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CATALYSIS AND THE INTERSTITIAL ELECTRON MODEL

VI. Surface Complexes in Catalysis by Metals^{*})

By

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Abstract

In the absence of a full theoretical treatment of the chemical binding in a surface complex on a metal surface which is active in catalysis, it is important that qualitative descriptions be as rigorous as possible. When valence bond theory is used, it should be used for both metal and surface complex, and similarly band theory of metals should be used with M.O. theory of molecules. The interstitial-electron model, which is a M.O. model, is used here to characterize surface complexes since it is especially suited for the representation of delocalized binding. Careful studies by different research groups on a Ni(100)-S butadiene hydrogenation catalyst, a Pt(111)-Ca dehydrocyclization catalyst, the W(100) and W(110) planes for C₂H₄ hydrogenation and the Ag ethylene oxide catalyst make it possible to formulate the surface complex in some detail for these catalysts. The information used to characterize the surface complex includes data from LEED, AES, INS, XPS, flash desorption, IR, O₂ exchange, adsorption kinetics, and changes in ϕ on chemisorption. Although these characterizations lack some details of geometry as well as energy levels for binding electrons, they represent a major advance in catalysis and offer considerable insight into activity and selectivity determination in a catalytic system.

Introduction

Since its characterization by BERZELIUS catalysis has been an elusive subject, and at any period of time there have been promising prospects for understanding the phenomenon. In the early days of metal film work many researchers were convinced that lattice spacings were the key variable. Later, when experiments on alloys indicated effects of the metal band struc-

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ture, electronic explanations were predominant. At present both theory and experiment are converging on some description of the chemisorption bond as a localized binding which also has contribution from the metallic conduction bands. This will be treated in the present paper from the point of view of delocalized electrons in binding.

There seems to be sufficient information at present about the surface complex in catalysis to make fruitful interaction between theory and experiment. The kind of progress already made in this respect for homogeneous catalysis can be anticipated. This paper will describe the systems for which a skeletal description of the surface complex is available. The further information required for full characterization of the active species in catalysis will be indicated. Since the chemical binding in the surface complex is at the heart of any description this aspect will be discussed first.

Descriptions of Chemical Binding

There are various treatments of chemical binding in metals and in chemisorption of molecules on metal surfaces. It will simplify the task of describing them to point out first the essential features of all chemical binding¹⁾. These can be listed as follows:

1. Potential energy is lowered as bonding atoms approach.
2. P.E. is lower because \bar{e} now move near +charge of 2 or more nuclei in *molecular orbitals*.
3. Vacant or 1/2 filled valence orbitals become binding regions.
4. Combination of 2 atoms with 1/2 filled orbitals have ΔE of 30-130 kcal/mol (higher if \bar{e} more strongly attracted by one atom or if \bar{e} completely transferred to an anion).
5. Combinations of atom with vacant orbital and atom with $(\bar{e})_2$ have ΔE of 10-50.

Both the Valence Bond Theory and Molecular Orbital Theory offer approximations to the energies of binding electrons and describe the essentials of chemical binding in different ways. However, it is important to emphasize that for characterizing surface complexes on a metal the same type of description be used throughout. If valence bond theory is used for the reactant molecules, then a valence bond theory of metals must be used with it for a rigorous treatment of binding. If the band theory of metals (M.O.) is used, then M.O. theory also must be applied to the reactant molecules. Various consistent descriptions are listed in Table 1. The ENGLE-BREWSTER Correlation²⁾ is taken as the most comprehensive valence

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TABLE 1 Descriptions of Chemical Binding of Catalyst Components

Metal Surface	Molecule to be Chemisorbed	Surface Complex
Band Theory (\bar{e} in potential field of all metal positive ion cores, with special surface states)	Molecular Orbital Theory (Energy level correlation diagrams)	Virtual Bound States (DEWAR-CHATT Model?)
Interstitial-Electron Model (\bar{e} in region above surface corresponding to interstices)	Electron Density Model (Spatial locations of binding electrons)	Delocalized (\bar{e}) ₂ used in binding
ENGLE-BREWER Correlation (Promotion of electrons)	Valence Bond Theory (hybridization)	Localized Binding (orbital overlap)
GOODENOUGH-Bond Model (Crystal Field Theory for d-orbitals at surface)	M. O.	DEWAR-CHATT Model

