTLER and DORGELO[48].

V. Reaction of Hydrogen Molecules

V-1 p-H_2 Conversion

Differences in catalytic activity can occur between the H atom reactions already discussed and the p-H_2 conversion since the latter includes the additional step of dissociation of H_2 molecules to form H atoms on the metal catalyst surface.
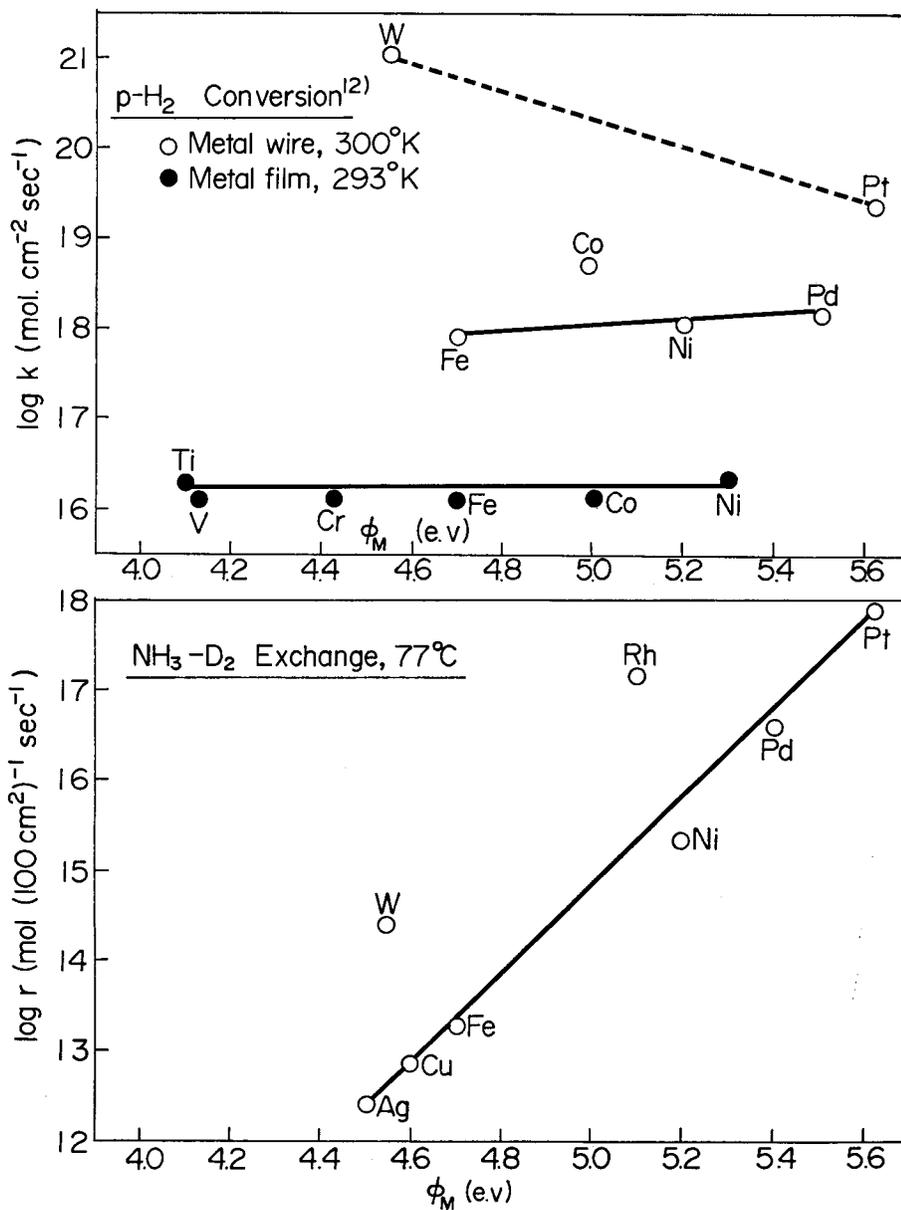
Fig. 7. Activity for p–H_2 conversion and NH_3–D_2 exchange as a function of ϕ_M.

The p–H_2 conversion has been studied in detail for 1st row transition metals by ELEY and SHOOTER[49], and in contrast to the H atom recombination there is about constant activity across the row. There are changes in order of reaction with temperature and pressure, but in general the mechanism appears to be a recombination of surface H atoms on sites of minimum energy. There is support for taking the rate determining step in p–H_2 conversion as the combination of H atoms on the surface in the following experiments. There is the very close parallel in activity of Au–Pd alloys for H atom recombination and p–H_2 conversion as observed by COOPER and ELEY[50]. This has been pointed out by BOND[42]. The second observation is the similar gradation in activities of these two reactions on different crystal planes of a given metal. VOLTER[51] has observed the following activation energies in kcal/mol for p–H_2 conversion:

	ΔE	ϕ_M		ΔE	ϕ_M
Ni_{111}	3.2	5.35	Cu_{111}	9.1	5.54
Ni_{110}	5.2	5.04	Cu_{100}	13.5	5.15
Ni_{100}	6.4	5.22			

(The use of Activation Energies for comparing activities is discussed in ref. 8 b.)

These are the same gradation as given above for H atom recombination for Cu; Ni_{110} differs for the two reactions. The variation in activity for the p–H_2 conversion correlates very well with work function for the different lattice planes of Cu and Ni; however, for different metals the correlation depends on row in the periodic table. The activity of 1st row transition metals for p–H_2 conversion is about constant (with a lower value only for Mn) but considerably lower for Cu and Zn (not shown). The latter values reflect the non-dissociation of H_2 on these metals. In the 3rd row transition metals W has very high activity and Pt a higher activity than Ni or Pd. In their discussion of p–H_2 conversion ELEY and SHOOTER[35] postulate a minimum in energy of adsorption for W_{110} and connect high activation energy and frequency factor with narrow $3d$-bands in Ti, V, Cr, Mn, and Fe. However, recent photoelectron spectroscopy results[52] indicate no such difference in band widths. It is suggested that the p–H_2 conversion for a series of metals does not correlate well with ϕ_M because it occurs at high coverage where the increase in ϕ_M due to chemisorbed hydrogen on the surface leads to only very small difference in ϕ for the H covered surface. This requires a special reason for high activity of W and Pt as mentioned

above. The previous paper[33] on chemisorption on metals postulated chemisorption over W^{6+} ion cores via d-electrons for W_{100} and similar chemisorption or bridging chemisorption on W_{110}. This much weaker chemisorption on W (the 110 plane is expected to predominate for polycrystalline W) can explain its high activity for p-H_2 coversion. Pt has also been reported to show a decrease in ϕ_M with hydrogen chemisorption. In any event the high ϕ_M for Pt leads to very weak chemisorption. This weak chemisorption will be discussed further in Section V-2.

V-2 H_2-D_2 Exchange and H_2-D_2 Equilibration

Transition metals show exchange of H_2 and D_2 at temperatures below 100°C while non-transition metals show exchange only above 300°C. This is another example of difference in activity due to the difficulty of H_2 dissociation over non-transition metals. For metals like Cu, Ag and Au there may be promotion of d-electrons to s-bands at the higher temperatures to form sites which dissociate H_2.

There is surprizingly little data on these reactions for a series of metals. SCHUIT et al.[53] found the following order of decreasing catalytic activity on metals supported on SiO_2 for the H_2-D_2 exchange reaction at 0°C.

> Pt, Rh, Ru>Ni, Co>Fe, Cu

The data of SCHUIT et al. indicate a tendency toward a dependence on ϕ_M, i. e., Ni and Co to be more active than Fe or Cu. Experiments on metal films have been summarized by BOND[12] for the equilibration reaction and show about constant activity for H_2-D_2 equilibration for 1st row transition metals, very high activity for W and higher activity for Pt than Pd or Ni. As expected the gradations of metal catalyst activity for the H_2-D_2 equilibration are very similar to those of the p-H_2 converion. In the above discussions of the latter reaction, weak chemisorption of hydrogen was considered to explain the high activity for W and Pt. On the basis of the earlier study of chemisorption[33] this weak chemisorption is chemisorption directly over a metal ion or in bridging positions, in either case at positions of unoccupied d-orbitals. This is in partial agreement with DOWDEN's suggestion for the socalled Type-C chemisorption on metals. W and Mo occupy a unique position of being the only metals with unoccupied d-orbitals $\perp$ to surface of BCC structure (where the 110 plane is important); Cr has a smaller extension of d-orbitals and a different direction of orbitals[4].

V-3 NH_3-D_2 exchange

There is quite a good correlation between ϕ_M and activity of metals for NH_3-D_2 exchange (See Fig. 7). This correlation was previouly pointed

out by KEMBALL[21] and explained on the basis of NH_4^+ formation. An alternate explanation consistent with other reactions of H_2 would be that exchange of chemisorbed NH_3 and H (or D) atoms depends on the ease of movement of chemisorbed H which is inversely proportional to ϕ_M.

