

Importance of Electronic Ligand Effects in Metal Alloy Catalysts

ROBERT BURCH

Department of Chemistry, The University, Whiteknights, Reading, RG6 2AD, England

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It would be difficult to exaggerate the importance of catalysts, since almost nine-tenths of the chemicals manufactured throughout the world involve the use of catalysts at some stage in the manufacturing process. Yet for all its importance and longevity—the first reported conscious use of catalysts was by Berzelius¹ in 1835—the catalytic process is still poorly understood. Catalyst users are faced with a bewildering variety of data, concepts, and theories, having little apparent order or organization.

Historically, the first theory of catalysis was developed by Sabatier² (~1918), who adopted a chemical approach and emphasized the importance of considering the catalyst as part of a chemical system in which a transitory, unstable intermediate was formed on the catalyst surface. This was followed by the geometric theory based mainly on the work of Balandin³ (~1929), who suggested that the activity of a catalyst was determined by the presence on the surface of appropriate multiplets (i.e., groups) of atoms having the correct geometry and lattice spacing to accommodate reactant molecules and facilitate their dissociation.

Developments in solid-state physics, and from this the evolution of electron band theory, resulted in a swing away from the geometric models toward an electronic theory. Around 1950, several theories were advanced⁴⁻⁶ which tried to correlate changes in catalytic activity with variations in some electronic property of the solid. In the case of metals, parameters such as the percentage d character, the number of holes in the d band, the density of states at the Fermi level, etc., were considered, but none proved to be entirely satisfactory. Recently the pendulum has swung back again to a chemical approach and, stimulated by the work of Schuit et al.⁷ and of Rooney and others⁸ support is now increasing for a localized model.

It is generally accepted that the best way of interpreting the differences in the catalytic properties of metals is by considering only the local environment of the active site. The individual surface atom model,⁹ which expresses this view, emphasizes the unique properties of each metallic element and draws comparisons with well-established principles in organometallic chemistry.

Research on metal alloy catalysts has highlighted further the inadequacies of the older electronic models. These treated an alloy as a homogeneous material with each atom having identical properties—properties, in-

centally, which were determined by averaging the properties of the parent metals. More recent theories consider that each individual metal atom in an alloy retains its identity and has virtually the same electronic properties as in the pure metal. Chemisorption processes, catalytic activity, and so on are believed to be affected if the process under consideration requires the presence of groups (ensembles) of similar metal atoms on adjacent lattice sites.

Dowden¹⁰ has combined the basic ideas of the ensemble model and the electronic model by proposing that the heat of adsorption on a particular metal atom is affected by the nature of the other metal atoms making up the ensemble which surrounds this particular metal atom. Other workers, notably Ponc and Sachtler,¹¹⁻¹³ have preferred a pure ensemble model in which it is assumed that adsorption is affected by the availability of the correct ensembles of metal atoms, the individual atoms being more or less unaffected by their environment. Of course, these workers have been aware that changes in the electronic properties of an atom may be caused by changing the ligands,^{13,14} but in general they have concluded that electronic ligand effects are only of secondary importance.

It is our opinion that this view is incorrect, and it is our intention in this paper to demonstrate that electronic ligand effects are important and to present a model¹⁵ which allows an alternative interpretation of trends in the activity of alloy catalysts. To assist in presenting the evidence in support of an electronic ligand effect it is helpful to summarize how previous electronic models came to be rejected.

The Simple Electronic Model

The earliest electronic theories were based on the rigid band model of metals. This simple model proposed that in alloys formed by combination of a transition metal (having a partially filled d band) with a

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(2) P. Sabatier, "La Catalyse in Chemie Organique", Librairie Polytechnique, Paris, 1913.

(3) A. A. Balandin, *Z. Phys. Chem.*, **132**, 289 (1929).

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(9) W. M. H. Sachtler and P. van der Plank, *Surf. Sci.*, **18**, 62 (1969).

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(14) See, e.g., R. A. van Santen and W. M. H. Sachtler, *Surf. Sci.*, **63**, 358 (1977).

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Robert Burch was born in Ballymena, North Ireland, in 1943. He attended The Queen's University Belfast, being awarded a 1st class Honours degree in 1965 and a Ph.D. in 1968. He is now Lecturer in Solid State and Inorganic Chemistry at the University of Reading. His research is concerned with investigating the role of the support in catalysis by metals and alloys, with preparing selective bimetallic Fischer-Tropsch catalysts, and with investigating the properties of mixed sulfide hydrotreating catalysts.

nontransition metal (d band fully occupied) the electron bands had the same shape and position with respect to the Fermi level as in the pure metal. However, since the alloy (e.g., between Pd and Ag) would contain more valence electrons than the pure metal (e.g., Pd), there would be a gradual filling up of the vacant electronic states in the d band until at some critical composition the d band became filled. Across the whole range of compositions of such alloys it was assumed that all the metal atoms had identical properties.