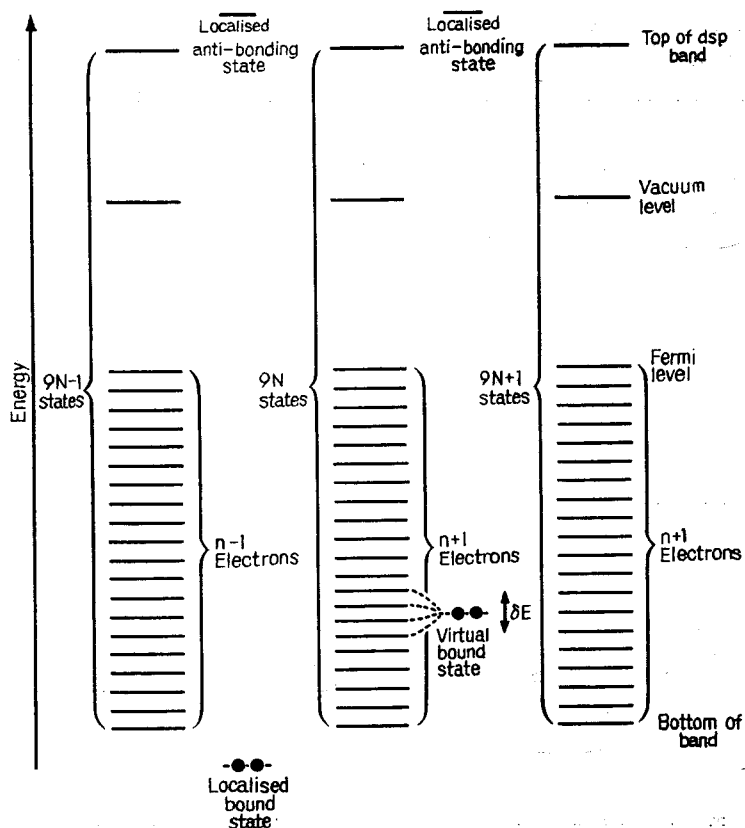


Fig. 1. Types of Chemical Binding to a Metal Surface; Localized Bound State, Virtual Bound State and Metallic Binding.

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bond treatment of metals. The Interstitial-Electron Model³⁾ and Electron Density Model⁴⁾ are M.O. treatments which place emphasis on the spatial location of electron density in binding regions. Each of these consistent description schemes has advantages in interpretation of certain types of data and, thus, supplement each other.

The diagrams in Fig. 1. give a band theory interpretation of three kinds of surface complexes. The first is a localized bond, and the binding electrons are shown below the energy band of itinerant electrons. The electron density model would show this as $(\bar{e})_2$ between H^+ and M^+ on the surface, with the possibility of variation between final states of H^{2+} and H^{-} . The third example in Fig. 1. is a metallic type bond with valence electrons of the surfaces complex becoming part of the conduction band. The equivalent description of the Interstitial-Electron model, *e.g.*, for Cs, has Cs^+ on the surface with the valence electron becoming part of the itinerant electrons in metal interstices. The second type of binding in Fig. 1. was first described by FRIEDEL as a virtual bound state and represents interaction of valence electrons and metal conduction electrons. This is the

