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Surface Composition and Selectivity of Alloy Catalysts

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I. Introduction

Interest in heterogeneous catalysis by alloys was very strong in the heydays of the "electronic factor" concept in the 1950s, when it was hoped that the rigid-band model of binary alloys would describe and predict their catalytic behavior. In this model it was assumed that in an alloy the valence electrons of both constituents form common bands consisting of one d-band and one s,p-band overlapping the former. As the holes in the d-band of transition metals were assumed to be responsible for adsorption and catalysis by these metals, a filling of these holes by alloying would drastically influence the adsorption capacity of the alloy. No adsorption of, e.g., hydrogen would be possible for alloys with a filled d-band, unless specific excitation processes would again create the required d-band holes.

An increasing number of results, either contradictory to this model or requiring additional ad hoc assumptions, weakened the faith in such a simple model for the prediction of heterogeneous catalysis, with, as a result, a decrease in research effort devoted to this subject.

Interest in alloy catalysis was, however, revived in the late 1960s and the early 1970s. A number of causes can be cited for this renewed interest, which include the following:

(1) The discovery that some bimetal systems exhibited a higher catalytic activity than either of their constituents. It is not absolutely clear, however, whether this enhanced activity applied to the initial state of the virgin catalyst or to its steady state, where a lower degree of poisoning by strongly adsorbed by-products would create a higher apparent activity. In this case the lower poisoning of an alloy as compared to its pure components would be due either to a lower rate of the reaction creating this poisoning by-product or to an enhanced relative rate for its removal. In either case the rate of the main reaction per unit of unpoisoned surface area might be equal to, or smaller than, that for the unalloyed metal; the apparently enhanced activity would, in other words, result from a change in selectivity.

(2) The finding that the selectivity of alloys often differs very strongly from that of their components or any mechanical mixture of them. In particular, the reactions involving C–C fissions are often affected much more severely by alloying than reactions that leave the carbon number of the organic molecule unchanged.

(3) The important discovery that supported bimetal and multimetal catalysts when used under severe industrial conditions often display a stability distinctly superior to that of their monometal counterparts.

(4) The ascertaining by classical and modern methods that the surface composition of alloys can strongly deviate from the composition of the bulk. These methods have opened up the possibility of correlating catalytic phenomena with catalyst surface composition, thus removing a major drawback of older studies with alloy catalysts.

(5) The discovery by ultraviolet photoelectron spectroscopy that the rigid-band model is not even applicable to the bulk of alloys such as Ni–Cu and Pd–Ag. The d-electrons of copper or silver in such alloys experience a potential that is predominantly the same as in the metals before alloying. For instance, upon alloying the d-bands of copper and nickel remain discernible in the alloy and no common d-band is formed, as is supposed by the rigid-band theory.

The coherent potential approximation for a disordered alloy (*1*, *2*) provides a satisfactory framework for describing the effect of alloying within two extremes: on the one hand, the rigid-band approximation, which supposes that band shapes do not alter upon alloying, and on the other hand, the minimum polarity model, which supposes the electron distribution of the elements forming an alloy to be similar to that in free atoms.

Even before the results discussed later were known, chemisorption data had shown the inadequacy of the rigid-band model in describing the chemistry of surface reactions. Highly diluted alloys of nickel or platinum in metals such as copper, silver, or gold proved capable of chemisorbing gases such as hydrogen and CO in amounts that were roughly proportional to the concentration of the transition metal element in the alloy surface. These results led to the "individual surface atom" approach of chemisorption (*3*), where every atom is assumed to retain its chemical identity although the quantitative parameters describing bonds with this atom may be somewhat modified by its near neighbors in and below the surface. For alloy systems where this modification is weak, the individual surface atom approach provides the basis for chemisorptive titration, i.e., the transition metal atoms in an alloy with a nonadsorbing element can be counted by measuring the number of CO molecules or hydrogen atoms chemisorbed by the alloy. The individual surface atom approach parallels the minimum polarity model developed in the electron theory of alloys.

We stress that this point of view implies that it is mainly the immediate environment of the atoms, active in the particular catalytic reaction under study, that determines their chemical properties. It is, therefore, the surface composition of an alloy that determines its catalytic properties.

We have chosen to present a review of experiments and the theory of surface enrichment before dealing with the catalytic properties of alloys and discussing the existing evidence for the relevance of changes in the electron distribution in catalytically active atoms.

II. Surface Composition of Equilibrated Alloys

Ever since it was demonstrated, both experimentally and theoretically, that in equilibrated Ni–Cu films the surface composition can differ substantially from that of the bulk (*4a–4d*)—and this was also found for alloy powders (*5*)—it has been generally accepted that a catalytic study of alloys should be accompanied by a study of the surface concentration of the alloys.

Equilibrium in the surface layer will in practice often be reached, because it has been shown (*6*) that the surface of thin metal films can be equilibrated by heating for about 30 min at a temperature of $0.3T_m$, where T_m is the melting point (K).

Of course, researchers had wondered about the surface composition before. Takeuchi *et al.* (*7a*, *7b*) were the first to provide experimental evidence of the surface composition being different from the bulk composition in Ni–Cu catalysts by reaction with HCl. In a later paper (*7c*) they concluded that the amount of hydrogen adsorbed, the heat of adsorption, and the catalytic activity of granular Ni–Cu alloys are related to the nickel concentration at the surface.

A difference in composition between surface and bulk had been suggested by Tuul and Farnsworth (*8*) in order to explain the decreases in activity of Ni–Cu alloys upon heat treatments at high temperatures (500°C). However, the possibility cannot be ruled out that these results were due to impurities in the surface (*9*).

Recent developments in the use of Auger electron spectroscopy (AES) have improved the possibilities for a quantitative study of the surface composition (*10a–10d*). By employing an internal standard (*11*) many of the ambiguities of previous applications have been eliminated. The application of AES has greatly improved the reliability of surface composition determinations compared with previous results.

A drawback of the AES method (*12*) is that it samples a weighted average over several outer layers of the sample, depending on the escape depth of the measured electrons. A comparison of results of this technique and chemisorptive titration (*13, 14*), in which chemisorption takes place selectively on one of the constituent atoms, has been made for the Pt–Sn system. This has provided information on the concentration profiles near the surface.

It should be realized that selective chemisorption titrates only atoms on the surface, but that the surface composition can be changed upon adsorption (*15*). A difficulty in the interpretation of chemisorptive titration is the possible presence of electronic effects, which can alter the chemical nature of the titrated atoms. Adsorbates can also show strong interactions with each other on pure metals, and decreases in this interaction can cause an increase in the number of molecules adsorbed per active metal atom exposed. The surface composition of active metal atoms deduced from these measurements will then be too high.