V-4 Summary of reactions of hydrogen

In the reactions of hydrogen on metal catalysts the H electrode reaction, H atom recombination and NH_3–D_2 exchange show a good correlation with ϕ_M. In all these cases activity appears to be dependent on the attachment of H atoms in an interstitial position as $H^{\delta-}$. These reactions are considered to take place at low coverage of H. For H_2–D_2 equilibration and p–H_2 conversion, activity was about the same for 1st row transition metals and Pt and W showed greater activity. Under the conditions of high coverage of hydrogen, ϕ_M approaches a constant higher value of ϕ_M previously designated[33] as $\phi_{terminal}$, so little dependence on ϕ_M is expected at high coverage. The higher activity for W and Pt are connected to chemisorption as $H^{\delta+}$ or Type-C chemisorption. The parallel behavior for these two types of hydrogen reaction (H atom recombination *vs.* equilibration) on Pd–Au could be due to low surface coverage of hydrogen on Pd–Au alloys.

VI. Hydrogenation of Olefins

Hydrogenation of several olefins and diolefins will be discussed below with emphasis on new interpretations by the interstitial-electron model. Considerable use has been made of the comprehensive discussion of hydrogenation catalysis by BOND[12], BOND and WELLS[54], THOMAS and THOMAS[11], KEMBALL[21], KOKES[30], ANDERSON and BAKER[55] and KNOR[56], and for the most part the model offers theoretical bases and makes additions to the interpretations in the literature. Aims of the present discussion will be to formulate olefin surface complexes as precisely as possible, to assess the usefulness of ϕ_M as a parameter in the more complex hydrogenations of olefins and other hydrocarbons, and to see what clarifications the classification of transition metals into class I, II, III or IV (depending on d-orbital orientation and occupancy) provides.

VI-1 Ethylene

A critical review of the extensive data on ethylene hydrogenation over transition metals has been recently published by HORIUTI and MIYAHARA[23]. Some of the observations on metal oxides have been discussed by TANAKA, NIHIRA and OZAKI[57] and by KOKES[30,58]. An attempt will be made here to relate this reaction of H_2 and an unsaturated hydrocarbon to the gradations

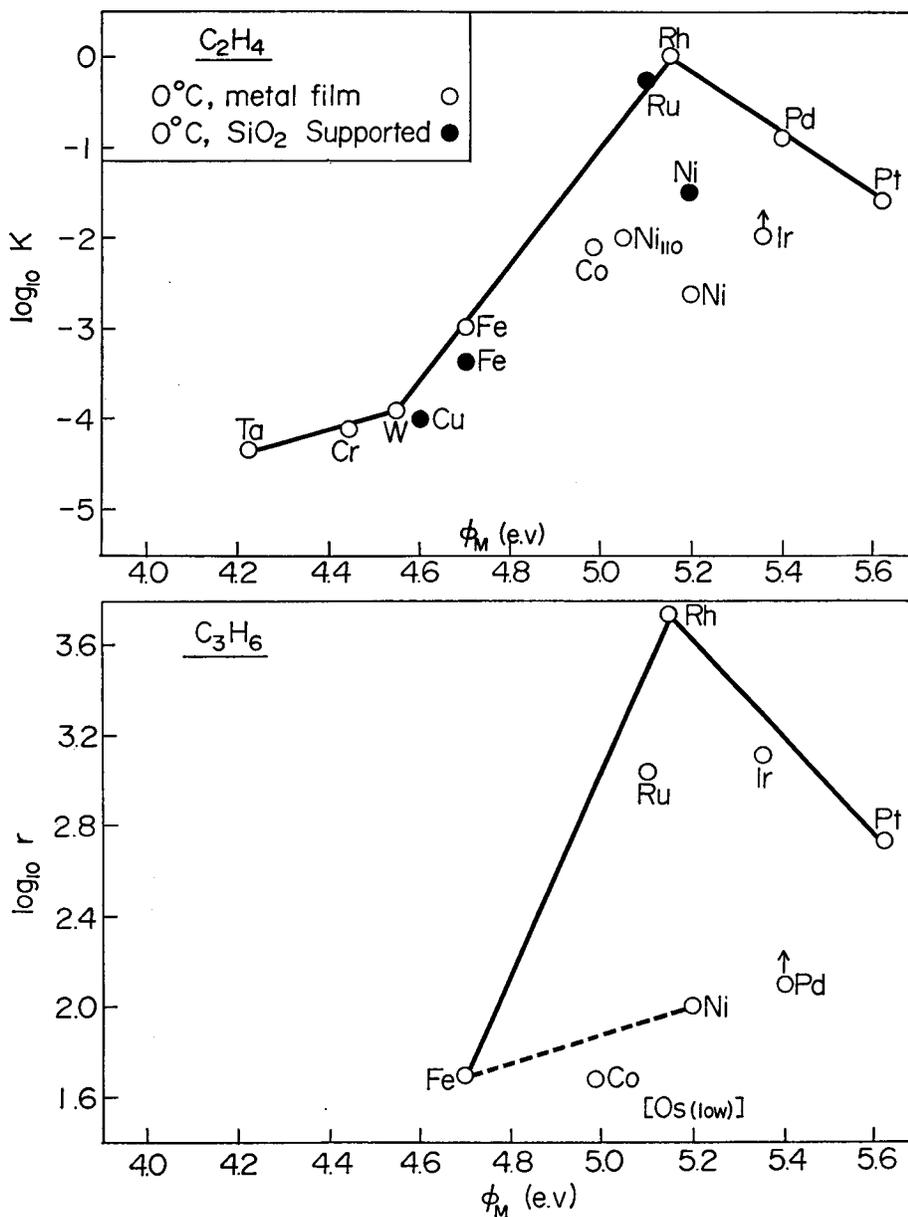**Fig. 8.** Activity of metals for hydrogenation of C_2H_4 and C_3H_6.

of activity already discussed for H atom recombination, p–H_2 conversion and H_2–D_2 exchange as well as to activities of transition metal complexes as homogeneous catalysis and of metal oxide catalysts.

Correlations of ethylene hydrogenation activity with d-character[7] of transition metal or to d-character times valence[8] and to initial heat of adsorption[6] of H_2 or of ethylene are well known. The role of lattice spacing has also been assessed[5,11].

Of the above correlations probably the one with ΔH is the only one of basic significance to catalyst activity. It is of interest that in the extensive study of kinetic pathways for ethylene hydrogenation, HORIUTI and MIYA-HARA[23] have predicted possible activity greater than that for Rh on the basis of parameters related to ΔH of chemisorption and to repulsion effects within the activated complex. They conclude the rate determining step in the ethylene hydrogenation to be the step of addition H to an alkyl chemisorbed species above optimum conditions and the step of dissociation of H_2 below optimum.
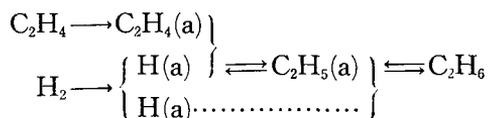
The correlation of ethylene hydrogenation activity with ϕ_M, as was already done for H_2 reactions, will be considered first to see if there are some general trends for metal catalysts. The early data of BEECK[7] remains the only ethylene hydrogenation measurements on series of metal film catalysts. There is data on oxide supported metal catalysts by SCHUIT and VAN REIJEN[53]. The log of activity for both these sets of data relative to Rh metal is plotted against ϕ_M in Figure 8. Although there is some scatter of data the data can be fitted to a volcano type curve with a maximum at Rh. Measured ϕ_M values for Ni are highly divergent, and the most recent ones on single lattice planes[59] are considerably higher than the ϕ_M value accepted for polycrystalline Ni[60]. The ϕ_M given by SACHTLER and BOUW-MANN[43] is used in Fig. 8 and the activity value for Ni_{110} by BEECK[7] with ϕ_M from ref. 69.

The indication of an optimum ϕ_M will be seen below also for other hydrogenations of hydrocarbons. A simple interpretation is that below this optimum, surface complexes of C_2H_4 and H are more strongly bound by the metal surface than optimum for high catalytic activity and that above this optimum ϕ_M, they are more weakly bound than optimum for high activity. This is equivalent to explanations based on volcano curves of activity *vs.* heat of formation of hydrides. ROONEY and WEBB[18] have suggested that since the surfaces under consideration strongly adsorb C_2H_4 it is likely that attachment of hydrogen to the metal surface will be the critical factor. However, it has already been stressed that the strength of binding of hy-

drogen is indirectly affected by both C_2H_4 chemisorption and formation of acetylenic residues which both increase ϕ_M. The picture the model gives of the electron interactions on the metal surface of H and ethylene species makes the observation on effect of pretreatment of catalysts understandable since residual materials on the catalyst surface can affect subsequent chemisorption.