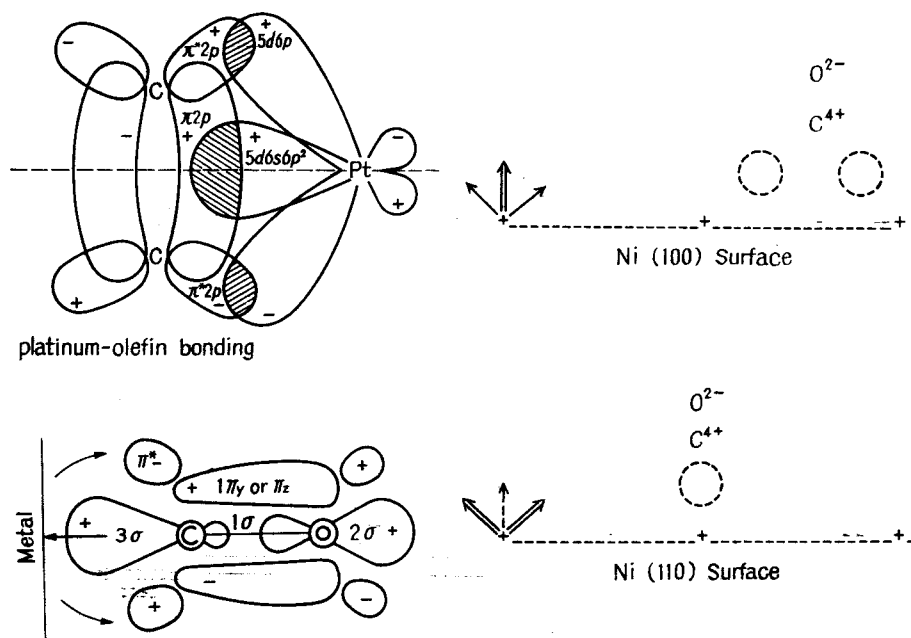


Fig. 2. Dewar-Chatt Model for Chemisorption of Olefin and CO. Interstitial-Electron Model for CO Chemisorption on Ni. (\rightarrow = 1/2 filled d-orbital, \Rightarrow = filled d-orbital.)

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type of chemical binding encountered in surface complexes of catalytic interest and is the one toward which most theoretical calculations are directed. The Interstitial-Electron model uses the characterization of "delocalized electron pairs" to describe this type of surface complex. Figure 2 shows this characterization along with the DEWAR-CHATT Model for CO on metals and the equivalent C_2H_4 -Pt complex also applied to C_2H_4 on metal surfaces.

Redistribution of Electrons in Chemisorption

In most cases chemisorption studies involve a spectrum of surface complexes and do not give specific data for the one responsible for catalysis. However, the information given by chemisorption studies can be expected to apply to the active species in qualitative respects. The experimental

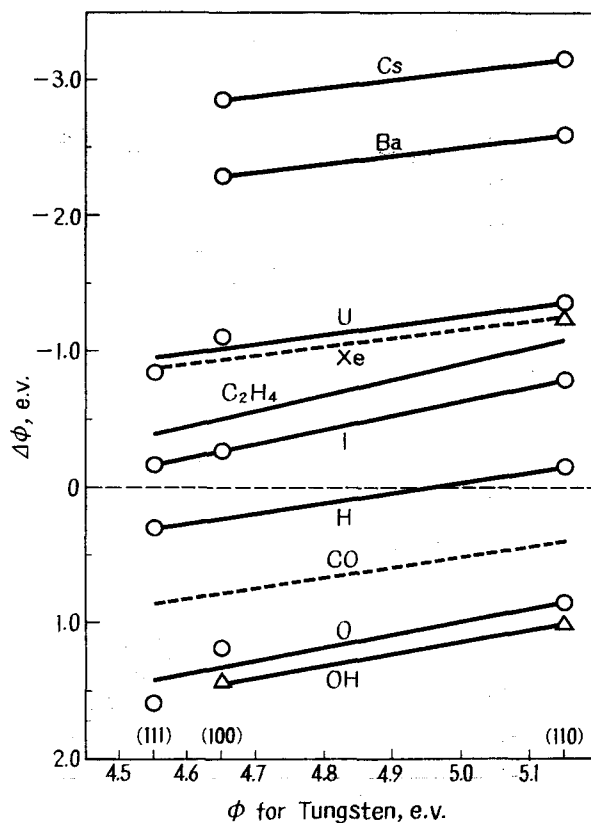


Fig. 3. Change in Work Function on Chemisorption of Various Gases on Single Crystal Planes of Tungsten Metal.

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techniques which give information on electron density around chemisorbed molecules are the measurements of electrical resistance, work function and the data of XPS (X-ray photoelectron spectroscopy or ESCA). Since most data is available on the work function changes on chemisorption those will be used to demonstrate the conclusions that can be drawn about the surface complex from such measurements.

There are available accurate measurements of the change in work function (ϕ) on different single crystal planes of tungsten for the chemisorption of a series of different substances. In Fig. 3. such data taken from SARGOOD, TOMPKINS and HOPKINS⁵⁾ show the linear relation⁶⁾ of $\Delta\phi$, the change in ϕ on chemisorption, with ϕ . An increase in ϕ indicates removal of \bar{e} from the metal surface, and a decrease in ϕ indicates donation of \bar{e} to metal by the chemisorbed molecule. Cs donates an \bar{e} and becomes Cs^+ on the surface of W. Xe is polarized by the $+$ ion core of W, and electrons are thus attracted to the metal region. Oxygen atoms strongly attract electrons to