It is obvious that chemisorptive titration is most ideally applied under such conditions of pressure and temperature that only adsorbates bonded to one surface atom exist. If, in addition, there are surface species bonded to several surface atoms, selective chemisorption applies if

$$\begin{aligned} |\Delta H_{\text{ads}}| &\gg RT, && \text{as long as} \quad \theta \leq x, \\ &\sim 0, && \text{if} \quad \theta > x, \end{aligned}$$

where θ is the surface coverage of adsorbate defined as the amount of molecules adsorbed divided by the total number of surface atoms present, x the surface concentration of the atoms that are titrated by selective chemisorption, and ΔH_{ads} the heat of adsorption. In Section IV this condition will be discussed in more detail.

Changes in the work function can also be used as a sensitive probe for differences in composition of the outer layers (*4*). If used with care, it is a valuable tool in the study of surface composition, as is shown in the work on Ni–Cu alloys.

It has been demonstrated (*15, 16*) that in general there is no linear relationship between surface composition and work function Φ. Data on work functions can, however, be useful to draw the following conclusions:

(1) Different Φ's after equal sintering treatments point to different surface compositions.

(2) Equal Φ's mean equal surface compositions.

(3) A change in Φ upon chemisorption is a qualitative measure of the extent of adsorption.

Mössbauer spectroscopy (*17*), too, has been used in combination with chemisorption in order to determine surface enrichment on supported alloys.

The phenomenon of surface enrichment in liquid solutions has been known for a long time. For instance, in a mixture of soap and water, the concentration of the soap will be higher at the surface than in the middle of the liquid.

In a two-component system, the difference Γ_1 between surface and bulk composition of component 1 is given by Gibbs' rule (*18*):

$$(\partial\gamma/\partial n_1)_{T,V,A_s,n_2} = -\Gamma_1(\partial\mu_1/\partial n_1)_{T,V,A_s,n_2},$$

where γ is the surface tension, n_1 and n_2 the concentrations of components 1 and 2, respectively, μ_1 the chemical potential of component 1, and A_s the surface area. For a critical discussion of the concepts of surface and surface tension we refer to the work of Linford (*19*). From Gibbs' rule we read that if the surface tension decreases, Γ_1 will increase with increasing concentration n_1 because

$$(\partial\mu_1/\partial n_1)_{T,V,A_s,n_2} > 0.$$

Assuming an ideal solution and a high temperature, the following equations are valid:

$$\mu_1 = \mu_1{}^0 + RT \ln x_1, \tag{1a}$$

$$\gamma \approx x_1\gamma_1 + x_2\gamma_2, \tag{1b}$$

where x_1 and x_2 are the partial concentrations of components 1 and 2, and γ_1 and γ_2 their surface tensions, respectively. One then finds

$$\Gamma_1 = (x_1/RT)(\gamma_2 - \gamma_1)aN, \tag{2}$$

where a is the average surface area of the components and N Avogadro's number. Equation (2) is the mathematical expression of the intuitive rule that enrichment occurs in that component which has the lower surface tension. A great deal of work has been done to improve on approximations (1). For a review of this work we refer to Defay *et al.* (*20*) and Ono *et al.* (*21*).

Most interesting for the purpose of discussing surface enrichment in alloys is the so-called cel model of a liquid. In this model the liquid is assumed to be a close-packed crystal. The surface is found by cutting the crystal and it is characterized by the number of neighbors of the surface atoms. If one uses only nearest-neighbor interactions and a binary solution, the energy depends on only three parameters: E_{11} and E_{22}, the bond energies of the equal components, and E_{12}, the bond energy between two different components. Another assumption is that the mixture is homogeneous and disordered. This assumption is reasonable for liquids but is not always acceptable for alloys. The solution is considered to be ideal if α is zero. α is defined by:

$$\alpha = E_{12} - \tfrac{1}{2}(E_{11} + E_{22});$$

α is proportional to the heat of formation. If α is fully taken into account in the computation of enthalpy changes, but is neglected in the calculation of the entropy of mixing, the computational model is called a *regular* solution.

The discussion of surface enrichment in alloys presented here is an extension of this model for the alloy. Surface enrichment is dependent on the phase diagrams of the alloys. If $\alpha < 0$, alloy formation is an exothermic process and there is a critical temperature T_C below which the alloy is ordered and above which it is disordered. The standard example is the β-phase of the Cu–Zn alloy, with $T_C = 470°C$. A system of catalytic interest that belongs to this category is the Pt–Sn system (*14*). For a particular stoichiometry it forms ordered compounds (*22*). The critical temperatures for disordering of these compounds are higher than their melting points. If $\alpha > 0$, alloy formation is endothermic. In this case there is a concentration range for which a critical temperature exists below which demixing occurs and above which the alloy forms a solid solution.

Although it has been thought for a long time that the Ni–Cu system does not have a miscibility gap, which was one of the reasons of the popularity of the Ni–Cu system for catalytic studies, closer inspection of the surface composition of these alloys (*4*) has shown that the Ni–Cu system does have a miscibility gap at low temperatures. This is in line with the endothermicity of this alloy system (*23a*, *23b*). Moreover, the clustering observed upon neutron bombardment of a solid Ni–Cu solution shows that the latter is metastable at room temperature (*24*).

The precise temperature T_k at which the miscibility gap closes is still a question of some dispute. The value 322°C measured by the National Physical Laboratory in Teddington (*25*) is often quoted. Disagreements on the surface enrichments can often be traced to

(a) a temperature of annealing high above the miscibility gap (*10b*, *27a*–*27c*),

(b) a selective removal of one of the alloy components by cleaning procedures, such as argon ion sputtering (*10b*, *27a*–*27c*),

(c) chemisorption-induced surface enrichment (*7c*, *15*), if no ultrahigh vacuum is used,

(d) the presence of impurity-stabilized surface complexes (*28*).

Ni–Au (*29*, *30*) and Pt–Au (*31*, *32*) belong to the same category as Ni–Cu.

We will restrict our discussion to the case where effects related to the particle size of the alloy can be neglected, but it should be remarked that the phase diagram of an alloy can change considerably if the particle size decreases. Although the phenomenon of surface enrichment in the Cu–Ni alloy is explained from its phase diagram, surface enrichment in small particles can differ widely from that in large particles.

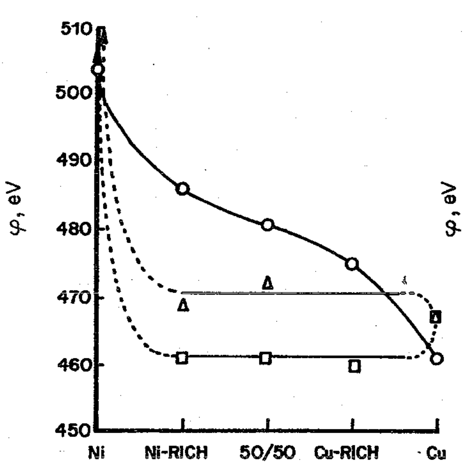
Anderson *et al.* (*33*) found that the surface composition can be a function of particle size in supported Pt–Cu and Rh–Ag alloys. Bartholomew and Boudart (*17*) did not find enrichment in highly dispersed Pt–Fe catalysts.