It soon became apparent that many data on alloy catalysts were not consistent with this simple model. The introduction of more sophisticated experimental procedures and the development of more realistic theoretical models led to a further decline in support for an electronic model. Electronic spectroscopy has shown that in alloys the band structure resembles quite closely the weighted average of the electron bands in the parent metals.¹⁶ Current theories of metal alloys, such as the coherent potential approximation,^{17,18} which assume that atoms retain their individuality in an alloy, give good agreement with experimental data on band structures.

Spectroscopic and chemisorption data seemed to confirm that the identity of metal atoms in the surface of an alloy were hardly affected by changing the nature of their neighbors. Occasional results were obtained, such as the observed shift in the infrared absorption bands of CO adsorbed on alloys, which indicated an influence of the near-neighbor metal atoms—a ligand effect—but it was generally assumed that the ligand effect was of only secondary importance.

The Ensemble Model

Nevertheless, for many reactions the activity, and especially the selectivity, of alloy catalysts is different from that of the parent metal, or of an "averaged" alloy. To account for this change in catalytic properties on alloying it was proposed¹³ that some "demanding" reactions (such as hydrogenolysis, self-poisoning, etc.) required large ensembles of metal atoms, and so these reactions would be more susceptible to alloying than other "facile" reactions which required only single metal atoms for reaction (hydrogenation, isomerization, dehydrogenation, etc., fall into this category).

Much of the early support for an ensemble effect derived from the work of Sinfelt et al.¹⁹ on Ni/Cu alloys. They observed that a small addition of copper to Ni produced a large decrease in activity for ethane hydrogenolysis but hardly any change in activity for dehydrogenation of cyclohexane. Ponc and Sachtler¹¹ have obtained similar results for reactions of hexane over Ni/Cu alloys. Martin and co-workers²⁰⁻²² have determined the kinetics of the hydrogenolysis of ethane, propane, and butane over supported Ni and Ni/Cu alloys. They have concluded that an ensemble effect

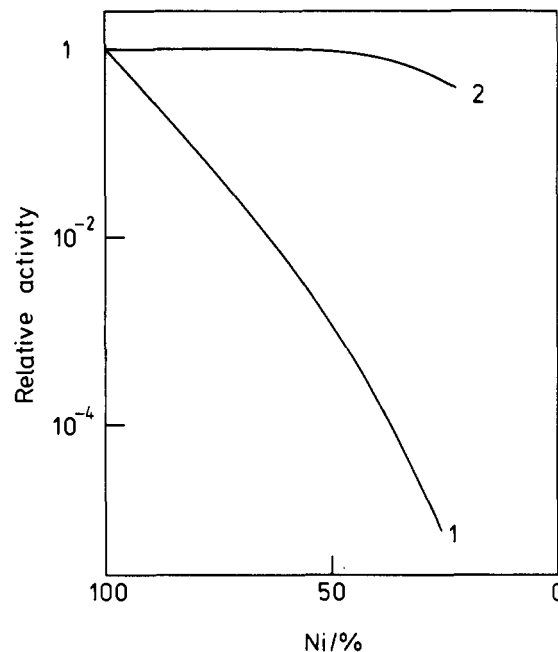


Figure 1. Comparison of the relative activities of Ni/Cu¹⁹ (curve 1) and Ni/Pd²⁶ (curve 2) alloys for the hydrogenolysis of ethane.

operates and that the number of Ni atoms required for these hydrogenolysis reactions is 12, 16, and 20, respectively. They have shown also that hydrogen adsorbed on Ni atoms in the surface has an effect almost identical with that of copper on the hydrogenolysis reaction, and this is taken as further evidence of an ensemble effect. On the other hand, Prinsloo and Gravelle have investigated these same Ni/Cu alloys by microcalorimetry and found^{23,24} that the heat of adsorption of hydrogen decreases both with hydrogen coverage and with copper content. They suggest that these effects must reflect changes in the electronic properties of the surface atoms and suggest a correlation with changes in the density of electron states at the Fermi level for surface Ni atoms.

Similar differences of opinion are apparent when one considers theoretical models of bonding of adsorbates at surfaces.²⁵ Calculations of adsorbate-adsorbent interactions indicate that the most appropriate model to describe a specific system depends on the strength of the adsorbate-adsorbent interaction. If the interaction is weak, quantum calculations suggest that an electron band (delocalized) model is best. If the interaction is strong, the calculations suggest the surface molecule (localized) model is best. Of course, in practice the best model will be a compromise between these two extremes.

The crucial question is, which model is appropriate to catalyzed reactions? The present consensus¹¹⁻¹³ is that the surface molecule description is adequate, and it is assumed that the major effect of adding elements such as Cu is to dilute the active metal and so reduce the number of large ensembles. However, there is growing evidence that in a great many alloy systems (e.g., Ni/Pd,²⁶ Ru/Cu,²⁷⁻³⁰ Os/Cu,³¹ Pt/Sn,^{32,33} Ni/Sn³⁴

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(25) For a recent review, see S. R. Morrison, "The Chemical Physics of Surfaces", Plenum Press, New York and London, 1977.