To provide a meaningful description of ethylene hydrogenation the above correlation must be connected to specific surface species as well as to the overall kinetics of the reaction. The associative mechanism developed by HORIUTI and POLANYI[61] and used extensively in this laboratory to explain complex observations in C_2H_4 hydrogenation, offers a suitable framework for the present discussion.

$$C_2H_4 \longrightarrow C_2H_4(a) \left.\begin{array}{c} \\ \end{array}\right\rangle$$
$$H_2 \longrightarrow \left\{\begin{array}{c} H(a) \\ H(a) \cdots\cdots\cdots\cdots \end{array}\right\} \rightleftharpoons C_2H_5(a) \left.\begin{array}{c} \\ \end{array}\right\rangle \rightleftharpoons C_2H_6$$

The species written above as $C_2H_4(a)$ in our microscopic description can be σ-bonded in at least 2 different ways by group (II) and group (III) metals. To it should be added still a third species, a π-bonded species, $M \leftarrow \|_{C}^{C}$, which is likely at high coverages. It should also be emphasized that the binding energy of all of these species is expected to decrease with increasing coverage. These "surface complexes" were shown in Fig. 4, and suggested type preference for different metals in Table 3.

It is proposed that the reversibility of the alkyl formation step will be very different for the 3 species (see Section VI. 3). Group III metals will have easy reversibility since bonding electrons are already in place. Group II metals will show less reversibility since extensive shifts of itinerant electrons are required for formation of bonds. Conversely it is likely that the possibility of electron shifts to facilitate addition of 1 hydrogen is also what makes these Group II metals highly active. However, the rate controlling step for hydrogenation of C_2H_4 on these metals may be associated with the H_2 dissociation step[18,23]. These metals all have high ϕ_M and weak attachment of chemisorbed species will accompany the relatively difficult dissociation of H_2. This interrelation of attachment of olefin and H shows that comparisons to metal-olefin bonds in Complexes are an oversimplification[63a].

It is of importance to consider the experimental data which gives direct indication concerning species on the surface active in ethylene hydrogenation. It is known from infra-red adsorption studies[62] that on a surface covered

with H atoms, adsorption as C_2H_4 occurs while on a bare metal surface
there are also $-\overset{\text{H}}{C} = \overset{\text{H}}{C}-$ species, called acetylenic residues. ALEXANDER, FORD
and PRITCHARD[63] have followed changes in work function of Cu during
hydrogenation of ethylene. Ethylene chemisorbs on Cu to give a decrease
in ϕ_M of 0.8 ev. (thus, $C_2H_4^{\delta+}$) while hydrogen chemisorbs with an increase
in ϕ_M of 0.35 ev. During hydrogenation at 0°C the changes in ϕ_M clearly
show that the ethylene species which gives the decrease in ϕ reacts with
H to form ethane. These observations agree with some tentative data for
Ni reported by MIGNOLET[64]. These data clearly establish that weakly chemi-
sorbed ethylene ($\Delta H = 17.5$ kcal/mol) is hydrogenated by H on the Cu (and
Ni) surface.

An extensive study by RYE, HANSEN and coworkers[38] of the $C_2H_4-H_2$
system on tungsten by flash desorption shows some of the details of hydro-
genation on tungsten. These data show that 110 tungsten has adsorption
sites than can adsorb either H_2 or C_2H_4 while the 100 plane has independent
sites for chemisorption of H_2 and C_2H_4. From the analyses of chemisorption
presented in Paper IV[33] the bridging sites on W_{110} (see Fig. 4) or edge sites
on W_{100} can accomodate either $(C_2H_4)^{\delta+}$ or $(H)^{\delta+}$, but the center of a face of
the unit cell can chemisorb $H^{\delta-}$ only. These flash desorption studies also
have demonstrated that the above species are involved in hydrogenation of
ethylene on W.

Some temperature programmed desorption experiments on Pt reported by
CVETANOVIC and AMENOMIYA[65] show that out of 5 different chemisorbed
species of hydrogen, the weakly bound H (or H_2) gave H_2-D_2 equilibration,
and the more strongly bound H gave only D_2 exchange while the most
strongly bound H was inactive. For comparison, similar data on ZnO show
two chemisorbed species of C_2H_4 on ZnO, but only the more weakly chemi-
sorbed species of both C_2H_4 and H participating in the hydrogenation reac-
tion. This is in agreement with the conclusions of KOKES[58] who proposes
that the reactive $(C_2H_4)^{\delta+}$ is chemisorbed on O^{2-} (see below), and upon addi-
tion of 1 hydrogen, shifts to chemisorption of (C_2H_5) on Zn^{2+}.

The above experimental evidence as well as the magnetic data of
SELWOOD[36] can be interpreted in terms of chemisorption of ethylene with
delocalized binding between $(C_2H_4)^{2+}$ and M^{n+} ion cores and electrons donated
by ethylene and metal itinerant electrons. This is similar to the binding in
transition metal complexes with the difference that greater electron density
in the region of M^{n+} is proposed for the chemisorption on metals. In metal
complexes proton shielding parameters[37] indicate net transfer of electrons to

Ag^+ in its olefin complexes but net transfer to olefin for other transition metal. For ZnO two types of olefin chemisorption occur. One is π-bonding by Zn^{2+} and the other a $(C_2H_4)^{\delta+}-O^{2-}$ complex similar to the olefin$^+$-trinitro-benzene$^-$ complexes[57]. Two forms of chemisorbed ethylene were also observed for Cobalt oxide[57]. It is concluded that $(C_2H_4)^{\delta+}$ is the bound species on metal, and it probably is held in positions of M^{n+} in the layer above the surface (over tet sites, marked as $\triangle$ in Fig. 4).

Data available for ethylene hydrogenation on single crystal planes of Ni will also be examined to see if they provide any clue to the complex behaviour. BEECK[7] observed a 4-fold increase (only partly due to increase in metal surface area) in ethylene hydrogenation over Ni (110) films as compared to a randomly oriented film. CUNNINGHAM and GWATHMEY[66] observed that below 100°C the sequence of activity Ni (110)>Ni (111)>Ni (100) after an initial decline in rate. Similar results were recently reported by IMELIK[66a]. Since Ni (110) has the lowest work function (opposite to the trend in Fig. 8) these results suggest that the most active Ni catalyst is the Ni lattice plane which has strongest attachment of H and C_2H_4. However, the ϕ_M for the other 2 lattice planes then do not have the same correlation with the activity gradation. An alternate explanation is that the special weak adsorption of hydrogen as $H^{\delta+}$ on Ni (110), postulated above for the H atom recombination reaction, leads to the higher catalytic activity for Ni (110). However, this probably would have a low activation energy which is not observed for Ni. Still another possibility is suggested by the D_2-hydrocarbon exchange study over nickel single crystal surfaces by ANDERSON and MACDONALD[69]. They concluded that polycrystalline Ni which probably contained some Ni (110) had sites which stabilized mono-adsorbed hydrocarbon while the Ni (111) and Ni (100) and sintered surfaces had none. A higher activity for ethylene hydrogenation would be expected on Ni (110), since mono-adsorbed species ($M-C_2H_5$) are a necessary step in the hydrogenation. The Ni_{110} plane has 2 different metal-metal distances which may be the basis of the difference in mono-and di-adsorbed species and indirectly for activity. See further discussion in Appendix.

There is considerable data on ethylene hydrogenation by alloys. The work was usually carried out to support the expectation that[1] activity was dependent on holes in the d-band. Although the early experiments[50] showed a striking decline in activity for Pd to which Au was added and no activity for alloys containing more than 60% Au, several alloy experiments show less clear gradations. The Band Theory of Metals indicates that addition of a d^{10} metal to Pd, $e.g.$ will cause a decline in paramagnetism. The

Catalysis and the Interstitial-Electron Model for Metals, V.

interstitial model separates out the effects of the localized d-electrons and indicates there will only be exchange which will affect paramagnetism when the d-electron have comparable energies and the required spatial extension. Some of the complexities of hydrogenation by alloy catalysts has been recently discussed by Moss and Whaley[68]. Alloy catalysis will not be discussed here, but some general criticisms of use of an over-simplified d-band model have been published separately (J. Catalysis, **28**, 503 (1973)).

It is remarkable for this well studied reaction that the precise mechanism and rate determining step are still in disagreement. A very general conclusion that weakly adsorbed $(C_2H_4)^{\delta+}$ and $H^{\delta-}$ or $H^{\delta+}$ are involved in the rate determining step seems warranted. The constant activation energy of the hydrogenation (except for the low values for W and Ta) makes ethylene hydrogenation an untypical reaction for olefin hydrogenation. Knor[56] has expressed the similar idea that there may be greater variety of adsorption sites available for simple molecules than for larger or more complex reactant molecules. A possible reason for the similar activation energy for C_2H_4 hydrogenation is the tendency for a metal-adsorbate interaction to approach a constant terminal ϕ_M[33]. In the case of ethylene the strong adsorption of ethylene as $(C_2H_4)^{\delta+}$ leads to about the same ϕ_M values at high coverage for all metals, and thus to a closely similar chemisorbed $H^{\delta-}$ for all metals with the possible exception of $H^{\delta+}$ on tungsten. For other olefins the different activation energies for hydrogenations on different metals will be discussed below as well as the interesting selectivities in D_2 exchange and isomerizations during hydrogenation.