Hoffman (*34*) argued that if there is a significant difference in atomic size, phase separation will not occur in very small particles. Sinfelt (*35*) showed that metals that do not form bulk alloys form metal clusters when they are finely dispersed on a support.

As long as the temperature of equilibration is higher than the temperature of disordering or demixing, the alloys will form solid solutions both if $\alpha < 0$ and if $\alpha > 0$. Ag–Au (*36*, *37*) and Pd–Ag alloys (*6*) are examples of catalytic interest that form solid solutions.

A. BIPHASIC ALLOYS

We will only briefly discuss the surface enrichment model proposed for the Ni–Cu alloy, since it has been reviewed several times elsewhere (*38*, *39*). The phase diagram of this alloy has a miscibility gap. Figures 1 and 2 show the results of two experiments, which demonstrate composition differences between bulk and surface in Ni–Cu alloys (*4a*, *4b*). The alloys are films deposited under ultrahigh vacuum. After sintering the binary systems all have nearly the same work function, despite the fact that the overall Cu:Ni ratio in the copper-rich system is about four times that of the metal-rich system.



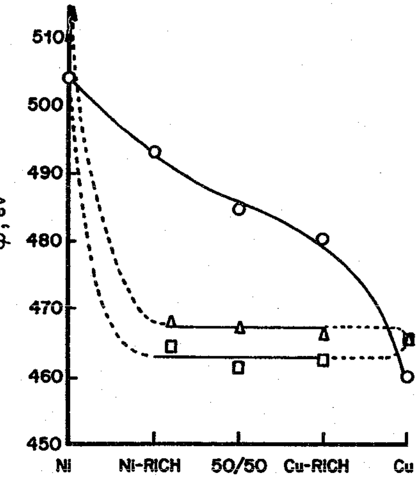


FIG. 1. (*left*). Work functions of films prepared by evaporation of nickel on top of a copper film, followed by sintering and admission of carbon monoxide. ○, Fresh; □, after sintering (200°C); △, after admission of CO (3 × 10^{-8} Torr). From Sachtler and Dorgelo (*4b*).

FIG. 2. (*right*). Work functions of films prepared by evaporation of nickel on top of a copper film, followed by sintering and admission of carbon monoxide. ○, Fresh; □, after sintering (200°C); △, after admission of CO (5 × 10^{-9} Torr). From Sachtler and Dorgelo (*4b*).

X-ray diffraction work showed the existence of two phases. The work function data suggest that the copper-rich alloy in the two-phase system is located at the surface and the nickel-rich phase below the surface. To check this, CO was admitted at a pressure of 10^{-8} Torr. The gas is strongly adsorbed on nickel, but not on copper at such low pressures. The work function of copper was not altered. The binary alloys showed a constant increase in work function between 0.04 and 0.11 eV. Therefore, the adsorbing surface belonged to the copper-rich phase. Chemisorption of H_2 on Ni–Cu films (*40*) leads to essentially the same conclusions. At temperatures below the miscibility gap, several classes of alloy systems characterized by their concentration ranges can be distinguished (*4c*), as illustrated in Fig. 3:

Range 1: $x_2 \leq x \leq 1$. Equilibrium is established after all the nickel has been dissolved. A homogeneous alloy, rich in copper, is formed and the concentration of either metal at the surface is equal to the surface enrichment proper to the concentration of the metal in the segment (see Section II, B).

Range 2: $x_1 < x < x_2$. Equilibrium is established after the copper has been consumed, resulting in a two-phase system. Each crystallite consists of a kernel of almost pure nickel ($x = x_1$), enveloped in a skin of alloy with

RANGE	a_x	NUMBER OF PHASES	PHASE	x IN OUTER PHASE
1	$x_2 < x < 1$	ONE		$x \geqslant x_2$
2	$x_1 < x < {}_2$	TWO		x_2
2a	$x_1 < x < x_1 + \Delta x$	TWO		x_1 AND x_2
3	$0 < x < x_1$	ONE		$x \leqslant x_1$

FIG. 3. Location of phases in Ni–Cu alloys. a_x, atomic fraction of copper in alloy; x_1, x_2, phase concentrations. From Sachtler and Jongepier (*4c*).

$x = x_2$. [This has been called the cherry model (*41*).] Which of the two phases will form the outer envelope is determined by the surface energy of that phase. The final surface composition will be determined by surface enrichments occurring in this outer layer, according to the model we will discuss later for a solid solution. The concentration of either metal in the surface phase will always be the same, irrespective of the overall composition.

Range 2a: $x_1 < x < (x_1 + \Delta x)$. Small patches of alloy with $x = x_2$ cover crystallites of almost pure nickel ($x = x_1$). The alloy skin does not completely surround the nickel crystallites.

Range 3: $0 \leq x \leq x_1$. A homogeneous alloy is formed, containing more than 95% nickel.

Analogous results have been found for Pt–Au (*42*) and Pt–Ru (*43*) films, which also have a miscibility gap. Each time, enrichment takes place because that phase which yields the lower surface energy will form the outer layer. Therefore, enrichment occurs in the component having the lower sublimation energy.

Recently Franken and Ponec (*44*) have published photoelectric work functions of Ni–Al alloy films. Since the phase diagram contains many intermetallic compounds, the surface composition will now be determined by that compound which yields the lower surface energy, in this case the compound having the largest amount of aluminum. Indeed after an initial steep decrease in work function over a limited concentration range, a plateau of constant work function is found.

B. MONOPHASIC ORDERED ALLOYS

An illustrative model of a monophasic ordered system is the Pt_3Sn compound (*45*). This alloy remains ordered up to its melting point at 1365°C. Experimental evidence of surface enrichment in Pt_3Sn stems from AES (*11*) and selective chemisorption (*14*). Both techniques indicate surface enrichment of tin, the element with the lower heat of sublimation. Table I shows that AES yields lower values of surface enrichment than surface titration. This is not surprising because AES scans not only the atoms of the surface layer, but also those of lower-lying layers. However, a quantitative comparison of AES and chemisorption data (*14*) shows that the results can only be matched if enrichment occurs by inversion of the outer layers, i.e., if depletion of tin atoms occurs in layers next to the outer layer enriched in tin atoms.

TABLE I

Comparison of Surface Compositions as Measured by AES and Chemisorption[a]

	Pt atoms ($\times 10^{17}$ m^{-2})		
Alloy	Theory	AES	Chemisorption
Pt_3Sn	49.1	68.3	44.1
PtSn	—	32.6	16.7

[a] From Verbeek and Sachtler (*14*).