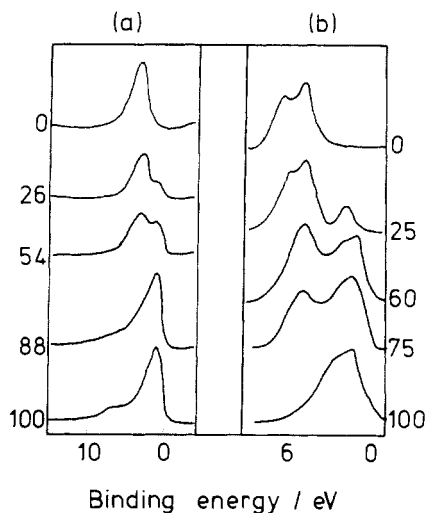


Figure 2. Electron band structure of (a) Ni/Cu³⁹ and (b) Pd/Ag⁴⁰ alloys derived from photoelectron spectra. Numbers beside curves indicate the Ni or Pd content of the alloy.

Ni/Mo,³⁵ Pd/Au,³⁶ Pt/Re,³⁷ etc.) some degree of electronic modification may coexist with an ensemble effect. As an example of the discrepancies which exist, Figure 1 shows how the specific activity of Ni/Cu and Ni/Pd alloys for the hydrogenolysis of ethane varies with alloy composition. Although both Cu and Pd are inert as compared with Ni, Figure 1 shows that the addition of Cu has a much greater effect than the addition of Pd. It is hard to explain these differences using a simple ensemble model. The results could be rationalized in terms of the ensemble effect if it is assumed that reaction may proceed on *mixed* ensembles. However, it would be surprising if the activity of a mixed ensemble was the same as that of a pure Ni ensemble. Some form of electronic effect would seem more appropriate. It is relevant to note that Sinfelt, whose early work stimulated interest in an ensemble model, has stated³⁸ that, although geometric (ensemble) models offer a reasonable explanation of the effect of adding Cu to Ni, it is difficult to exclude the possibility that electronic effects may be responsible.

It is our opinion that there is sufficient evidence in support of this view to justify a reexamination of the electronic ligand effect in catalysis. To avoid confusion, it should be made clear that we define *the electronic ligand effect* as the change in the *local* electronic, and therefore by implication the catalytic, properties of a central metal atom brought about by varying its near-neighbor atoms, and we do not imply, or require, any long-range band effects.

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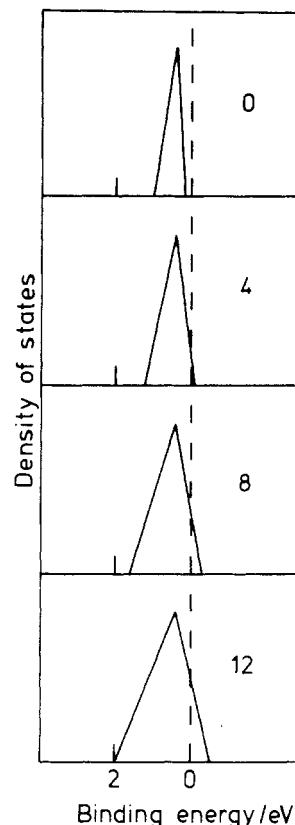


Figure 3. Schematic representation of the variation in the local density of states at Ni atoms in Ni/Cu alloys as a function of the number of near-neighbor atoms which are Ni. (The number of near neighbors is indicated on each diagram.)

Electronic Properties of Bulk Metals and Alloys—Effect of Near Neighbors

The photoelectron spectra of alloys show (see Figure 2) that the band structure of a binary alloy is similar to the weighted average of the band structure of the parent elements, providing the parent metals have similar atomic numbers, e.g., Ni/Cu,^{39,40} Pd/Ag,⁴⁰ etc. (More substantial variations are observed for alloys formed from widely different elements.³⁴) This has led to the conclusion in the case of Ni/Cu alloys, for example, that the copper atoms have little influence electronically on their Ni neighbors and, consequently, that the catalytic properties of a Ni atom in a copper matrix are essentially the same as for a Ni atom in a Ni matrix.