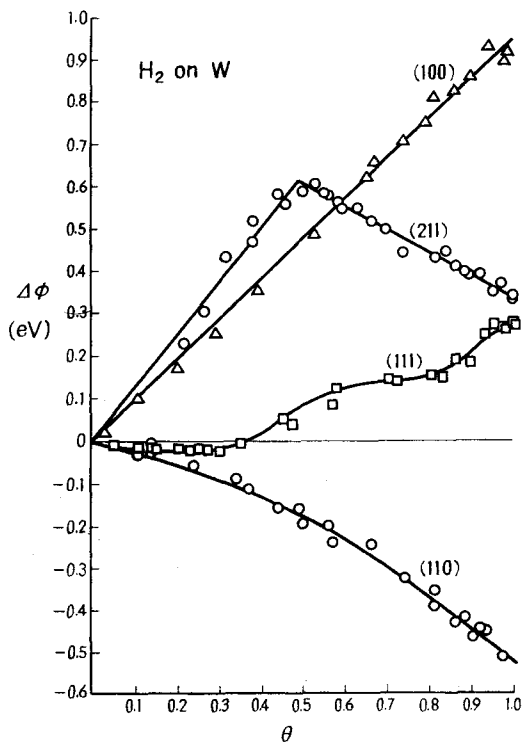


Fig. 4. Work Function Change vs Coverage for H₂ on W (110), W (100), W (211) and W (111).

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become O^{2-} on the surface (probably approaching O^{2-}).

In the relation $\Delta\phi = c - a\phi$, c can be defined⁶⁾ as a terminal ϕ of the chemisorbed molecule, and it is the ϕ value of metal which will give no change in ϕ upon chemisorption of that molecule. Terminal ϕ values determined from plots of $\Delta\phi$ vs. ϕ for several metals are the following: benzene, 3.2 eV; C_2H_4 , 4.25; Xe, 3.6; H, 5.0; CO, 5.8; O, 6.0.

The sign of the $\Delta\phi$ (see Fig. 4) can show whether the chemisorbed molecule is $(S)^{\delta-}$ or $(S)^{\delta+}$. The direction of electron transfer can also suggest changes in the binding energy of the metal. Addition of itinerant electrons to the metal (which accompanies formation of $S^{\delta+}$) will increase metal binding energy and stabilize low index planes. Removal of electrons from metal (and with $S^{\delta-}$) will decrease metal binding energy and destabilize low index planes at the surface.

In general the data on electrical resistance and the small amount of data from XPS agrees with the electron shifts indicated by $\Delta\phi$. In order to relate this data to chemical binding of the surface complex one of the models in Table 1 can be used. The DEWAR-CHATT model describes the electron redistribution of the chemisorption bond as involving an attraction of σ -electrons by metal ion core and a back donation of metal d-electrons to vacant π -orbitals on the chemisorbed molecule (see Fig. 2). The electron-density model suggests a description in terms of delocalized electron pairs in binding such as was given for CO chemisorption on Ni in Fig. 2. This description follows from the expectation that the chemical binding in chemisorption is intermediate between that in transition metal complexes and that in metals. It has been shown⁴⁾ for both the positive ion cores in transition metal cluster complexes and in transition metal complexes that such delocalized electron pairs can be distributed according to the geometry of the molecules to give a reasonable binding. These electron pairs are delocalized in multiple ion core binding regions, and only in special cases are they located between 2 ion cores as in a covalent bond. There is sufficient information both on the geometry of the surface species and the electronic changes in chemisorption to characterize 4 different types of surface complexes.

Well-Characterized Surface Complexes

The flash desorption technique has given considerable insight into surface species on several metals. Some of the early work was done by CVETANOVIC and AMENOMIYA⁷⁾ who showed that out of several hydrogen species chemisorbed on Pt it was the weakly bound H which participated