It appears that ϕ_M is a useful parameter for a very general assessment of catalysts *i.e.* that low ϕ_M metals are not efficient hydrogenation catalysts and that also metals of very high ϕ are less active than those of optimum ϕ_M. More detailed reasons for this dependence are probably the following. The strong adsorption of H atoms by low ϕ_M metals involves electron attraction by H and leads to $H^{\delta-}$. Adsorption of C_2H_4 by these same metals involves surface complex formation with rearrangement of electrons (large ΔH) but small net change in dipole of C_2H_4 (small $\Delta\phi$ and $C_2H_4^{\delta+}$ with small δ value). On the other hand, as already discussed, a high ϕ_M metal may interact with H atoms to form $H^{\delta+}$ and the electron transfer in the ethylene chemisorbed complex gives $C_2H_4^{\delta+}$ with a relatively high $\delta+$. (This can involve less metal electron rearrangement and thus a small ΔH). There is clearly an optimum position between these 2 extremes, and this analysis suggests it will be for metals that give a relatively weak $H^{\delta-}$ attachment. The way in which different surface planes d-orbitals can affect this have

already been suggested.

In addition to suggesting the use of ϕ_M as a correlating parameter, the model has suggested a wider variety of chemisorbed species than usually discussed, but has also proposed specific "surface complexes" involved in ethylene hydrogenation. Different surface binding is suggested for Class I, II and III metals and although differences are not strong for ethylene hydrogenation, it will be seen that for higher olefins the selectivity is markedly affected by metal class. Also part of the model is a role for occupied d-orbitals in chemisorption of H at high coverages where d-electrons have comparable energies to itinerant electrons.

VI-2 Propylene and Higher Olefins

The rate of hydrogenation of propylene[12] over a Ni catalyst is only about 1/10, and that for butene about 1/30, of that of ethylene.

The activation energies for hydrogenation of propylene[69] vary from 7~17 kcal/mol over different metals, and activation energies for butene[12] hydrogenation are 2~3 kcal/mol as compared to 12 kcal/mol for ethylene hydrogenation for all metals except W and Ta. BOND has pointed out that in contrast to the 1st order kinetics for ethylene and zero order for hydrogen, both reactants show 1/2 order kinetics in the hydrogenation of 1-butene.

BOND concludes from this that hydrogen is more readily adsorbed in presence of higher olefins than with ethylene. Since acetylene is more strongly adsorbed on Ni-pumice than methyl acetylene (see Section VIII), it is also likely that ethylene will be more strongly adsorbed on metals than propylene. With propylene the possibility of a π-allyl type of adsorption must also be considered. An allyl complex is considered to be present in hydrogenation of C_3H_6 and C_4H_8 over ZnO[58] but not Co_3O_4[57].

Fig. 8 shows the gradations with ϕ_M in hydrogenation activity for propylene hydrogenation. The ϕ_M $vs.$ activity curve shows a maximum at Rh, but first row transition metals all are low. There is an indication of higher activity for Class II metals than Class III metals (which may form allyl species).

As with ethylene, propylene is expected to chemisorb as $(C_3H_6)^{\delta+}$ with a larger δ value than C_2H_4 due to electron donation ability of the additional CH_3 group. The variations in ΔE for hydrogenation suggest a different rate determining step than for C_2H_4, in this case possibly the $(C_3H_6)_{ads} \leftrightarrows C_3H_7$ step. A variety of different $(C_3H_6)_{ads}$ species could lead to the range of ΔE values.

When propylene adsorbs on a metal surface the same sites postulated for ethylene can be occupied in a 2-point attachment. In addition the CH_3

group now close to the metal surface is susceptible to dissociative bonding to form a 3-point attachment of propylene to the surface (cf. Fig. 5). The tendency for this to happen is probably similar to the tendency for exchange of CH_4 and D_2 over metals, a process which involves attachment of CH_3 to the surface. The order of metals in increasing CH_4–D_2 exchange is $W > Rh > Pt > Pd > Ni > Co > Fe$. Now such a 3-point attached propylene can switch to a π-allyl species by electron delocalization, and the following reaction paths are possible in propylene hydrogenation.

$$
\begin{array}{c}
\underset{H_2C=C-CH_3}{\overset{H}{}} \;\rightleftarrows\; \underset{M\quad M}{\overset{H\;H}{H\,C-C-CH_3}} \;\underset{-H}{\rightleftarrows}\; \underset{M\quad M\quad M}{\overset{H\;H\;H}{H\,C-C-CH}}
\end{array}
$$

$$-H / +H$$

$$+H \mid -H$$

$$
\underset{M}{\overset{H}{C}}\;\diagdown\;\underset{M}{\overset{H}{C}H}
$$

$$\uparrow\downarrow +H$$

$$C_3H_8 \overset{+H}{\longleftarrow} \underset{M}{C_3H_7} \overset{}{\underset{+H}{\longleftarrow}} \qquad \underset{M\qquad M}{\overset{H\quad H_2\quad H}{H\,C-C-C\,H}}$$
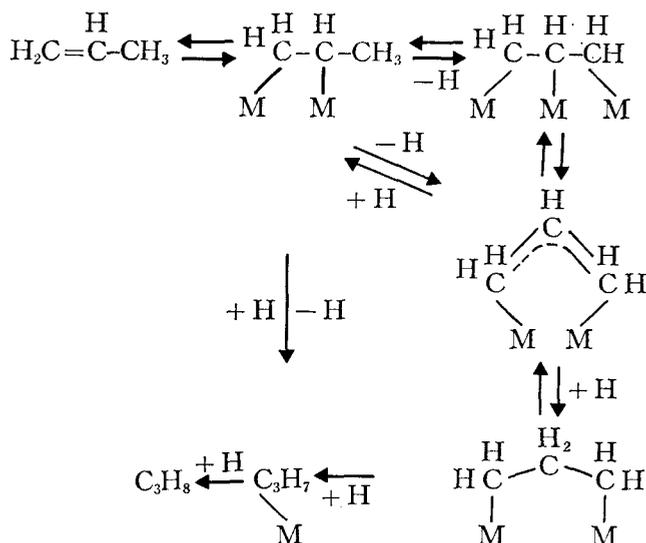
In addition there can be isomerization of the two different C_3H_6 surface complexes.

Some unusual features of propylene hydrogenation to explain are the low activation energies for Ru, Os and Fe and Co and low activities of Fe, Co, Ni and Pd and Os, already mentioned.

One feature of the close packed surface for Ru, Os, and Co is the presence of a potential tet interstitial sites $\perp$ to the ion cores in the surface. Since the normal interstice in HCP would have the other $3M^+$ in the missing next layer, this will not be a region of high $\bar{e}$ density, but rather will be a region in the surface which has a high $+$ field. [This effect is the opposite to the presence of lone pairs of electrons in molecules]. This situation is expected to lead to a very weak binding of propylene over Ru, Os, and Co (HCP metals) and can be connected to low activation energy for hydrogenation. Alternatively, when partially occupied d-orbitals are used for binding,

stronger but labile binding is expected for Fe, Co, Ni, Pd, Pt. The opposing trends for the same metal can lead to the complex gradations in activity.

An allyl ligand will donate 3 electrons as a $(C_3H_5)^{3+}$ species which would form on the metal surface only after dissociation of 1 hydrogen. ROONEY and WEBB[18] have pointed out that Fe, Pd, and Co are the metals which convert σ-olefins to π-allyl complexes most readily, and if this is the case it would mean a stronger chemisorption for Fe, Co and Pd and a resulting lower activity.

The above considerations strongly suggest that in hydrogenation of propylene, the low activity for Fe, Co, Ni and Pd are connected with formation of π-allyl surface complexes. The special properties of HCP lattices have given the only explanation thus far for the low activation energy of propylene hydrogenation for Ru, Os and Co. The low activation energy for Fe is not explained.

VI-3 Diolefins

The data on hydrogenation of butadiene gives important information on selectivity in hydrogenation. The metals Fe, Co, Ni, Pd and Cu (Class III metals + Cu) are the only metals which hydrogenate butadienes almost exclusively to butenes[70]. For these metals yields of n-butane are 0% for Fe, Co and Cu and 0.3% for Ni and Pd. Class II metals like Rh and Ir give considerably more n-butane.

There is a clearly greater selectivity for butene formation for Group III metals than Group II metals, which must be connected to the use of partially occupied d-orbitals in the binding of the surface complex of Group III metals. Cu is also included with these metals, but probably it shows high selectivity because of its low activity for olefin hydrogenation. ROONEY and WEBB[18] have postulated π-allyl complexes for Pd and Co to explain some of the stereochemistry. However, the general difference in selectivity probably has a more general explanation and lies in the manner of chemisorption of the diolefin. From the possible chemisorbed species shown in Fig. 5 it appears difficult for both double bonds to be chemisorbed via available d-orbitals on Class III metals but possible by delocalized binding for Class II metals. BOND[12] has reviewed the evidence from competitive reactions which shows that dienes are more strongly adsorbed than olefins.