This is not strictly correct. There is much evidence from investigations of binary alloys that there is a substantial modification of the properties of a central atom caused by substituting its near-neighbor atoms with foreign atoms (see later). What the photoelectron spectra show, again taking Ni/Cu as an example, is that a Ni atom does not become *equivalent* to a Cu atom as the Cu content increases—this is where the simple rigid band model is misleading—but retains many of the characteristics of a Ni atom in pure Ni. However, this is not the same as saying that a Ni atom in a Cu matrix is *identical* with a Ni atom in a Ni matrix. Indeed, it is most improbable that this would be so, and neither the photoelectron spectra nor the most reliable theo-

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retical calculations are consistent with such an idea. Figure 3 shows schematically how the shape of the 3d band in Ni varies as the number of near-neighbor Ni atoms is decreased. The data, taken from published photoelectron spectra,^{39,40} show, as predicted by the coherent potential approximation,¹⁶ that the *width* of the d band is largely due to interaction with like near-neighbor atoms (i.e., near-neighbor Ni atoms) and so varies as Cu is substituted for Ni. Although the *position* of the d band peak maximum hardly changes (and this is why it is generally assumed that Ni atoms remain unaltered on alloying), the change in the band width means that as the Cu content increases both the local density of states and the number of unfilled d states on a Ni atom decrease. Therefore, there is a progressive change in the electronic properties of a Ni atom as its near neighbors are replaced by foreign atoms. For an alloy of given composition there will be a statistical distribution of Ni atoms having from 0 to 12 near-neighbor Ni atoms. The bulk properties—magnetic susceptibility, electronic specific heat, etc., will reflect this average state. However, *at the local level* the electronic properties of each Ni atom will vary right across the range from a low density of states $3d^{10}4s^0$ atom (when surrounded only by Cu atoms), to a high density of states $3d^{9.5}4s^{0.5}$ atom when surrounded exclusively by Ni atoms. Fuggle and Zolnieriek⁴¹ have recently shown from an analysis of the intensities of XPS satellite peaks that band filling occurs in alloys of Ni or Pd with electropositive elements.

Direct evidence that the electron density at a metal atom is dependent on its near neighbors comes from Mössbauer spectroscopy. Data for ⁵⁷Fe, ¹⁹⁷Au, ¹¹⁹Sn, and ¹²¹Sb in dilute solution in Pd, Pt, Ni, and their alloys are typical of many other systems.⁴¹⁻⁴³ The results, which are confirmed by magnetic⁴⁴ and photoemission studies,^{45,46} show two important effects. First, there is clear evidence that the charge on a solute atom is screened out within its own atomic volume, as originally proposed by Friedel.⁴⁷ Second, and especially important in the present context, the extent to which *self-screening* is sufficient to produce complete screening of the solute nucleus is variable and will frequently be incomplete, so that the residual charge will be felt by *neighboring* atoms. For example, in Ni/Cu alloys the large difference in electron density of states between Cu and Ni cells is too large for complete self-screening of the Cu solute atoms. The extra nuclear charge introduced with each Cu atom will be weakly screened, and the d states on adjacent Ni atoms will be affected. The effect will be larger for solute atoms having higher valencies. This can be seen by comparing the electronic spectra of Ni/Cu and Ni/Sn alloys.^{39,34} Although in Ni/Cu alloys there is little change in the position of the Ni d band, in Ni/Sn alloys quite large changes are observed.

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The important point to be taken from these results is that the electronic properties of a metal atom in an alloy are mainly affected by the local potential so that rigid band models are invalid. However, at the same time it must be recognized that changes *do* take place at the local level. The important question in the context of catalysis is, what is the magnitude of the effect?.

Effect of Near Neighbors on Chemical Properties of Atoms in Alloys

Atoms in the bulk. One extremely useful chemical probe of electronic properties at the local level in a bulk metal is a hydrogen atom. We now consider some recent data for the *absorption* of hydrogen in transition-metal alloys to demonstrate that although atoms retain individual identities, as anticipated from the discussion above, there is, in addition, a chemical effect which depends on the identity of the near neighbors. Few data exist for the absorption of hydrogen by Ni alloys, so we consider other related alloys.

Palladium and iron form an ordered alloy Pd₃Fe having a cubic close-packed lattice in which there are special octahedral sites surrounded exclusively by Pd atoms (Pd₆ sites) and a disordered alloy in which each octahedral site has a statistical distribution of near-neighbor metal atoms. Hydrogen dissolves to a much greater extent in the ordered alloy and is located in the special Pd₆ sites.^{48,49} This indicates that hydrogen atoms can differentiate between different types of metal atom and confirms that atoms retain some of their individual identity in alloys, in agreement with current thinking.

However, whereas for pure Pd the standard enthalpy of dissolution of hydrogen is -19 kJ mol^{-1} , for the ordered Pd₃Fe alloy it is $>+10 \text{ kJ mol}^{-1}$. Thus, although the environment of a H atom in the Pd₆ site in Pd₃Fe is apparently identical with the environment of a H atom in pure Pd, the interaction with the H is different, and the enthalpy differs by at least 30 kJ mol^{-1} . This gives some indication of the order of magnitude of what we have described as an electronic ligand effect. These results indicate that the Pd atoms adjacent to Fe atoms are modified electronically, i.e., their local density of states is changed so that they can no longer interact so strongly with H atoms. Apparently, this change in the enthalpy reflects differences in the two sites because in one case the Pd atoms have only Pd atoms as near neighbors (pure Pd) whereas in the other case (Pd₃Fe) they have 8Pd and 4Fe atoms as near neighbors.