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in H_2 - D_2 exchange. RYE, HANSEN and coworkers⁹⁾ have identified the active sites on W(100) and W(110) by a combination of flash desorption studies and studies of change in work function on chemisorption of H_2 and C_2H_4 . They showed that there was chemisorption of the two components on common sites on W(110) and on independent sites on W(100). Fig. 5 shows the surface complexes in terms of the interstitial-electron model with surface d-orbitals and itinerant electron density (\bar{e}) indicated. On both tungsten planes C_2H_4 is chemisorbed probably as a di- σ -bonded species with decrease in ϕ indicating $C_2H_4^{\delta+}$ on the surface. In the case of hydrogen, as shown in Fig. 4, there is an increase in ϕ on W(100) and a decrease on W(110)⁹⁾ indicating $H^{\delta-}$ and $H^{\delta+}$, respectively. The actual location of surface complex is suggested by location of vacant orbitals. The 4-center position for $H^{\delta-}$ has been discussed previously. From the partial charges suggested it can be anticipated that C_2H_4 is more strongly chemisorbed on W(110), the high ϕ plane, and that H is more strongly chemisorbed on W(100). This would bring $(C_2H_4)^{\delta+}$ and $H^{\delta-}$ to similar energies on the W(100) surface and explain the higher catalytic activity for hydrogenation by W(100). The tungsten surface also contains several carbide species. These may play a role in defining the specific reaction site, as will be seen below for sulfur

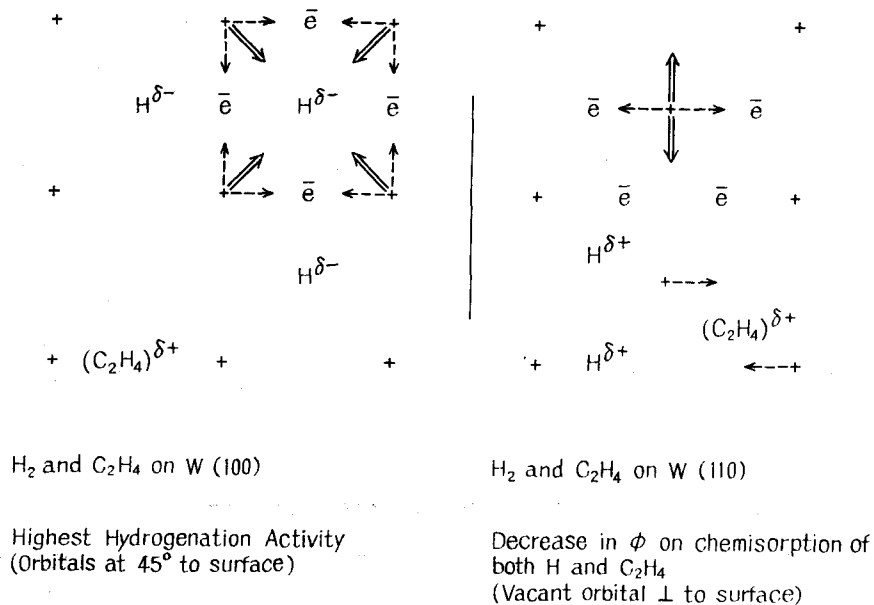


Fig. 5. Surface Complexes of Chemisorbed H and C_2H_4 on W(100) and W(110).
(-----) = vacant d-orbital, \Rightarrow = filled d-orbital)

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on Ni but, it is believed that tungsten carbides are sufficiently metal-like to insure that the catalytic reaction still takes place on metal sites. The carbides are not shown in Fig. 5 since their surface location and amount are not known. The delocalized electron pairs (\bar{e}_2) used in binding are also not shown in Fig. 5. They would be in positions similar to those shown for CO on Ni in Fig. 2 as dashed circles.

Two surface complexes for a Ni and a Pt catalyst have been characterized by McCARROLL and coworkers¹⁰⁾ at British Petroleum using LEED studies along with INS, APS, XPS, UPS, AES, ion emission and chemisorption studies by other workers using radioactive S. For a sulfur treated Nickel catalyst which is selective for hydrogenation of butadiene to butene, it was shown that there was surface reconstruction of Ni(111) to Ni(100)-S. The authors have not discussed the surface reconstruction, but it can be understood in terms of number of binding electrons. Other studies have shown that S chemisorption increases ϕ , *i. e.*, removes \bar{e} from the metal surface. This decreases the number of binding electrons and should decrease metal binding energy and thus destabilize Ni(111). Fig. 6 shows the butadiene surface complex on Ni(100)-S with S dispersed on the surface in