The physical cause of this phenomenon (*45*) can be most easily explained by means of a one-dimensional chain with equal concentrations of the elements, as an analog to the three-dimensional alloy. The theoretical results can be extended to a three-dimensional system. They are only applicable to a true alloy if lattice strain effects are negligible.

The surface energy in a one-dimensional chain can be considered to be half of the difference in energy between a closed and an open chain. This energy difference is one bond energy and, hence, the surface energy is half of it. If the chain is built up of equal numbers of A and B atoms, then in the ordered alloy there are only bonds between atoms A and B. Therefore, formation of the open chain gives the same result, regardless of where the closed chain is broken. In the open chain, one end atom is an A atom and the other a B atom. In this model surface enrichment takes place if the end atoms become equal. We will now compute the energy differences between these situations.

Let us consider a row with an equal number of A and B atoms, assuming $\alpha < 0$ and $T < T_C$. The system should then be ordered and can be represented by

$$\text{Model 1a:} \qquad \mathrm{A\ B\ A\ B} \cdots \mathrm{B}$$

Surface enrichment occurs in this model if one of the end atoms, say A, is replaced by an atom B. This can take place in two ways. First, end atom A can interchange with its neighbor B (process 1), giving rise to the situation

$$\text{Model 1b:} \qquad \mathrm{B\ A\ A\ B} \cdots \mathrm{B}$$

The energy cost of this process is

$$\Delta E_1 = \tfrac{1}{2}(E_{AA} - E_{BB}) - \alpha. \tag{3}$$

Second, interchange can occur between an A atom and a B atom from the bulk (process 2), giving rise to the situation

$$\text{Model 1c:} \qquad \mathrm{B\ B\ A\ B\ A\ A} \cdots \mathrm{B}$$

The energy cost of this process is

$$\Delta E_2 = \tfrac{1}{2}(E_{AA} - E_{BB}) - 3\alpha.$$

A peculiarity of one-dimensional models is that they may involve so-called Umklapp processes (*46*) annihilating, for instance, the situation of model 1b. However, as there are more than two neighboring atoms in three dimensions, we assume that in our example such a process will not occur.

If no enrichment takes place, the surface energy is

$$\gamma_0 = -\tfrac{1}{2}E_{AB}.$$

This is, of course, positive because $E_{AB} < 0$. If enrichment occurs, the surface energy becomes

$$\gamma_1 = -\tfrac{1}{2}E_{AB} + \Delta E_1, \tag{4a}$$

or

$$\gamma_2 = -\tfrac{1}{2}E_{AB} + \Delta E_2, \tag{4b}$$

depending on which of the two processes takes place. Hence, there is surface enrichment if $\Delta E < 0$, where ΔE can be either ΔE_1 or ΔE_2. We note that

$$\Delta E_2 - \Delta E_1 = -2\alpha.$$

Since $\alpha < 0$, process 2 requires -2α more energy than process 1. This is the energy necessary to replace two AB bonds by one AA and one BB bond. Therefore, in an ordered system only process 1 will occur. Physically, this means that if surface enrichment takes place, it will be by interchange of atoms in a surface layer with atoms from the first monolayer under it. It then follows from Eq. (4) that surface enrichment takes place if $\Delta E_1 < 0$. This, together with Eq. (3), gives

$$\tfrac{1}{2}(E_{\mathrm{AA}} - E_{\mathrm{BB}}) < \alpha, \tag{5a}$$

or

$$E_{\mathrm{AA}} - 2\alpha < E_{\mathrm{BB}}. \tag{5b}$$

We are dealing with the case where $\alpha < 0$. In consequence, there is a possibility of surface enrichment if the bond strength of a BB pair is smaller than that of an AA pair. Here we touch upon the rule that surface enrichment occurs in the component with the *lower heat of sublimation*. This effect can, however, be counterbalanced if α is highly negative. If Eq. (5) is not satisfied, there will be no surface enrichment, even if $T = 0$.

For another explanation we revert to the closed chain. This chain can only be broken such that the open chain represents the situation depicted in model 1b if two AB pairs are replaced by an AA and a BB pair. Hence, some disordering has to take place in the closed chain. As a result, the energy in the closed chain is raised by -2α. If less energy is required for breaking the closed chain between a BB pair than between an AB pair, we have a decrease of the difference in energy between the surface-enriched system and the one where no surface enrichment took place. The condition under which this will occur is given by Eq. (5).

For the actual Pt_3Sn compound, the surface enrichment of (111) and (100) planes has been computed (*45*) by assuming that it only takes place by inversion between surface atoms and neighboring atoms. Since in this calculation only interaction between nearest neighbors was taken into account, this assumption was justified. However, if interactions are of longer range, the layers that interchange atoms with atoms from the surface can extend deeper into the solid.

The degree of surface enrichment can be derived by subtracting from the change in enthalpy the change in entropy of demixing and by minimizing this expression. This is basically the procedure that has been followed. There is, however, an essential difference between the entropy expression to be used here and that used in the case of a solid solution, to be dealt with below. This is because in the case of an ordered compound, the entropy of the surface layer is not independent of the entropy in the layer next to it. As we have seen, surface enrichment takes place by interchange between nearest neighbors, a restriction that is not valid for solid solutions.

The expression for surface enrichment in the (111) plane is

$$\tfrac{1}{3}x_a/(\tfrac{1}{4} - x_a) = \exp(-\Delta E/kT),$$

where x_a is the change in the percentage composition of those atoms which have the lower concentration, and

$$\Delta E = \tfrac{3}{2}(\epsilon_{\mathrm{Pt-Pt}} - \epsilon_{\mathrm{Sn-Sn}}) - 7\alpha$$

Values for ϵ and α have been derived from the cohesive energies of platinum and tin and the estimated heat of formation of Pt_3Sn. The final result is that in Pt_3Sn at 500°C a complete inversion of the outer layers is predicted, as illustrated in Fig. 4 (*45*). This is in accord with the experimental findings quoted in Table I.