Since the selectivity patterns[18] for metals are very similar in the hydrogenation of 1-3 butadiene, allene and acetylene it is important to see if the above explanation holds for all three hydrogenations. ROONEY and WEBB[18] have suggested that since the selectivity should be a function of ratio of rate of desorption of olefin and rate of further addition of hydrogen to the

adsorbed olefin, the increase in selectivity from Ru to Rh to Pd and from Pt to Pd indicates decrease in stability of olefin complex in those directions. This explanation does not include the first row metals Fe, Co and Ni, and BOND[12] has shown that ethylene and acetylene can compete for surface sites on Os and Ir. The suggestion, which can also be the underlying reason for strength of adsorption, that Class III metals give high selectivity because surface complexes are readily formed and readily desorbed due to σ-binding via partly occupied d-orbitals can hold for both dienes and acetylene. It is consistent with the similar explanation of high isomerization and exchange by Class III metals because of easy reversibility of the alkyl formation step. The possibility also remains that in presence of acetylene or di-olefin and product olefin, the dissociation and adsorption of more weakly bound hydrogen is the determining factor.

Rhodium shows the isomerization and exchange behavior of Class II metals at temperatures $>80°C$ only and platinum exhibits properties of both Class II and III. Two comments can be made about Pt as a catalyst. First, it has been described by BOND and WELLS[54] as exhibiting facile alkyl reversal but difficulty in desorption. The former is a Class III metal property associated with partially occupied d-orbitals, and the latter can account for a lower exchange activity and isomerization activity than other Class III metals. BOND and WELLS[54] have also concluded that there is no evidence for π-allyl species with Pt. The second comment has to do with metal structure. Although there is strong evidence for unpaired d-electrons in Ni and Pd, the evidence for Pt is primarily the existence of a paramagnetic region for Pt metal (as for Pd and Ni). It is possible that although in the paramagnetic region there are $Pt^{10+}(d^7)$ ion cores with one unpaired electron, the normal metal has both $Pt^{10+}(d^7)$ and $Pt^{10}(d^6)$ ion cores; the latter would not have unpaired electrons and would have properties of Class II metals (vacant d-orbitals).

Within the group of metals giving high selectivity for butene formation, the amount of 1,4-addition varies from 15% for Cu, 40% for Pd, 50% for Ni to 70% for Co. The ratio of trans-butene-2 to cis-butene-2 is high for Co and Pd and low for Cu and Ni, and has been explained by π-allyl formation for Co and Pd by JOICE, ROONEY, WELLS and WILSON[70]. The interpretation of the stereochemistry of hydrogenation using the present model will be discussed in a subsequent paper.

There are not sufficient data to compare activity levels for butadiene hydrogenation for a series of metals. The very high selectivity for hydrogenation to butene by H Co(CN)₅ catalysts is connected with complexing of

a single double bond, and the ratio of 1–2 to 1–4 addition is markedly influenced by number of CN groups coodinated[71]. The model used in the present paper suggests that on Group III metals there can be conversion of the species adsorbed at one double bond to a π-allyl surface species by loss of 1 hydrogen, which would add Fe, Ni, and Pt to the metals Co and Pd considered by ROONEY *et al.*[70]

VII. Cyclopropane Hydrogenation

There is considerable delocalization of the binding electrons in cyclopropane, and it is probably initially bound to metals as a π-complex. This π-complex can dissociate 1 H to form a π-bonded cyclic compound which can either rearrange to relatively stable allyl forms or fragment. According to MERTA and PONEC[72] the activities of metals for hydrogenation of cyclopropane decrease in the order Pd, Pt $>$ Rh $>$ Ni $>$ Mo $>$ Fe. The activity for fragmentation (cracking) decreases in the order Ni $>$ Mo $>$ Rh $>$ Fe $>>$ Pd, Pt. Of these metals only Pd and Pt give propane as the only hydrogenation product. Pd and Pt show partially dehydrogenated 3C species on the surface which can be displaced by CO. Ni, Fe and Mo show neglible displacement of dehydrogenated species although H_2 is displaced.

These gradations as discussed by MERTA and PONEC[72], KNOR[56] and also by BOND[12] can be explained by π-adsorption of cyclopropane by Pd and Pt and dissociative adsorption by Ni, Mo and Fe. These tendencies also can exist in other hydrogenations and explain some of the gadations. For comparison, another measure of dissociative adsorption (in the case of C_2H_4) is the carbon retention by the catalyst of the interaction with ethylene. For alumina-supported metals there were found to be following order[73] of increasing dissociation (C retention): Pt $<$ Ir $<$ Rh $<$ Ni $<<$ Pd. Other results[7] show the above order as Rh $<$ Pd $<$ Ni. The relatively high value for Ni is found for both C_2H_4 and cyclopropane dissociative adsorption.

The dissociative adsorption by Ni, Mo and Fe causes their activities to be low for cyclopropane hydrogenation. The usual patterns found in olefins are obscured by this susceptibility of cyclopropane to dissociation of H and to cracking.

VIII. Hydrogenation of Acetylenes

The order of decreasing activity for metals in the hydrogenation of acetylene is for pumice-supported metals[74] Pd $>$ Pt $>$ Ni, Rh $>$ Co $>$ Fe $>$ Cu, Ir $>$ Ru, Os. The order for metal films[75] is essentially the same but with
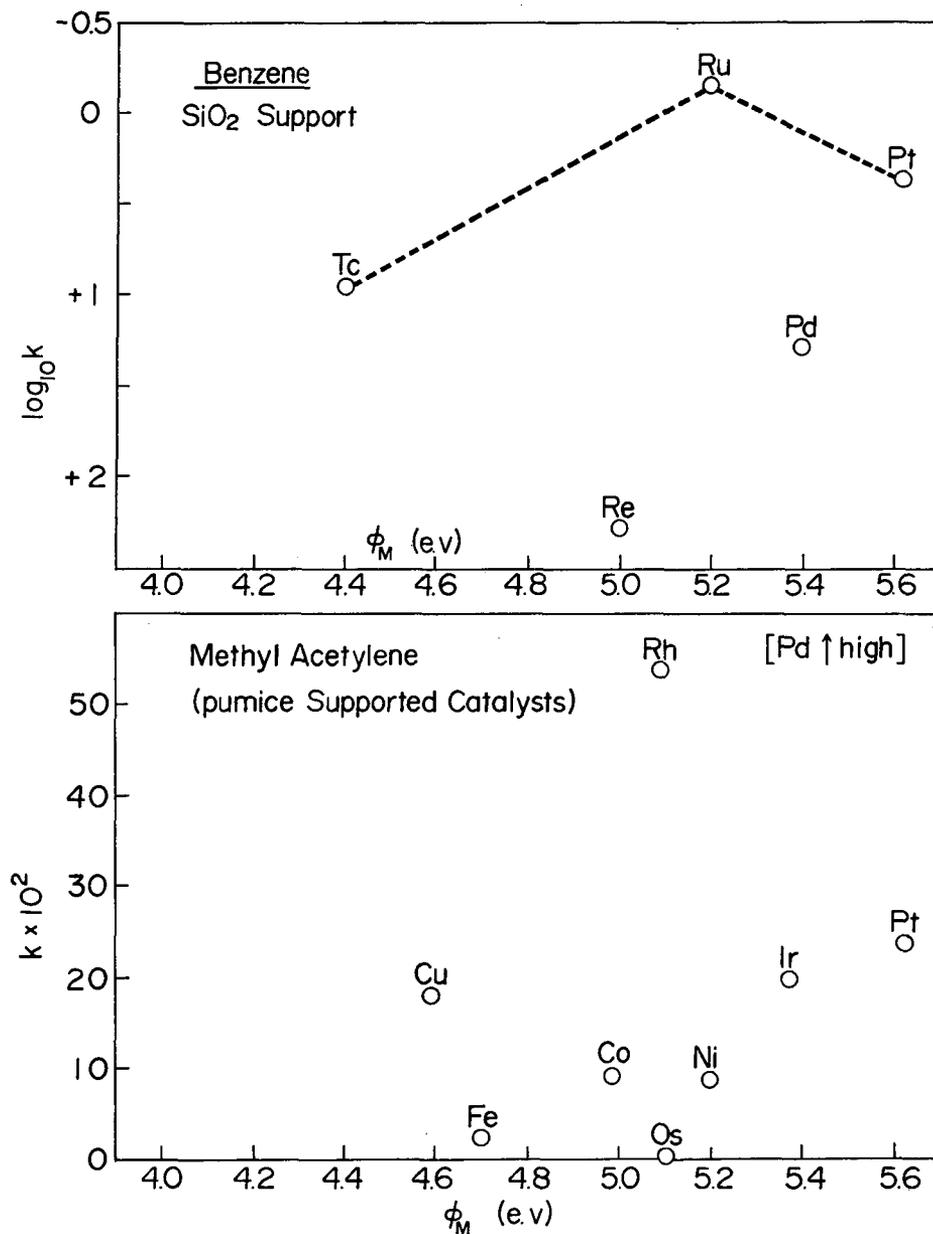
Rh, Pt>Ni>>Fe, W. The activative energy of acetylene hydrogenation is 6~7 kcal/mol, and rates of hydrogenation are, *e.g.*, for Ni, 100 times lower than for ethylene hydrogenation.