Similar effects are observed in other Pd alloys.^{50,51} Figure 4 shows results for a variety of alloys of Pd. In the case of PdAg alloys, the H again initially chooses only Pd-type sites, yet the enthalpy is found to decrease by about 2 kJ mol^{-1} for each 1% Ag added. Figure 4 shows that even larger effects are observed with other additives. These results also show that there are differences between transition- and non-transition-metal additives, the former in general reducing the affinity for hydrogen, the latter having the opposite effect. The results for

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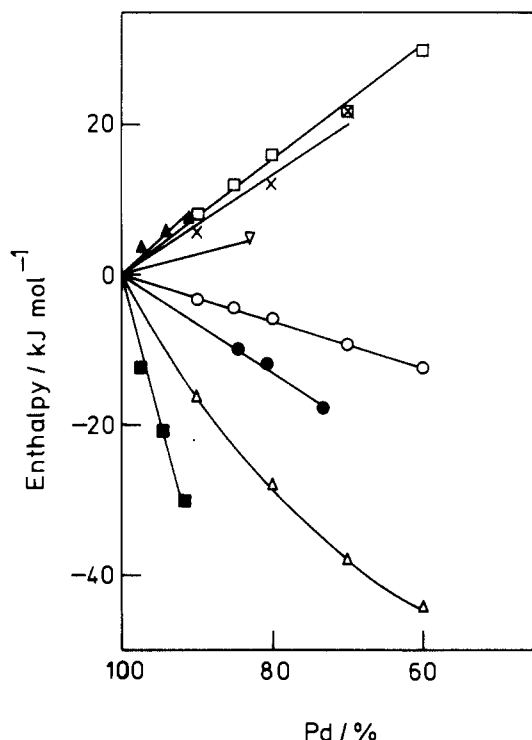


Figure 4. Variation in the relative partial molar enthalpy of hydrogen in Pd alloys. Data have been corrected to take account of differences in the physical properties of the alloys. (□) Rh; (△) Ir; (×) Pt; (▽) Ni; (○) Cu; (●) Au; (△) Ag; (■) Pb.

Pd/Cu alloys appear anomalous, but this is because in these alloys the H is situated in mixed PdCu sites where the binding is weaker. Once again it is clear that the effect of an added element depends on which additive is used.

Many other systems could be cited as evidence of changes in the electronic properties of metal atoms in alloys, but two further examples will suffice. Pd and V separately absorb hydrogen very readily, whereas alloys of these elements absorb very little hydrogen.⁵² The effect is quite dramatic. As little as 6% V in Pd can almost completely suppress the absorption of hydrogen. At this concentration of V there will still be many Pd_g-type sites in the lattice, but apparently these can no longer bind H atoms. In the case of Fe and Ti, the opposite is found to happen. Fe does not absorb hydrogen, yet in the intermetallic alloy TiFe the H is situated adjacent to Fe atoms.⁵³ Once again we have evidence of changes in the electronic properties of metal atoms in alloys.

We conclude that near-neighbor metal ligands can cause an electronic ligand effect which alters the enthalpy of solution of hydrogen by about 20–30 kJ mol⁻¹.

Atoms on the Surface. The adsorption of hydrogen on metal surfaces has been studied extensively.⁵¹ One general observation is that up to a coverage of about 50% of a monolayer the enthalpy of adsorption is constant and then decreases rapidly. Since the spacing between the H atoms is too great to allow direct H–H repulsive interactions to occur, it has been suggested that the decrease in the enthalpy of adsorption occurs via a “through-bond” interaction involving the orbitals

on the metal atoms in the surface.^{54–56} For adsorption of H on the W(100) plane it has been estimated that this interaction is of the order of 15–30 kJ mol⁻¹. This is of the same order of magnitude as the variation in the enthalpy of absorption due to changes in near-neighbor metal atoms. It would seem that in both cases a change in the electronic properties of a metal atom (caused either by changing its near-neighbor atoms or by binding an adsorbate atom to a neighboring atom) leads to a substantial change in the affinity for hydrogen. Prinsloo and Gravelle^{23,24} have measured directly the heat of adsorption of H on Ni and Ni/Cu alloys and found that it decreases smoothly when either H or Cu is present at sites adjacent to a Ni atom. Their results show that although H adsorption still occurs at isolated Ni atoms the heat of adsorption is affected by the local environment. Although the Ni atom retains many of the characteristics of a pure Ni atom, it is not exactly the same, and there is a decrease of 10–20 kJ mol⁻¹ in the binding of an adsorbed H atom. Such a change in binding energy would be expected to produce a change in catalytic activity, especially in reactions such as hydrogenolysis where strong metal–adsorbate bonds are necessary.