As can be seen in Table II, measurements of the adsorption of D_2 on PtSn and Pt_3Sn (*14*) show that far less D_2 is adsorbed than can be expected on the basis of the adsorption found for CO. Since for the same surface concentration H_2 has been found to adsorb well on Ni–Cu (*40*) and Pt–Au (*31*) alloys, this could be due to the occurrence of a d-band filling effect in PtSn, as will be discussed in Section IV. It is also possible that the large decrease in H_2 adsorption compared with that of CO is related to the very large decrease in the number of platinum atom pairs found on the surface, because of the large heat of formation of Pt_3Sn and PtSn. Indeed, owing to short-range ordering (*45*) it is expected that for equal surface concentrations Ni–Cu and Pt–Sn the number of nickel atom pairs at the surface of the Ni–Cu alloy is much larger than that the number of platinum atom pairs expected at the

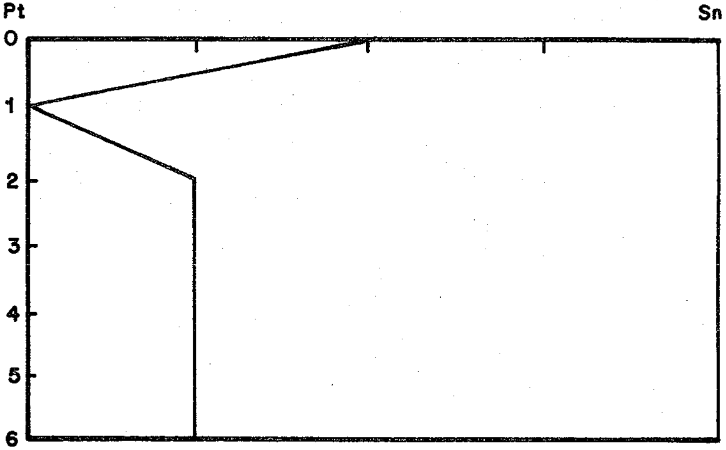


FIG. 4. Composition of (111) layers in Pt_3Sn ($T \ll T_C$). From Van Santen and Sachtler (*45*).

TABLE II

Maximum Coverage on Platinum and Some of Its Alloys by CO, C_2H_4, and D_2

		Number of molecules ($\times 10^{17}$ m^{-2})		
Alloy	Adsorbate	Adsorbed	Desorbed	Nondesorbable
Pt	CO	90.8	57.0	33.8
Pt_3Sn	CO	44.1	28.3	15.8
	C_2H_4[a]	15.7	15.7	—
	D_2	8.1	<8	≥
PtSn	CO	16.7	11.8	4.9
	C_2H_4[a]	3.5	3.5	—
	D_2	1.9	<1.9	≥
$PtSn_2$	CO	<1	<1	—
	C_2H_4	—	—	—
	D_2	—	—	—

[a] In contrast with what was found with platinum itself, no hydrogen, methane, or ethane was produced.

Pt–Sn surface. Even if hydrogen needs more than one transition metal atom in order to dissociate, this would only explain the large decrease in hydrogen adsorption if the possibility of spillover is largely reduced on the alloys. The ligand effect, to be discussed in Section IV, would have to be present for this assumption.

It has also been found (*14*) that ethylene does not dissociate on Pt_3Sn and PtSn, whereas it does on platinum.

It may be of interest to note that as far back as 1934 Rienäcker (*47*) reported that the decomposition of formic acid over Au–Cu alloys is influenced by long-range ordering of the alloys.

C. SOLID SOLUTIONS

A large number of alloys will form a solid solution when heated above a critical temperature if their melting point is not too low.

It has been shown that for a liquid alloy of silver and gold near its melting point, the regular solution model gives surface tensions that correspond well with measured values (*48*). To calculate the surface concentration and profile of a solid alloy, this model has been applied to the Fe–Cu system (*49*), account being taken of enrichment in several outer layers.

Recently, a detailed disscussion has been given (*50*) of surface profiles and their dependence on the heat of formation. If the heat of formation is zero, only enrichment in the surface layer will be found and the surface composition y can be computed from the bulk composition x using (*20*)

$$\frac{y}{1-y} = \frac{x}{1-x} \exp \frac{(\gamma_2 - \gamma_1)a}{kT}. \tag{6}$$

It is of interest that McLean (*51*) employs a similar equation to discuss equilibrium grain boundary segregation. However, he ascribes the driving forces entirely to releases in strain energy. In that case, surface enrichment should depend on the difference in size and compressibility of the atoms in the lattice. In an investigation of Au–Cu alloys it has been shown that these effects become significant (*52*) only if the radii of the atoms differ by 10% or more. Equation (6) has been used by Berglund and Somorjai (*28*) in a study of the liquid Pb–In alloy system. The computed enrichment in lead proved to be too large.

One can improve Eq. (6) by again restricting surface enrichment to the outer layer, but taking into account the heat of formation. One finds (*20, 53*)

$$kT \ln \left\{ \left(\frac{y}{1-y} \right) \left(\frac{x}{1-x} \right)^{-1} \right\} + a_1\gamma_1 - a_2\gamma_2 + \frac{\Omega}{1+m} \left\{ (2l+m)x - 2ly - \frac{m}{2} \right\} = 0, \tag{7}$$

where l is the number of nearest-neighbor bonds per atom parallel to the surface plane, m the number of nearest-neighbor bonds per atom in the bulk outside the plane parallel to the surface plane, and Ω the heat of formation of the alloy. The conditions under which Eq. (7) is valid have been discussed in detail by Van Santen and Boersma (*36*).

Using the broken-bond model of surface enrichment one derives (*36*)

$$kT \ln \left\{ \left(\frac{y}{1-y} \right) \left(\frac{x}{1-x} \right)^{-1} \right\} + \frac{m}{4}(\epsilon_2 - \epsilon_1) + \alpha \left\{ (2l+m)x - 2ly - \frac{m}{2} \right\} = 0. \tag{8}$$

The first term in Eq. (8) is due to the difference in entropy between surface layer and bulk. The decrease in entropy on enrichment is balanced by the gain in enthalpy, determined by the difference between the numbers of bonds broken in the surface and bulk on enrichment. ϵ_2 and ϵ_1 are the bond energies and can be computed from the heat of sublimation. In an extensive review, Overbury *et al.* (*12*) have shown that the surface energy of a metal is proportional to the heat of sublimation of the metals.

From Eq. (7) it follows that enrichment in the component with the lower heat of sublimation increases with decreasing coordination of the surface atoms. Enrichment decreases with temperature. One can correct (*52*) for the delocalization of the electrons in the metal by using for ϵ_i the values derived from the surface energy according to Skapski (*55*) instead of the sublimation energy. The resultant decrease in surface enrichment can become quite important.

Defay and Prigogine (*56*) pointed out that Gibbs' rule, the exact thermodynamic law that determines surface enrichment, can be satisfied only if changes in the two outer layers are taken into account. If one takes into account two layers instead of one, the surface layer composition is given by Eq. (9a) instead of Eq. (8):

$$kT\ln\left\{\left(\frac{y}{1-y}\right)\left(\frac{x}{1-x}\right)^{-1}\right\}+\frac{m}{4}(\epsilon_2-\epsilon_1)+\alpha\left\{2(l+m)x-2ly-\frac{m}{2}-my'\right\}=0. \tag{9a}$$

The concentration y' in the second layer is given by

$$kT\ln\left\{\left(\frac{y'}{1-y'}\right)\left(\frac{x}{1-x}\right)^{-1}\right\}-\alpha\{-(2l+m)x+2ly'+my\}=0. \tag{9b}$$

Equations for more than two layers are easily found from Eqs. (9a) and (9b) (*49, 50*).