BOND[12] and BOND and WELLS[54] have suggested several schemes for hydrogenation of acetylene one of which may involve a vinyl radical:

$$C_2H_2(g) \longrightarrow HCCH \xrightarrow{+H} \underset{H}{\overset{H}{C}} = C \xrightarrow{H \ +H} C_2H_4(g)$$

Since the pathway via vinyl radical leads to chemisorbed ethylene, further hydrogenation to ethane may be a consequence of this pathway. The selectivity for C_2H_4 formation also decreases in the order of activities except that Ru and Os show higher selectivities than Ir. BOND[12] has given an explanation of the gradations in selectivity for ethylene formation in terms of a combination of strength of adsorption of ethylene (thermodynamic factor) and activity of the metal for hydrogenation of ethylene. This accounts for the abnormally low selectivity of Ir by an especially weak operation of the thermodynamic factor[12] for this metal. An alternate explanation already discussed for butadiene is the expectation of high selectivities for Group III metals which have more restrictive bonding sites. For acetylene, binding of acetylene either as M–C=CH (with H above) or as a π-bonded species on the surface will not readily shift to a di-σ-bonded ethylene, whereas on Group II metals which use itinerant electrons in binding, such a shift can take place.

From studies of acetylene-D_2 reaction[12] it appears clear that the vinyl reversal step is most likely for Ru, Os, Rh and Ir and hydrogenation of vinyl to ethylene more likely for Ni, Pd and Pt. This can be explained and related to the opposite behavior of these metals for alkyl reversal (Sect. VI. C) if over Class II metals (Ru, Os, Rh, Ir) a vinyl radical attached to 1 metal site is formed and over Class III metals (Ni, Pd, Pt and also Fe and Co) a vinyl radical attached to 2 metal sites is formed. There is some evidence for this in the greater polymerization during acetylene hydrogenation for most Class III metals.

The gradations in activity for methyl acetylene[78] show no correlation with ϕ_M (see Fig. 9). Heats of chemisorption on different metals are not known. It is of interest to compare the gradation in activity with the ease

Fig. 9. Activity of metals for hydrogenation of benzene and
methyl acetylene as a function of ϕ_M.

of oxidation of the metal in low valent complexes[76] where $Os > Ru > Fe$, $Ir > Rh > Co$, $Pt > Pd > Ni$, Au. This measure of electron donating ability would also measure interaction of acidic H of acetylene with metals. On this basis strong interaction of acidic protons of acetylene with the more basic metals would lead to low activity in hydrogenation. This explanation of activity gradation which may be the basis for the thermodynamic factor also provides for the possibility of surface complexes such as $M-C \equiv CH$ or $M^+(\bar{e}) HC \equiv CH(\bar{e}) M^+$. BOND *et al.*[12] have postulated a polar interaction of acetylene to explain acetylene-acetylene-d_2 exchange patterns.

The basic nature of a metal surface has been directly investigated by SHEETS and BLYHOLDER[77] by BF_3 adsorption. The infra-red spectra and the ease of displacement of BF_3 by CO placed the metals investigated in the following order of decreasing basicity, $V > Fe$, $Ni > Cu$, the same as the ease of oxidation given above.

It is of interest that activities for acetylene hydrogenation appear to be affected by acid-base interaction between acetylene and the metal surface. This is another point of similarity between metals and metal oxides where in the case of ZnO the H abstraction by oxide was considered by KOKES[58] to be important in olefin hydrogenation.

For Methyl Acetylene the order of decreasing activities[78] is Ir, Rh, $Co > Pt > Ni > Fe > Cu$. The main differences from acetylene are the high activity for Ir and Co. It is of interest that methyl acetylene in competitive hydrogenations[12] appears to be more weakly adsorbed than acetylene.

IX. Hydrogenation of Aromatics

The previous discussion of binding of ligands in complexes can lead to some suggestions for the ways benzene and other aromatics can be bound to the metal surface. The early discussions of benzene hydrogenation[79] were in terms of 6 point adsorption of benzene flat on the surface. BOND[12] has concluded that in presence of hydrogen during hydrogenation, benzene is adsorbed as phenyl radicals and partly as diadsorbed species. The magnetic data reported by LEE and SELWOOD[80] that benzene has 3–5 times the effect of H atoms in reducing magnetic susceptibility of Ni is compatible with a 2 point adsorption with some H dissociation. Also, the Ni surface will have a considerable fraction of electrons in interstitial positions available for delocalized bonding which also would give the magnetic effect found by SELWOOD.

Benzene which gives up 6 electrons to molecular orbitals in formation

of π-arene complexes has rather stringent requirements for the binding electrons in such a complex in a metal surface complex. The delocalized electrons in the metal complex are, according to the scheme described in Section II, *e.g.* for $Cr(C_6H_6)_2$, $[Cr^{6+}(\bar{e})_{18}(C_6H_6)_2^{6+}]$. Electrons or electron pairs would be expected to be distributed with $6(\bar{e})_2$ on a trigonal prism arrangement and $3(\bar{e})_2$ axially distributed. In this scheme there are no localized d-electrons to restrict the position of these binding electrons and it is in keeping with the preponderance of arene complexes for Group VI, Group VII positive ions, and di and tripositive ions of Group VIII. Also, the latter complexes only form with mesitylene, not with benzene. This suggests that a π-benzene surface complex would form most readily on Group VI metals and that when d-orbitals extending above the surface block a trigonal arrangement of sites, there will be no π-complex formation. Class II metals (Rh, Ir, Ru and Os), thus can form π-complexes because they all have vacant d-orbitals over alternate interstitial positions above the surface. Class III metals would be expected to give 2-point attachment of benzene as in an olefin complex. Class I metals (Mo, and W) may not readily form π-benzene surface complexes because the ion cores are probably $M^{6+}(d^4)$ in these metals, and the occupied d-orbitals can interfere. For Mo and W the vacant d-orbital $\perp$ to the surface may give preponderance of adsorption as phenyl radicals. The consequences of these different types of aromatic adsorption for activity and selectivity in exchange of hydrogens in toluene will be discussed after the activity patterns are examined.

The order of activities observed for benzene hydrogenation over transition metals is:

$$Ru > Pt > Tc > Pd > Re > Co > Ni > Fe$$
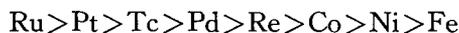
The order of metal activities for the hydrogenation of toluene[81] are $Rh > Mo > W \sim Co \sim Pt > Ni > Fe > Pd$. The exchange of D_2 with ring hydrogens follows the order of rates $Rh > Mo > Co > W > Ni > Fe > Pt > Pd > Mn$. A study[82] of Pt, Ni and Pd showed rates in the rates $18 : 7 : 1$ but activation energies 13, 34 and 14 kcal/mol.

The order of activities for hydrogenation of aromatic is not as well established as for the olefins. There appear to be effects of supports which may be espected for a molecule like benzene. In general from the sequences given, Rh, Ru, Mo, W have higher activity the Fe, Co, Ni, Pd which would mean Class I and II metals are more active catalysts for hydrogenation of benzene than Class III metals with the possible exception of Pt.

ROONEY and WEBB[18] have concluded that the slow step in hydrogena-

tion of benzene is the addition of the 2nd H atom to C_6H_7 on the surface. When the reverse reaction (formation of C_6H_6) is fast, only exchange is observed without hydrogenation (as in Ni at low temperatures). The stability of C_6H_7 on the surface is expected to increase from Ni to Pd to Pt. The more labile the C_6H_7 species the more exchange (more reversal to C_6H_7).

The above suggestions of π-bonding on Class II metals and di- σ-bonding on Class III metals can be brought into the scheme suggested by ROONEY and WEBB[18]. If addition of H to C_6H_7 is the slow step this would be expected to be rapid for Class II metal since the C_6H_7 will still be adsorbed flat on the surface as $(C_6H_7)^{5+}$. In the case of the σ-diadsorbed benzene on Class III metals addition of H to form C_6H_7 leaves localized orbitals available for the reverse reaction. These two kinds of bonding can explain the more rapid hydrogenation by Class II Metals. If Mo and W (Class I metals) chemisorb benzene as phenyl radicals, step wise addition of H can readily occur.

It is of interest also to relate these suggestions to the exchange of ring hydrogens and methyl hydrogens during the hydrogenation of toluene which has been reported by HORREUX et al.[81] Ring exchange would be expected to be rapid for π-adsorbed toluene on Class II metals and exchanges of all ring positions and side chain are very fast for Rh. For the di- σ-bonded adsorption by Class III metals which can be assumed to include the carbon having the CH_3 group, exchange of side chain hydrogens will be expected to be more rapid than ring hydrogens and more rapid than hydrogenation. This is the sequence observed for Pd, Fe, Co, Ni, and Pt. For Mo and W, if phenyl groups are formed, the ring positions of attachment relative to the CH_3 will determine the exchange pattern. In our view chemisorption of aromatics probably involves a net electron transfer to the aromatics and in this case the adsorption of a phenyl group would occur at the meta-position of toluene and not in the electron rich o- or p-positions. Steric hindrance would tend to favor the para-position. These two tendencies can explain the preponderance of meta- and para- over ortho- ring hydrogen exchange for toluene on W and Mo.