Adsorption of Other Reactants

Carbon Monoxide. CO is adsorbed by metals in two forms, linear and bridged, and the proportions of each varies with alloy composition.^{57–60} This is simply an ensemble effect and reflects a change in the relative numbers of isolated atoms and pairs of metal atoms. However, there is now, in addition, clear evidence of ligand effects in CO adsorption. Various workers^{57,59,61} have observed changes with alloy composition of the vibration frequency of adsorbed CO molecules. Moreover, Yu et al.⁶¹ have shown by temperature-programmed desorption that there is a decrease of 25 kJ mol⁻¹ in the Ni–CO binding energy when Cu is present. They conclude that the bond between Ni and CO is weakened by the presence of Cu atoms around the Ni atom. Dalmon et al.,⁵⁸ using combined IR and magnetic measurements, also find that Cu affects the electronic properties of adjacent Ni atoms. Toolenaar et al.⁶⁰ have recently collated the data for the adsorption of CO on alloys and suggested that the shift in IR frequency is somehow related to the density of states of the metal alloy, although it is now believed⁶² that the observed effects are due to a decreased dipole–dipole interaction as the concentration of adsorbed CO declines.

Organic Molecules. Little relevant data are available on the adsorption of organic molecules. However, from the point of view of catalyzed reactions, it is worth summarizing what changes are to be expected in the strength of metal–carbon bonds due to alloying. We restrict our attention to σ bonding since

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in hydrogenolysis reactions this will be the initial bond formed with the surface.

The formation of a σ bond between an sp^3 orbital on a CH_3 radical (itself formed during the initial adsorption process by loss of a H atom) and a surface metal atom would be expected to occur by overlap with a partially filled d orbital of appropriate symmetry. The most obvious "correct" symmetry would be an orbital normal to the surface plane. (Although it is a naive idea, it is perhaps relevant that whereas the Ni(100) and Ni(110) planes are active for ethane hydrogenolysis, the Ni(111) plane is very much less active.⁶³ The first two planes have d orbitals normal to the surface; the (111) plane does not. Incidentally, the fact that different surface planes have different activities is further evidence that the rates of demanding reactions are not just controlled by ensemble effects).

The requirement that the d orbital is partially filled is of direct interest in the present context. We have seen earlier that the properties of individual atoms in an alloy are dependent on their own environment. As foreign atoms are substituted at near-neighbor positions the d band of a transition metal narrows, slips below the Fermi level, and becomes filled. These atoms would not be able to form strong σ bonds to carbon, and so the catalytic activity would be drastically reduced.

The importance of considering the effect of the nearest-neighbor atoms on the ability of metal atoms to adsorb gaseous molecules has been emphasized by Frennet et al.⁶⁴⁻⁶⁶ These workers found,⁶⁴ for example, that the "landing site" for a methane molecule on a Rh surface consists of eight Rh atoms. The methane molecule is not bonded to eight Rh atoms, but rather the results show that in order for adsorption to occur on a central Rh atom (or atoms) it is necessary also to keep adjacent Rh atoms free of adsorbed species (such as H atoms). The results indicate that the ensemble size calculated from kinetic data probably includes not only the atoms directly involved in forming chemisorption bonds but also the other metal atoms in the nearest-neighbor positions. There are some similarities between the model suggested by Frennet et al. and our model, which is described below.

The Proposed Model

Our very simple model is as follows. It is known (see earlier discussion) that the electronic properties (i.e., density of electron states, type of electrons at the Fermi level, etc.) of a metal atom in an alloy are largely determined by interaction with its near neighbors. If these near neighbors are similar in character to the central atom (Ni and Pd are similar because of their similar crystal structures and electron band structures), there will be extensive interaction and broadening of electron levels. If the near neighbors are dissimilar (Ni and Cu are construed to be dissimilar in this context because the energies of their d electrons are very different), there will be very little interaction, and the central atom will have an electronic structure similar to that of a free

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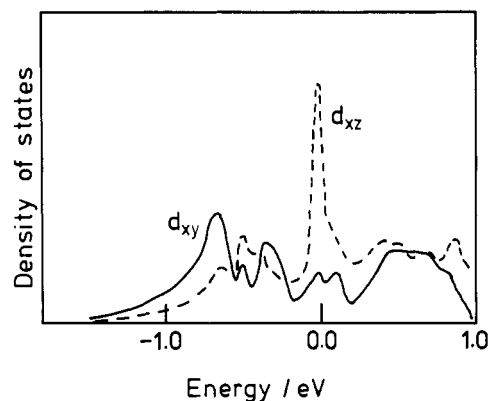


Figure 5. Calculated local density of states for the d_{xy} and d_{xz} orbitals of a Ni atom in the (100) surface plane.

atom. In band model terms there will be a narrowing of the d band as the number of like neighbors is reduced.