It is clearly seen from Eq. (9b) that an increase or decrease of the concentration in the layers next to the surface layers is determined by the sign of α, i.e., it depends on whether alloy formation is endothermic or exothermic. As long as the temperature is high compared with the critical temperature of demixing, the deviations in layers other than the outer layer are found to be small. They will be large if the temperature is near the temperature of demixing or disordering. If alloying is endothermic ($\alpha > 0$) enrichment in the second layer is also found. However, if alloying is an exothermic process ($\alpha < 0$) depletion in the second layer by the component that becomes enriched in the surface layer would occur.

Taking into account changes in concentration of four layers, Williams and Mason (*50*) have shown that if $\alpha > 0$, enrichment in the component with the lower heat of sublimation is enhanced compared to that found for ideal solutions. Near the critical temperature of demixing, the dependence of surface concentration on bulk would be highly reminiscent of this dependence for temperatures lower than the critical temperature.

If $\alpha < 0$, the enrichment is less than computed according to the ideal solution model (*45, 50*). For temperatures not too high compared with the temperature of disordering it has also been found (*50*) that there is depletion in the layer next to the surface. This situation resembles the enrichment by inversion (*45*), as found for the ordered system below the temperature of disordering.

In the hypothetical case that $2|\alpha|$ is larger than the difference $|\epsilon_2 - \epsilon_1|$ according to Eq. (9a), enrichment can occur in both components. Which component will be enriched then depends only on the relative concentration and the sign of α. For instance, if $x > \frac{1}{2}$, $\alpha > 0$, and $\epsilon_1 = \epsilon_2$, the surface concentration in x will decrease, but if $x < \frac{1}{2}$ its surface concentration increases.

However, for the alloys discussed in this paper it is always found that $|\epsilon_2 - \epsilon_1| > 2|\alpha|$. Hence, at equilibrium no reversal in surface enrichment can occur as a function of alloy concentration. Such an inversion, as reported by Takasu and Shimizu (*57*) for Ni–Cu alloys, has to be related to the particular conditions under which their experiment was performed. It is possible that their results were influenced by the presence of oxygen or carbon impurities in their alloy samples, which would cause enrichment in nickel.

There is very little experimental evidence pointing to enrichment in solid solutions. Bouwman *et al.* (*15*) studied the surface composition of Ag–Pd alloys by measuring the changes in work function of the alloys upon adsorption of CO. The result they obtained after brief exposition to CO at room temperature is shown in Fig. 5. Since the dependence on alloy concentration is nonlinear in the silver concentration, enrichment in silver is concluded, this enrichment being a function of the concentration of the alloys. After 16 hours' exposure to a CO atmosphere Bouwman *et al.* found an additional increase in work function, which they ascribed to chemisorption-induced enrichment

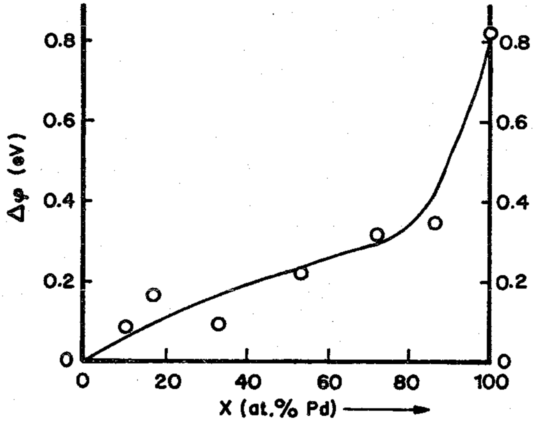


FIG. 5. Change of work functions of Ag–Pd alloy films caused by CO chemisorption as a function of overall composition. From Bouwman *et al.* (*15*).

of the surface with palladium, as this element forms strong bonds with CO molecules.

Chemisorption-induced enrichment has also been invoked by Moss and Thomas (*54, 58*) to explain enrichment with silver of Pd–Ag surfaces in contact with gaseous oxygen.

Christmann and Ertl (*59*) found increases in work function of the Pd–Ag alloys upon CO adsorption similar to those found by Bouwman *et al.* (*15*) after a short time. However, they also performed Auger electron spectroscopy measurements, from which they concluded that no enrichment occurs in equilibrated Pd–Ag alloys.

This seems to be inconsistent with ascribing the increase in work function upon chemisorption to surface enrichment. AES, however, measures a concentration averaged over several outer layers and since enrichment should occur by inversion between the outer layers, enrichments based on AES data are a lower limit to the actual surface composition. Moreover, another point of dispute might be the surface equilibration, which could be an extremely slow process for a low-index plane.

Williams and Boudart (*29*) measured the surface composition of Ni–Au alloys that had been preequilibrated above the miscibility gap and subsequently generated. They found large enrichments in gold. The surface composition measurements fit the surface enrichment calculated according to Eq. (8) rather well. They report enhancements of the nickel concentration by treatment with oxygen.

No enrichment for Ni–Cu and Pd–Ag is reported by Hardy and Linnett (*26*). Their Ni–Cu alloys were equilibrated at temperatures high above the miscibility gap of this system. Neither do Ertl and Küppers (*10a*) report enrichment for Ni–Cu alloys equilibrated at high temperatures, where phase separation is not expected.

At temperatures near the temperature of demixing, the catalytic activity of Ni–Cu alloys has been found to vary little with bulk composition over a large range (*60*). The trend of increasing enrichment on lowering the temperature is in accord with expectations derived from Eq. (6). The conversion of hexane proved to be relatively insensitive to the bulk composition, in contrast to the selectivities, which showed a clear dependence on the bulk composition. This may be due to the dependence of the probability of finding particular clusters of nickel at the surface on the composition of the alloy layers next to the surface layer or on enrichment in nickel due to the gas mixture.

Fain and McDavid (*16*) measured the surface composition of Ag–Au alloys with low-energy Auger electrons. The surface concentration proved to be linear and the work function nonlinear in the bulk concentration. This clearly shows that a deviation from linearity of the work function is in itself no proof of surface enrichment.

Assuming only enrichment in the outer layer, some enrichment in silver has been predicted for Ag–Au alloys on the basis of the regular solution model (*36*). The origin of this discrepancy is not very clear, especially since above the melting point the experimental surface tensions (*48*) agree well with that computed according to the regular solution model.

III. Selectivity of Alloys in Hydrocarbon Reactions

The catalytic activity of group IB metals in hydrocarbon catalysis is known to be greatly inferior to that of the group VIII metals. Following the previous review articles on catalysis by alloys written by Allison and Bond (*61*) and Moss and Whalley (*39*), results have been published showing that alloying a group VIII metal with a group IB metal affects hydrogenolytic reactions much more severely than reactions involving C–H bond rupture or formation (*62*, *63*). It is obvious that these drastic changes in selectivity upon alloying cannot simply be accounted for by a decrease in the number of surface atoms exposed to the reactants, and that changes in geometry of the reactive sites and changes in intrinsic activity of the metal surface atoms have to be considered.