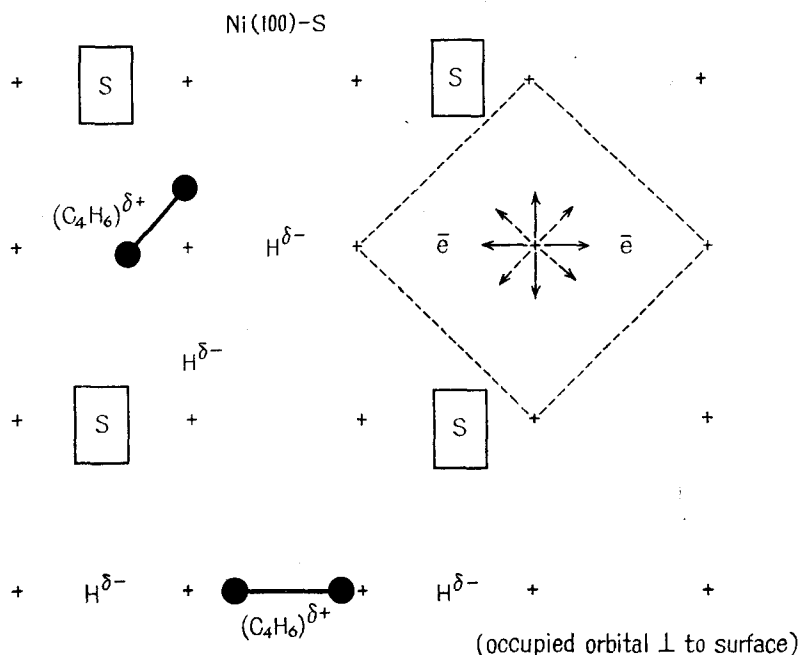


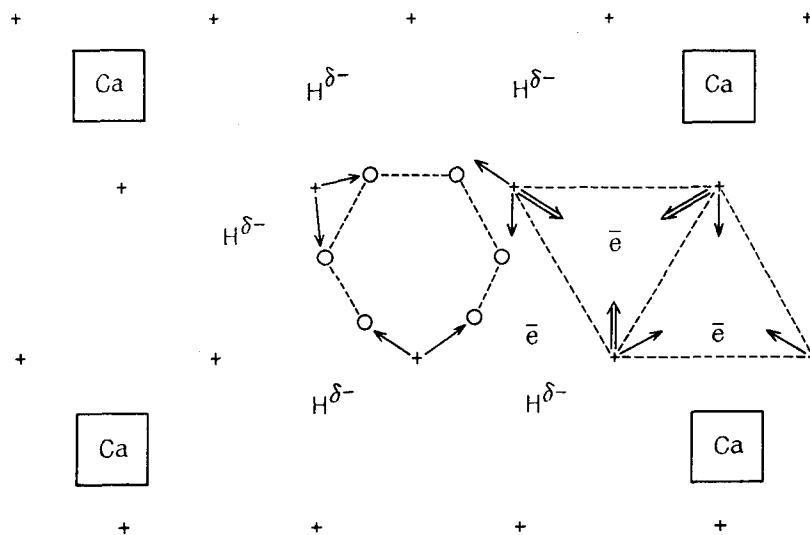
Fig. 6. Surface Complexes of H and Butadiene on Sulfided Ni (see caption to Fig. 2 and 5).

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bridge positions. MCCARROLL *et al.* showed the surface complex with S over Ni, but it is believed the bridge position is more likely. Fig. 6 also adds the pattern of d-orbitals and \bar{e} above the Ni(100) surface.

The other catalyst studied¹¹⁾ was a Pt dehydrocyclization catalyst for aromatization of hexane. The LEED work showed reconstruction of Pt(100) to Pt(111) for catalysts with Na or Ca added. In this case the additive donates electrons to the metal surface, thus increasing binding energy and stabilizing the (111) plane. For this catalyst the details of Ca distribution are not known, but a uniform distribution of 5% Ca leads to the picture of the surface complex shown in Fig. 7.

SOMORJAI¹²⁾ has also studied the dehydrocyclization reaction on single crystal planes and stepped planes of Pt and has noted especially high activity for the latter. It is the terrace of (111) orientation on the stepped planes which is associated with high activity; carbon deposits appear to play a role in maintaining catalytic activity. It has also been suggested that carbon deposits play an important role in providing "templates" for reaction^{12,13)}. Such a template effect has been reported in the enhancement of acetylene hydrogenation over a metal phosphide¹⁴⁾ after pretreatment with acetylene. As mentioned above for tungsten carbides, the electronic structure of



N-hexane on Pt (111)-Ca

Fig. 7. Surface Complexes of H and Hexane on Ca treated Pt (see caption to Fig. 2 and 5).