At the local atomic level we will observe changes in the local density of states of d and s electrons. Even in a pure metal we should expect to see variations in the local density of states. Schrieffer and Soven⁶⁷ have calculated the local density of states for the d_{xy} orbital (in the surface plane) and the d_{xz} orbital (out of the plane) for the (100) surface of Ni. Figure 5 shows that the d_{xy} orbital which has its lobes lying in the surface plane, and thus has four near-neighbor Ni atoms, is quite different from the d_{xz} orbital which has two lobes protruding into the vacuum, and thus has only two near-neighbor Ni atoms. This d_{xz} orbital has a narrow peak in the center of the LDS curve. This arises because the root-mean-square width of the distribution is proportional to the number of (like) near neighbors.⁶⁸

In an alloy, as we have indicated earlier, when the number of like near neighbors is reduced, we expect to get a further narrowing of all the d orbitals of the surface atoms. It is pointless with such a simple model to speculate on the effect that such changes in the LDS will have on the catalytic activity of surface atoms. However, judging from the data presented earlier from absorption and adsorption experiments, we would predict a variation in binding enthalpy of the order of 20–30 kJ mol⁻¹. Such a change in binding enthalpy will have a dramatic effect on the catalytic activity. For example, for a typical catalyzed reaction (activation energy 100–150 kJ mol⁻¹) operating at 500 K, the change in the rate of reaction, assuming a constant preexponential term, is about three orders of magnitude—sufficient to account for the largest changes in activity due to alloying yet observed.

Catalyzed Reactions

We consider first hydrogenolysis reactions over Ni alloys. Currently, an ensemble model is favored^{11-13,22-24} to explain the very large decrease in activity when Cu is added to Ni. It has been calculated²⁰ that the active site for ethane hydrogenolysis is an ensemble of 12 Ni atoms, and it has been suggested that the rate-determining step involves the simultaneous formation of six M–C and six M–H bonds. Such a complete dissociation seems improbable—a stepwise dissociation would appear more likely, but this would not require a 12-atom

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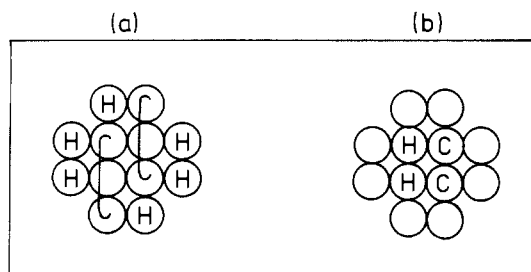


Figure 6. Comparison of the site requirements for ethane hydrogenolysis in (a) the ensemble model and (b) the electronic ligand model. H is a hydrogen atom bound to a Ni atom, C is a carbon atom bound to a Ni atom, [is a carbon atom bound to three Ni atoms.

ensemble since a single Ni atom could remove several H atoms in succession.

We propose that the active site consists of two Ni atoms per adsorbed C atom in the reactant molecule (i.e., Ni_4 for ethane, Ni_6 for propane, etc.). However, in order that these four Ni atoms can bind the ethane sufficiently strongly to activate the C-C bond, we suggest that these Ni atoms must only be surrounded by other "Ni-type" atoms. Figure 6 shows how our model differs from the ensemble model.⁶⁹ Although both "require" a 12-Ni-atom ensemble, the bonding of the ethane is very different. Substitution of any of the outer ring of Ni atoms by Cu atoms will prevent the central atoms from forming strong bonds to C, so the catalytic activity will decrease. If we assume that the activation energy for the dissociation of ethane increases linearly with the number of near-neighbor Cu atoms from the value of 60 kJ mol^{-1} for pure Ni²⁰ to a value of 350 kJ mol^{-1} for pure Cu (350 kJ mol^{-1} is the bond dissociation energy of a C-C bond, and assumes no catalytic effect of Cu), then the rate of reaction will decrease by a factor of 1000 for each Ni atom replaced by Cu. Obviously, the contribution of such ensembles to the total activity would be negligible, so the reaction will *appear* to occur only on pure Ni ensembles with a constant activation energy (as observed experimentally).

The complete hydrogenolysis of larger hydrocarbon molecules into C_1 fragments is thought to require even larger ensembles. However, Figure 7 shows how, once again, these results can be interpreted in terms of multiples of Ni_2 units in a protected environment.

In the case of Ni/Pd alloys we anticipate that Ni and Pd will form a common d band so there will be little change in the electronic properties of Ni atoms when Pd is substituted for Ni. Figure 1 shows that this is probably correct, since Pd has almost no effect on the activity of Ni in ethane hydrogenolysis.

Our model is in no sense restricted to Ni alloys. The following section briefly summarizes some relevant results on other alloys.