There does not seem to be a definite correlation of activity for hydrogenation of benzene or toluene with ϕ_M. This is not unexpected since with a complex molecule like benzene a dependence on surface orbitals will have a greater effect than the strength of attachment of metal electrons which is of predominant significance when there is attachment of the reacting molecule to single sites.

It is of interest that homogeneous transition metal complexes have not

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been found to hydrogenate benzene. This is not unexpected since some homogeneous complexes only hydrogenate activated olefins, and benzene is more difficult to hydrogenate than olefins. Also, the group of metals which most readily form π-aryl complexes are not among the most active catalytic metals. Whether more than 1 metal atom is a requirement may be found when metal cluster compounds can be prepared which are suitable for catalytic tests.

X. D₂ exchange with Hydrocarbons

The D_2 exchange with saturated hydrocarbons will be discussed here for the purpose of comparison with the exchange which occurs during olefin hydrogenation and for relating it to C–H bond breaking which occurs during dissociative chemisorption of olefins and dienes.

Exchange reactions are carried out in the temperature range of 150~200°C and at these relatively high temperatures it is likely that strongly chemisorbed species are involved in the reaction in contrast to the weakly chemisorbed species postulated as reactive intermediates for olefin hydrogenation. The reaction is complicated by decomposition of hydrocarbons to carbides which starts at 60°C for CH_4 on W, at 140°C for Ni and 170°C for Fe. The order of activities[12] for metals for D_2-exchange with CH_4 (or C_2H_6) is

$$W > Mo > Ta > Rh > V > Cr > Zr > Pt > Pd > Ni > Co > Fe$$
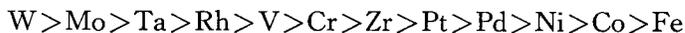
A plot of activity $vs.$ ϕ_M in Fig. 10 shows a volcano type curve with a maximum activity in the region of W (or $\phi_M = 4.6$). Fe, Co, and Ni show unexpectedly low activities on this basis. However, TRAPNELL[6] has shown that adsorption of hydrocarbons on these metals at 0°C is 50~100 times smaller than for the other metals in Fig. 10.

There are two interesting aspects of this reaction, the activity sequence and the occurrence of multiple exchange for certain metals. The metals of high activity (W, Mo, Ta, Rh) are metals of Classes I and II and those of low activity (Pd, Fe, Co, Ni) are of Class III. The pattern is quite similar to that in hydrocracking to be discussed in Section XI. However, it differs from the olefin hydrogenation pattern in the high activity of W, Mo and Ta for D_2-exchange. Also, for olefins both exchange and isomerization activities during hydrogenation are high for Pd and other Class III metals and low for Rh and Ir. In the olefin hydrogenation exchange depends on

the ease of the alkyl reversal step, H C–C H $\rightleftharpoons$ C–C H, and the model
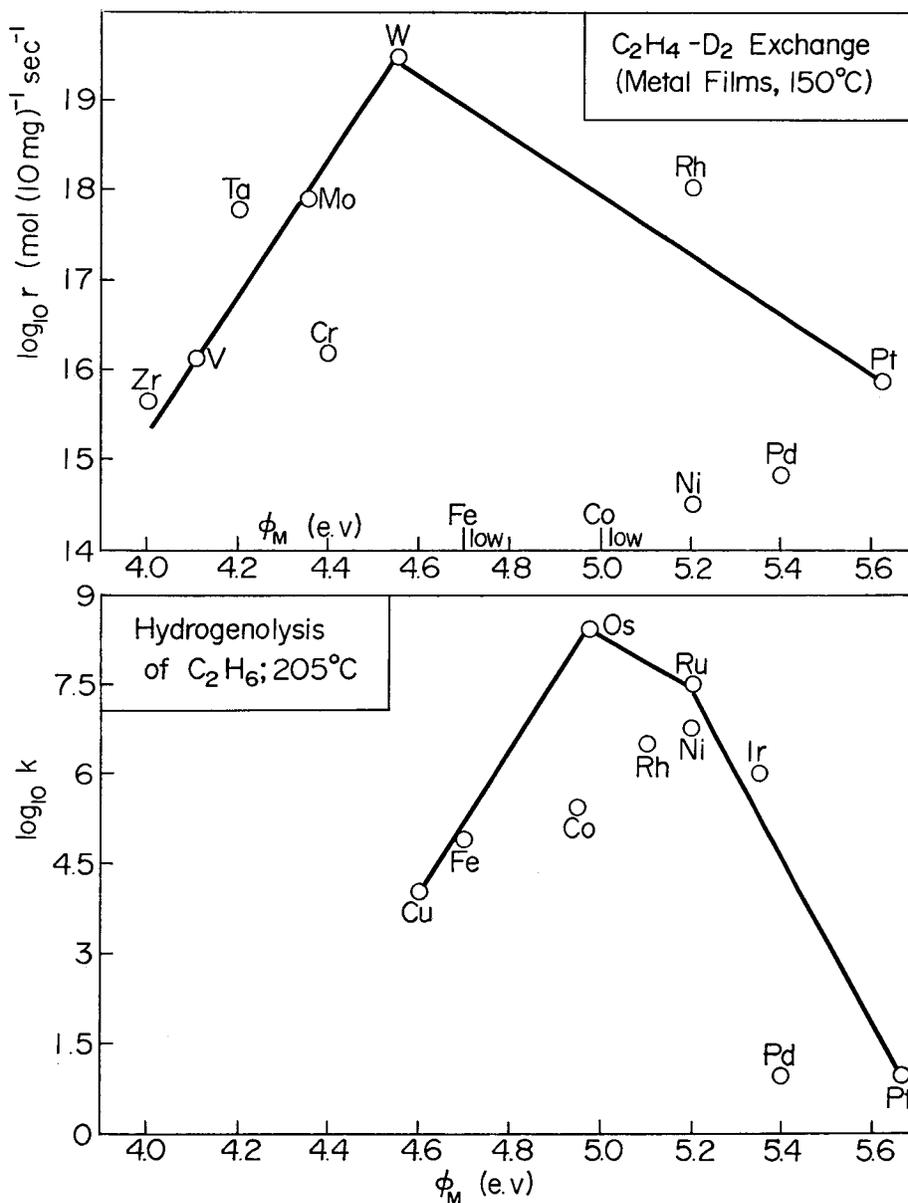
Fig. 10. Activity of metals for $C_2H_6-D_2$ exchange and for hydrogenolysis of ethane as a function of ϕ_M.

TABLE 4   Exchange of CH_4 with D_2 (Initial Distribution)[a]

Metal	Proportion of Isotopes			
	d_1	d_2	d_3	d_4
W	0.76	0.01	0.09	0.14
Rh	0.21	0.045	0.29	0.45
Pt	0.36	0.12	0.25	0.27

a) C. Kemball, ref. 21

given in Sect. VI indicated easy reversal in the ease of Class III metals. In D_2-exchange with saturated hydrocarbons the rate determining step is probably the dissociation of hydrocarbon (M$\overset{CH_4\ -H}{\diagup}$M–CH), and both rate of exchange with D_2 and degree of exchange are determined by the CH surface species.   For Class I metals strong attachment to a single metal as M–CH$_3$ (or M–C$_2$H$_5$) is expected, and this is borne out by the predominantly stepwise exchange pattern for W shown in Table 4.   For Class II metals, multiple attachment at interstitial sites is expected $\left(M\overset{M}{\underset{M}{\diagup}}\!\!\nleftarrow\!\!CH_2 \right)$, and this is the case for Rh which shows multiple exchange[21].   Metals like Pt (Class III) show intermediate behavior which indicates both kinds of hydrocarbon surface species, the major species is probably σ-bonded CH$_3$ and the second as given for Rh.   There is not sufficient data to suggest whether Class of Metal is decisive for diadsorbed species present for C_2H_6 on some metals.

XI.   Hydrogenolysis of Hydrocarbons

As with D_2-exchange of hydrocarbons, their hydrocracking will be discussed since it involves processes which can also occur during olefin hydrogenation.

A reaction such as the hydrogenolysis of ethane shows the interesting sequence of metal catalyst activities Os>Ru>Ni>Rh>Ir>Re>Co>Fe>Cu Pd=Pt.   SINFELT and YATES[84] have recently discussed this reaction and correlated activity with d-character of the metals.   Data tabulated by BOND[8] indicate a maximum in activity for group VIIIa of 2nd and 3rd transition series and probably group VIIIc for the 1st transition series.

This reaction differs from the reactions discussed above which required dissociation of ethane, $i.e.$, rupture of a C–H bond for chemisorption of an ethyl group.   The overall reaction of hydrocracking a hydrocarbon involves

stripping off hydrogens, rupture of C–C bonds, formation of surface radicals (CH_3, CH_2, CH) which are subsequently hydrogenated and desorbed. There are conflicting views[83] on whether C–C bond breaking or desorption of hydrocarbon fragments is the rate controlling step.