These selectivity changes with respect to destructive and nondestructive reactions will be discussed in this section. Changes in selectivity have also been reported for a different class of alloys, viz., those where both metals are either active or inactive for the studied reaction (*64a–64g*). Since for these alloys a rationalization of the scarce data is hardly possible, we shall not consider them here and confine ourselves to those binary alloys in which one constituent is active and the other is virtually inert with respect to the reaction considered under the conditions of pressure and temperature under which the alloy is tested.

It has been found that some reactions are sensitive to particle size while others are not, and the particle size dependence has tentatively been interpreted as a structure sensitivity (*65a–65c*). It will be shown that there is apparently a relationship between structure-sensitive reactions and reactions that are drastically reduced upon alloying (*66*).

The comparison of the catalytic performances of metals and their alloys is sometimes hampered by the different degree of deactivation by carbonaceous residues (*107*, *67*). Therefore, it seems appropriate to start with a discussion of the exchange reactions of the hydrogen isotopes protium and deuterium on platinum and Pt–Au films (*31*). A comparison of this reaction on platinum and its alloy shows that of the two reaction paths possible on platinum in the temperature region studied, one remains unchanged on the alloy but the other, which prevails on platinum except at very low temperatures, seems to be completely absent on the alloy. Although the $H_2 + D_2$ equilibration reaction does not reveal which fraction of the catalyst surface is active at the low temperatures where the reaction is not diffusion controlled, the number of participating sites is measured when the exchange of, e.g., gaseous protium with adsorbed deuterium is studied. This has been done on platinum and Pt–Au films prepared under ultrahigh vacuum in the temperature range 78–300 K.

Pt–Au alloys are known to have a miscibility gap (*68*). The measured ratio α of adsorbed hydrogen/adsorbed xenon is shown in Fig. 6 as a function of bulk concentration of the equilibrated films. The equality of the surface composition with the overall composition within the miscibility gap supports the cherry model discussed in the previous section. If one assumes that every surface platinum atom adsorbs a hydrogen atom, the surface composition of these films is 15 ± 5% Pt and 85 ± 5% Au, in fair agreement with the composition of the gold-rich phase of this two-phase system. The chemisorptive titration result is confirmed by catalytic data, showing the same activity per unit surface area for all Pt–Au alloys with compositions within the miscibility gap. The films were first saturated with adsorbed deuterium, then cooled to 78 K, and evacuated. The exchange of gaseous protium molecules with this adsorbate was then studied. For platinum films at 78 K a very fast exchange was found to take place over the first 15 sec; in this exchange the R″ reaction (*69*)

$$H_{2\,\mathrm{gas}} + 2D_{\mathrm{ads}} = D_{2\,\mathrm{gas}} + 2H_{\mathrm{ads}}$$

is significant. A similar behavior was found by Eley and Norton (*70*) with nickel. After 15 sec a slower exchange yielding HD and obeying first-order kinetics prevails (*71*). The rate constant and the fraction of adsorbed ex-

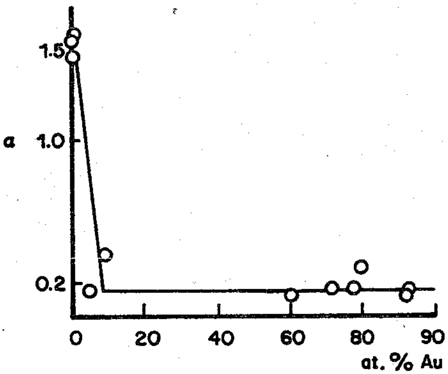


FIG. 6. α as a function of alloy composition. From Kuyers *et al.* (*31*).

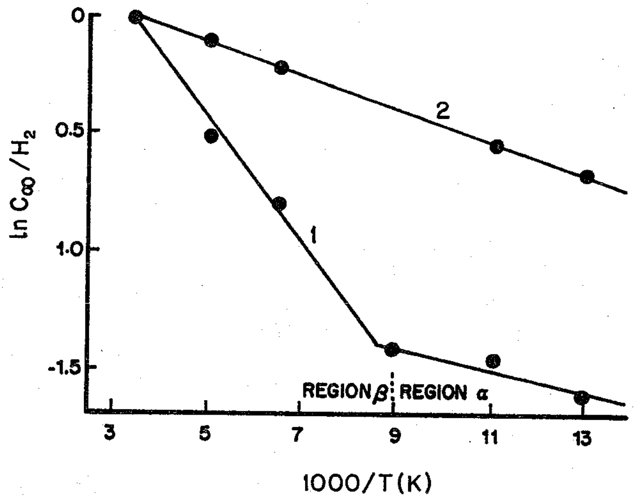


FIG. 7. Arrhenius plot for exchange reaction on platinum (curve 1) and Pt–Au (curve 2). H_2 is the hydrogen absorbing surface, C_∞ is the concentration of HD at $t = t_\infty$. From Kuyers *et al.* (*31*).

changeable deuterium both increase with temperature. The Arrhenius plots of the H/D exchange are shown in Fig. 7 and are linear for the alloys but show a distinct break for platinum at ~110 K. The apparent activation energy and reaction order are identical on the alloys and for the low-temperature reaction on platium. For $T < 110$ K, the apparent activation energy is found to be 0.07 kcal/mole; for $T > 110$ K the value is 0.6 kcal/mole. Breakspere *et al.* (*72*) in a study of hydrogen chemisorption and exchange on polycrystalline platinum wires observed a similar change in reactivity of platinum at $T = 110$ K. Both for platinum and the alloys the pressure dependence of the amount that is ultimately exchanged at a given temperature can be described by $c_\infty = ap_{H_2}^m$. For alloy films m is virtually independent of the temperature, whereas for platinum m decreases from ~0.9 at $T = 78$ K to ~2 at $T > 200$ K.

It is seen that by alloying platinum with gold the fraction of adsorbed deuterium that can ultimately be exchanged at 78 K is increased. This higher reactivity suggests that the heat of adsorption of deuterium and hydrogen is lower on these alloys than on unalloyed platinum. This seems to be a general phenomenon in alloying a group VIII metal with a group IB metal (*7c*, *73*, *74*). It has also been observed in the systems Pd–Ag (*75a*) and Ni–Cu (*75b*) with CO. The sharp break in the Arrhenius plot for platinum occurs around the temperature at which extensive surface migration sets in (*76*).

Three phenomenological criteria can be identified for the exchange reaction on the alloys:

(1) initial occurrence of D_2 in excess over equilibrium values, i.e., an R'' reaction;
(2) apparent activation energy $E \sim 0$;
(3) pressure coefficient $m \sim 1$.