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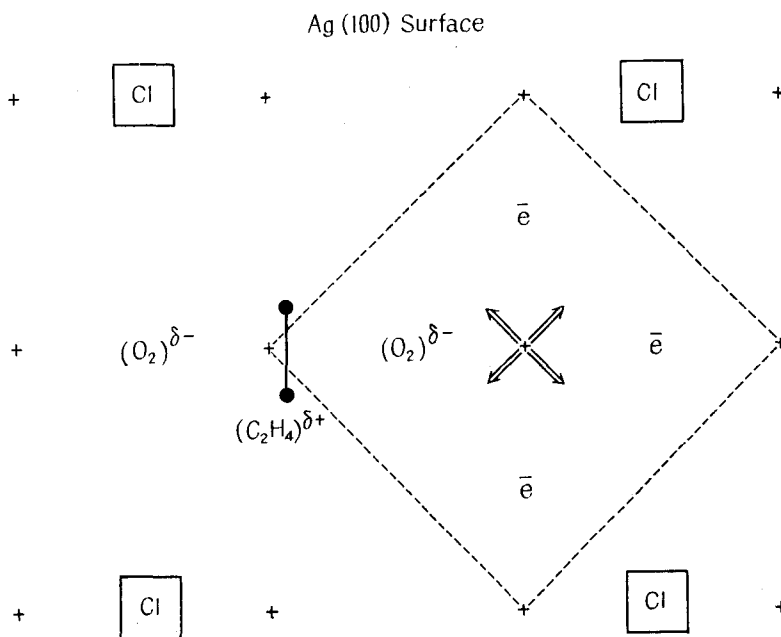


Fig. 8. Surface Complex of O_2 and C_2H_4 on Cl treated Ag (see caption to Fig. 2).

metallic carbides, borides, nitrides and phosphides provides for both interstitial anions and itinerant electrons in the vicinity of metal ion cores as in a metal.

Another system for which there is quite detailed information is the surface complex on the silver-ethylene oxide catalyst. The suggested surface complex in Fig. 8 is based on information from the studies of CZANDERA, IMRE, GEREI and SACHTLER¹⁵). It is known that Cl increases ϕ , and the arrangement of Cl on the surface as in Fig. 8 blocks the arrays of 4 Ag which are postulated by SACHTLER to lead to dissociation of O_2 to O^{2-} on the surface, with loss of selectivity to ethylene oxide. The Ag(100) surface is chosen since the removal of binding electrons by Cl will destabilize Ag(111). The increase in ϕ due to Cl should also tend to stabilize $(O_2)^{\delta-}$ species relative to O^{2-} . It is the low work function metals which appear to form O^{2-} and bulk oxides very readily. The chemisorption of C_2H_4 directly over Ag is the usual π -type binding, and the most likely site for O_2 is in the bridging positions which have high \bar{e} density. The model with 1/4 coverage by Cl leads to no more than 2 Ag in a group which are not attached to Cl. This in keeping with SACHTLER's explanation of

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selectivity, and the relative positions of C_2H_4 and $(O_2)^{\delta-}$ indicate ease of O_2 addition to ethylene to form ethylene oxide.

Although there is a certain amount of speculation in drawing the whole surface complex as is done in Fig. 5-8, these characterizations of the active complex represent a significant advance for catalysis. The implications of these results and the further characterization needed will be discussed in the Summary.

Surface Complexes on Metal Alloy Catalysts

Metal alloy catalysts are included in this discussion because recent advances have also made it possible to characterize the surface of metal alloys quite precisely and also to partly characterize the surface complex in catalysis by alloys.

The major clarification of metal alloy catalysis has been the recent precise characterization of the surface composition by AES, XPS or changes of work function with composition. For many alloys there is surface concentration of one component in preparation, and surface concentration can also occur when a reactant gas is strongly chemisorbed on one component of the alloy. Once the surface composition of an alloy catalyst is known precisely the effect of "ensembles" can be considered. Some recent infrared adsorption studies by SOMA-NOTO and SACHTLER¹⁶⁾ of the CO chemisorption on Pd-Ag alloys have shown a shift from linear CO chemisorption to bridged adsorption for alloys with more than 70% Pd. Earlier studies of the effect of CO chemisorption on work function of Ag-Pd alloys by MOSS and WHALEY¹⁷⁾ showed a large increase in ϕ at approximately 60% Pd with constant ϕ from 60 to 100% Pd. Both of these results can be explained by the rapid increase of $(AgPd_2)$ ensembles in the region 40-60% Pd. In general the catalytic activity of alloys appears to be explained by the surface composition and the kind of surface complex formed with reactant molecules. Vacant d-orbitals are important in defining the surface complex, but a property such as holes in the d-band does not appear to be relevant in the light of recent information.