Hydrogenolysis and cracking of ethane involves both M–H and M–C binding strengths as well as C–H binding. The reaction must also include multiple bonded adsorption of ($-CH_2-CH_2-$) and reaction with H atoms to form CH_4. The strength of adsorption of all hydrocarbon species is expected to be proportional to the M^{n+} field which is also proportional to ϕ_M; the attachment of H atoms have an inverse dependence on ϕ_M. The plot of ϕ_M *vs.* activity for ethane hydrogenolysis on Fig. 10 shows a maximum activity at ϕ of 4.9~5.0. The correlation with ϕ_M brings all metals into a common basis which was not true of the correlation with *d*-character discussed by SINFELT and YATES[84] or the variation with periodic group used by BOND[12]. The dependence of hydrocracking activity on ϕ_M with an optimum ϕ_M supports the conclusion that desorption may be rate controlling. As ϕ_M increases the interaction of CH_4 and metal electrons decreases and desorption can occur more easily. At very high ϕ_M there would be lower activity due to less dissociative adsorption.

The unusual feature of the reaction is the high activity for Ru, Os, W and very low activity for Pd and Pt. This is the same as the cracking activity sequence for cyclopropane reported by KNOR[56],

$$Ni > Mo > Rh > Fe > Pd, \quad Pt.$$
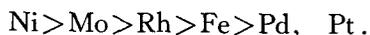
The observations on hydrocracking agree very well with previous observations of carbide formation during ethylene hydrogenation on W and Ni and was connected to presence of vacant *d*-orbitals $\perp$ to the metal surface on W_{110} and Ni planes. This may also be the explanation for Ru and Os where the close packed lattice normally would have a tet interstice above M^{n+} in the surface. This is absent at this surface layer but can be a region of high positive charge for HCP metal surfaces. These properties are reflected in ϕ_M values since attachment of $\bar{e}$ to the metal surface depends on M^{n+} field.

XII. Hydrogenation of Ketones

Strength of chemisorption of oxygen on metals follows the same order as H or olefins so the major difference expected for ketones is the possibly greater strength of attachment to metal of the oxygen group compared to carbon. The gradation of decreasing activity of metals, $Pt > Ni > Fe$, $W >$

Pd>Au appears similar to the gradations for hydrogenation of olefins. This indicates surface attachment of both carbon and oxygen. The product in all cases is isopropyl alchol.

Of interest is the hydrogenation of a molecule like acrolein, HC=C–C=O for which there can be a selectivity for either hydrogenation of C = C or C = O. Here the greater strength of C = O adsorption compared to C = C shows up in the high selectivity for C=O hydrogenations by catalysts such as Cu–Cd alloys (Class III–IV) which are poor olefin hydrogenation catalysts.

VIII. Discussion

The application of the Interstitial-Electron Model to hydrogenation catalysis has led to a great variety of explanations for the complex catalytic behavior of metals. These explanations, however varied, have a certain consistency and can be divided into two groups for the purpose of summarizing them. The first is based on metal properties and includes both geometric and electronic factors; an important aspect of these interpretations is the division of metals into 3 Classes with distinctly different catalytic behavior. The second kind of explanation involved properties of the surface complex as determined by properties of reacting molecules. These points of view have much in common with that of SCHUIT, VAN REIJEN and SACHTLER[53] who proposed one factor in catalyst activity related to heat of adsorption of product or reactants and a second factor related to stability of the activated complex, *i.e.* one related to metal electronic properties and the other not.

Within the first group of explanations based on metal properties, certain reactions such as simple H-atom reactions, D_2–NH_3 exchange, D_2-hydrocarbon and D_2-olefin exchange there was a good correlation between catalytic activity of the metal and metal work function or heat of adsorption of reactants. For more complex reactions like olefin hydrogenation there appeared to be an optimum ϕ_M for maximum catalytic activity, but specific effects of surface orbitals of each metal were considered to be more important in determining selectivity and probably partly responsible for determining activity level. For benzene the effects of orbital pattern far outweighed the electronic property of the metal as indicated by ϕ_M.

For the hydrogenation of acetylene and cyclopropane specific properties of the reactant appeared more important than the metallic properties indicated by ϕ_M or orbital pattern. These properties were the acidic nature of hydrogens in acetylene and specific effects of cracking behavior of metals for cyclopropane. These catalytic properties of metals reflect the dual character

of the metal surface; a metal has regions around ion cores with strong positive fields not completely screened by electrons and also regions of high electron density at interstitial positions above the plane of ion cores.

The model has established some theoretical basis for the groupings of metals which give isomerization and exchange during hydrogenation, and the division of metals into Classes I, II and III clarify observations on a large number of catalytic reactions. The connection the model makes between catalytic selectivity and orientation of d-orbitals is the same as made by OCHIAI[85] in his review of catalysis by metal complexes in homogeneous solution. The insight this clasification gives can guide choice of catalyst for the reactions for which metal class has been shown to be important. It also suggests Class II–Class III metal alloy combinations which may be far more important for catalysis than the much studied alloys between Pd or Pt and Group IB Metals. The Interstitial-Electron Structures for these types of alloys have not been formulated yet, except for cases where no change in metallic properties are anticipated[4]. Gradations in activity levels for a series of metals are even more complex than selectivity patterns. When the binding of reactants to the surface can be expected to depend on availability of metal electrons for chemical binding the most active catalysts can be expected to be those with highest ϕ_M (or lowest heat of adsorption). When reactants differ in attraction of electrons or when one reactant donates electrons to the metal and the other attracts electrons, activity can be expected to reach a maximum at some intermediate ϕ_M (or ΔH) value. When a reactant has some special property such as acidic groups which dominate the interaction with the metal surface then a corresponding property of the metal, in this case its basicity or electron donating ability, become important for activity.

This paper has not discussed many facets of hydrogenation catalysis. Modifications of some of the explanations may be required as additional data are considered. It was mentioned earlier that previous discussions had been incorporated to a large extent. As examples one can consider the discussion in this paper to offer some detailed surface species in place of $(C_2H_4)_{ads}$ as used in the extensive studies of ethylene hydrogenation by HORIUTI, MIYAHARA and coworkers[23] in this Institute. By use of the framework of the present discussion, many of their results should be transferable to other hydrogenations. The careful elucidation of thermodynamics of catalytic reaction and connections to heats of adsorption and heats of formation of related compounds by BALANDIN and coworkers[79] and SCHUIT, SACHTLER, VAN REIJEN *et al.*[53] can supplement (and be related to) our discussion of ϕ_M

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as a parameter. The extensive explanations by BOND, WELLS, ROONEY, SHOPOV and ANDREEV using π-complexes do have differences due to our different model, but many of the mechanistic explanations have been taken from their work. Although the present discussion uses a specific model, that of the Interstitial-Electron Model for the Metal Surface, an attempt was made to give the explanations in terms of electron transfer between reactants and metal surface which should be of general applicability in catalyst discussions.

Acknowledgement

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APPENDIX

d-orbital Patterns for Minor Lattice Planes

The orientation and occupancy of *d*-orbitals on the less prevalent lattice planes can also be described on the basis of the Interstitial-Electron Model for metals. Table 5 lists these characteristics for the 100 and 110 plane of CCP lattices and the 100 and 111 plane of BCC lattices. These *d*-orbital patterns can be of importance in modifying catalytic behavior especially if some special binding sites are present. In addition they can be of use in interpretation of results of catalysis on single crystal planes.

For BCC metals the 100 planes show similarity to the 110 plane given

TABLE 5   *D*-orbital orientation and occupancy for
different lattice planes of metals

Metal Lattice		Occupancy and Angle of *D*-orbital to Surface		
		Vacant	Partly Occupied	Occupied
CCP (100),	Ni	45	36	90
	Rh, Ir	90	—	45
	Pd, Pt	—	90	45
CCP (110),	Ni	90	45	45
	Rh, Ir	45	---	45, 90
	Pd, Pt	—	45	45. 90
BCC (100),	Cr	45, 90	—	45
	Mo, W	45, 90	—	45
	Fe	30	90	45
BCC (111),	Cr	13, 45	—	54
	Mo, W	45, 58	—	13
	Fe	13	45	58

earlier except for the vacant d-orbital 90° to the surface for Cr and the partially occupied orbital at 90° for Fe. This can impart tungsten like properties to Cr (100). On the 111 plane Mo and W have vacant orbitals at 58° instead of at 90° as on the 110 plane.

For the CCP lattice there is on the 100 plane a new vacant orbital at 90° for Rh and Ir and a partially occupied orbital at 90° for Pd and Pt. On the 110 plane there is a vacant orbital at 90° for Ni. There is also the difference of arrangement of d-orbitals on the 110 plane. It can be seen by comparing the orbitals for CCP (111) and BCC (110) in Fig. 4 that the difference is an edge orientation in 110 (orbitals at 90° each other) and orientation over a triangle of 3 M^{n+} in (111) (orbitals at 120° to each other).

The difference for Ni (111) and Ni (110) are thus rather great. The vacant d-orbital at 90° or Ni (110) can account for the greater carbide formation during ethylene hydrogenation (tungsten like behavior), and the more favorable orientation of partly occupied d-orbitals at 45° can account for the enhanced hydrogenation of ethylene on Ni (110). The pattern of D_2 exchange with CH_4 over Ni at low temperatures also follows a tungsten like behavior.