Group 8 Metal Alloys

The range of activity of the group 8 metals (and Re) span more than 7 orders of magnitude. The approximate relative activities are³⁸ Os (2×10^7), Ru (2×10^6), Ni (3×10^5), Ir, Rh, Re (10^5), Pd, Pt (1). We consider

(69) For simplicity, Figure 6 shows only a surface layer. Clearly, the requirement that active Ni atoms must be surrounded by other Ni atoms means that the first layer of atoms below the surface should also be taken into account.

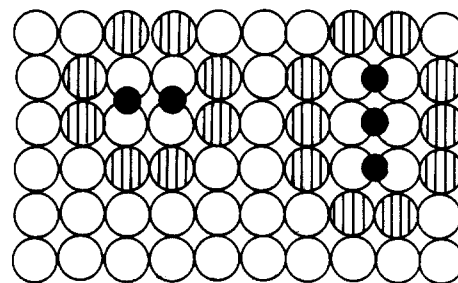


Figure 7. Active sites in the electronic ligand model for the hydrogenolysis of ethane and propane. (○) Ni; (●) C; (◐) near neighbor.

first the very active metals.

Os, Ru, Ir, and Re. Sinfelt and co-workers^{27,28} have demonstrated that the activity of Os and Ru is reduced by 3-4 orders of magnitude when Cu is added. Although Cu is not miscible with Os or Ru, it forms a surface layer partially covering the active metal. However, the metals still retain the ability to adsorb H, so the Cu does not merely poison the surface. It is concluded²⁷ that an electronic factor is involved. A similar conclusion can be drawn from the model studies of Christmann et al.^{29,30} on the Cu/Ru system. They observe that Cu is present as a partial overlayer on the Ru and that as a consequence each H adsorption site requires between five and ten Ru atoms. Obviously, a H atom will not be directly bonded to ten Ru atoms. It is more likely that for strong adsorption to occur the active Ru atoms in the alloy must be "protected" by surrounding them with other Ru atoms, in agreement with our model.

Ir/Cu alloys have been investigated³¹ for pentane hydrogenolysis, and similar results obtained. An electronic model has been postulated which correlates catalytic activity with the "softness" of the metal. For the reaction of butane over Ir/Au alloys, Foger and Anderson⁷⁰ find only a small decrease in activity as the Au content is increased (a factor of 100 up to 86% Au). They conclude that probably two Ir atoms constitute the active site. If the surface is homogeneous, this implies that when Au is added to Ir no "protection" of the Ir atoms is necessary, which is surprising. However, Brunelle et al.³¹ have indicated that Ir/Au alloys are similar to Ir/Cu alloys. Other Ir alloys of interest include Ir/Re³¹ which show a maximum in the activity as Re is added to Ir. It is suggested that this occurs because an Ir/Re alloy has similar electronic properties to Os, which is the most active pure metal. Ir/Pt alloys have been investigated,⁷¹ and it has been found that very small additions of Ir can completely suppress the self-poisoning of Pt. Once again an electronic effect appears to operate.

Pt and Pd. Pt and Pd are comparatively inactive for the hydrogenolysis reaction. Moreover, it is well established that they can catalyze hydrocarbon reactions at single metal atom sites. It is perhaps not surprising, therefore, that Pt and Pd alloys show smaller effects than those found with the active metals described above. Pt/Cu,⁷² Pt/Au,⁷³⁻⁷⁵ and Pd/Au^{36,73} alloys have

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been investigated, and in all cases the added elements have a small effect, which strongly suggests that the active site is small (perhaps only one or possibly two metal atoms). Data for hydrogenolysis over Pt/Sn alloys³² are interesting because they show that as compared with Cu the addition of only a small amount of Sn is sufficient to produce a particular change in properties. This difference between two inert additives is contrary to the ensemble model but quite acceptable on our model since we would expect the extra effective nuclear charge on a Sn atom to cause a larger change in the electronic properties of adjacent Pt atoms.

Further evidence has been obtained^{33,76} that a small amount of Sn can materially affect the catalytic properties of Pt in reforming reactions. This appears to support the electronic model,³³ although the alternative ensemble model has also been proposed.⁷⁶

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Conclusions

We conclude that the variation in catalytic activity of metal alloys for "demanding" reactions can be interpreted on the basis of electronic ligand effects. Ensemble effects operate, but to some extent they are a consequence of electronic ligand effects. For some metals, notably Pd and Pt, the active site may only be one or two atoms, and even in the case of the very active metals, the reactant molecule is probably bonded directly to only a small number of protected metal atoms. Ensemble effects are not excluded, indeed they must occur, but we emphasize that the size of ensembles calculated from kinetic data may not accurately reflect the bonding of reactant molecules.

Whereas for some alloys, such as Ni/Cu, where the two metals have similar effective nuclear charges, it may be difficult to distinguish between a direct and an indirect ensemble effect, alloys of quite different metals (Pt/Sn, Pt/Re, etc.) would be expected to show larger effects. There is already some evidence that this is the case. It will be interesting to see whether data for other such alloys can provide more definite "proof" of electronic ligand effects.