Summary of Properties of the Surface Complex and Catalytic Behavior

The information needed for a complete characterization of a surface complex in catalysis is listed in Table 2. The precise geometry is still lacking, and the energy quantities are not available for the surface com-

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TABLE 2. Complete Characterization of Catalytically Active Surface Complex, (S)

Information	Experimental
Number of other Surface Complexes (may be inactive or active for side reactions)	Flash Desorption, XPS, UPS, I.R., $\Delta\phi$
Geometry (M-S distance, single or multiple attachment to M, Pattern of S on surface, S-S distance, any changes in interatomic distances or angles in S)	I.R., LEED, FEM, FIM, estimates of radii
Electron Density around S and in binding region of surface complex	$\Delta\phi$, ΔR , XPS, UPS, AES
Energy Levels of Binding Electrons and Electrons in S	XPS, UPS, FES, INS, $\Delta\phi$, Emission Spectra
Strength of Chemical Bond in S	Heat of Adsorption, Flash Desorption

plexes discussed above. Theoretical calculations in connection with the various spectroscopies will be most helpful for this purpose. However, the data already available gives considerable insight into the way the properties of the surface complex are related to catalysis. A major catalyst property can be termed the binding strength of the surface complex. This is measured by heat of absorption and is also related to the work function measured under catalytic conditions. For the tungsten catalyst of Fig. 5 the relevant quantity is the ΔH or ϕ in the presence of both reactants, and for the Ni, Pt and Ag catalyst of Fig. 6-8 it is these quantities in the presence of the additives as well (S, Ca and Cl, respectively). It is suggested that binding strength of surface complex is the factor responsible for *activity* of a catalyst. Additives can either increase or decrease the binding strength of the reactant molecules in the surface complex; an additive effective for a given metal and reactants leads to the optimum in binding strength for high catalytic activity.

It is also of interest to consider the properties of the surface complex responsible for *selectivity* of the catalyst. In the case of homogeneous catalysts the high selectivity results from the stereochemical influence of ligands attached to the metal and also from the discrete energy change involved in the change in coordination number and of d-orbital occupancy on the metal during the catalytic reaction. In the surface complex the additives such as S or Cl appear to have the same stereochemical role as

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the ligands have in the transition metal complex of the homogeneous catalyst. In addition, through the change in ϕ of the metal surface, the additive can cause surface reorganization of the metal lattice with accompanying changes in itinerant electron localization and changes in d-orbital orientation. There has been recently given a detailed comparison of heterogeneous catalysts and homogeneous catalysts using the present models¹²⁾. For the surface complex the itinerant nature of metal electrons with their continuous range of energies (band structure) leads to a range of binding strengths for the reactants in the surface complex, and there is a lower selectivity than for homogeneous catalysts.

For ethylene hydrogenation there is expected a range of binding energies for both C_2H_4 and C_2H_5 species, and this can lead to easy reversibility in addition of H and also to additional reaction pathways, *e.g.*, exchange and isomerization. In this respect the additives on the metal surface modify ϕ and limit the possible adsorption sites and thus restrict the energy range for chemical binding of the reactants. This can also be described as occurring with a greater localization of binding electrons, and in this way also the surface complex approaches the electronic properties of a homogeneous catalyst. It is expected that the greater localization of itinerant electrons will restrict electron movement in and out of the binding region of the surface complex. The high specificity noted for stepped planes of Pt¹²⁾ with no additives present may be due to the geometry and limited area provided by the specific stepped plane, or it could be due to the unique spatial arrangement of surface d-orbitals above the stepped plane.

It can be concluded that modern techniques can characterize the geometry of the surface complex and indicate the kind of electron transfer which takes place in formation of the surface complex and during its reactions. However, the precise electron pathways which are decisive for high selectivity are still speculative and requires further development of theoretical background.

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