Although the equality of the three experimental criteria might be purely incidental, it appears more probable that the same molecular mechanism that prevails on platinum only at $T < 110$ K remains predominant on Pt–Au alloys up to the temperature where rates become immeasurable with the apparatus used. This reaction appears to include an appreciable contribution of a Bonhoeffer–Farkas exchange (*77*).

These results suggest that on platinum weakly bonded hydrogen atoms form a minority group in the population of adsorbed hydrogen; only at very low temperatures does this minority group, which exchanges with the lower activation energy, dominate the observed kinetics. On the Pt–Au alloys, however, the weakly bonded hydrogen prevails and consequently dominates the overall kinetics over the entire temperature range of the experiments. This conclusion is consistent with an earlier result found by Takeuchi *et al.* (*7c*) on Cu–Ni alloy catalysts. They observed an average decrease in heat of adsorption of hydrogen upon alloying nickel with copper.

It is important to observe the qualitative difference upon alloying between the change in the hydrogen isotope exchange reaction (i.e., H_2 with D_{ads}) and the ortho-para-hydrogen equilibration reactions (both molecules in the gas phase in quantities far in excess over the adsorbed hydrogen atoms). In the classic work of Couper and Eley (*78*) with ortho-para H_2 on wires of Pd–Au alloys, a sudden increase in activation energy was observed at 60% Au; later Couper and Metcalfe (*79*) observed a more gradual increase in activation energy on Pd–Ag alloys.

These results were often cited (*80*) to illustrate the occurrence of d-band filling. Although the detailed dependence on bulk concentration differs for the three alloys under discussion, they share the feature that the heat of adsorption of hydrogen decreases.

The increase in activation energy of the ortho-para equilibration reaction found by Couper and Eley could be due to an increase in activation energy of dissociation. This implies that the rate of adsorption is rate determining, which is only possible if the surface is sparsely covered or if equilibration occurs by a Rideal mechanism (*70*).

A logarithmic decrease in the rate of H_2–D_2 equilibration has been observed by Takasu and Yamashima as a function of nickel surface composition in a Ni–Cu alloy at 273 K. After heating at 800°C for 8 hours *in vacuo* these alloys were cleaned by argon ion bombardment to remove impurities from the uppermost surface layers. The alloy composition of the clean surface was determined by means of AES. The catalytic activity was observed to decrease appreciably upon annealing at 300°C, which is to be ascribed to enrichment in copper. The same authors (*81*) also measured the work functions of the same alloys before annealing and found a decrease linear in the copper surface concentration.

These results clearly illustrate the dependence of H_2–D_2 equilibration and work function on surface composition. The observation of a surface composition greatly dependent on the bulk concentration is only apparently in conflict with the cherry model discussed in Section II, since the surfaces studied by Takasu and Yamashima had not been equilibrated and their composition was entirely determined by the way in which they had been prepared.

The exchange reaction of methane with deuterium has been found to show a decrease in specific activity upon alloying of palladium with gold (*82*), reflecting the decrease in number of reactive surface metal atoms upon alloying.

The hydrogenations of acetylene over Pd–Au (*83*) and Ni–Cu (*64d*), and of methylacetylene (*84a*) and 2-butyne over Ni–Cu (*84b*) and Pd–Au (*85*) have also been studied. The selectivity for consecutive hydrogenation was found to be little influenced by alloying (*64a*). Rushford and Whan (*85*) did not find any correlation of their data with d-band filling. They postulated that catalysis in their system is associated with palladium centers in the alloys, with gold acting merely as an almost inert diluent. They found a linear correlation between the frequency factor for hydrogenation and the probability of finding clusters of four atoms. So their work strongly suggests that the ensemble effect, to be discussed in Section IV, determined changes in selectivity upon alloying.

Whereas in one of the first papers on the hydrogenation of ethylene over nickel and Ni–Cu alloys (*86*) the reaction had been reported to be relatively insensitive to alloying up to a copper concentration of 80%, 15 years later Best and Russell (*87*) reported large increases in activity. Some of the contradictory evidence has been clarified by Takeuchi *et al.* (*88*), whose discussion has been extended recently by Takusu and Himiru (*89*), who showed that the catalytic activity may be very sensitive to the ways of preparing the alloys.

Takeuchi *et al.* prepared films by the evaporation of copper and nickel metals or their alloys on a substrate cooled by liquid oxygen. Prior to use, the film was treated in vacuum at 30 or 250°C. The catalytic activity was tested by the hydrogenation reaction of ethylene. Their result is illustrated in Fig. 8. Essentially similar results have been reported by Völter and Alsdorf

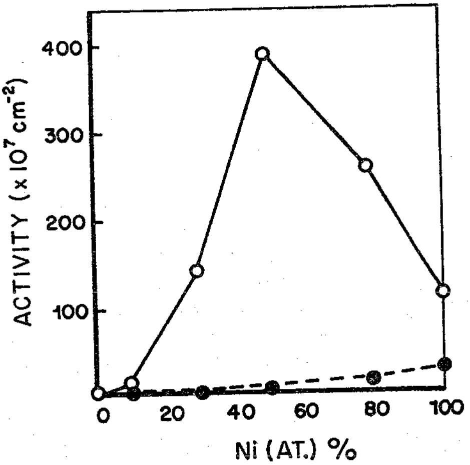


FIG. 8. Catalytic activities of hydrogenation reaction of ethylene at 30°C on films treated at 30 and 250°C. ○, Films treated at 30°C; ●, films treated at 250°C. From Takeuchi *et al.* (*88*).

(*90*). It is seen that the film evaporated on the low-temperature substrate shows a strong dependence on composition of the Ni–Cu concentration and a large increase in activity compared with pure nickel. However, the films treated at 250°C show a gradual decrease upon alloying. The treatment at 250°C apparently equilibrates the alloy, and the behavior can be understood on the basis of the cherry model disscussed in the previous section.

A similar behavior independent of bulk composition has been found by Campbell and Emmett (*91*) over Ni–Au films. These alloys also have a miscibility gap. Takasu *et al.* suggest that the large increase in activity of the low-temperature films is due to an abundance of lattice imperfections. The absence of impurities can also be a reason, because this has been shown to increase activities (*92a–92c*). Furthermore, in some previous experiments (*87*, *91*, *93a*, *93b*) large amounts of hydrogen may have been adsorbed by the catalysts, because they were cooled in the presence of hydrogen. This might cause an enrichment of the surface with nickel (*94*).

Another possibility that explains increases in activity upon alloying is a reduction in the degree of poisoning. If this were true in this case, however, it is not obvious why the equilibrated alloys do not also show strong enhancements.

Recently (*64a*, *67*) new light has been shed on the problem of poisoning. Van Barneveld and Ponec (*67*) studied the hydrogenation of benzene on nickel catalysts with 5% Cu and 10% Cu, where the copper is fully soluble in nickel at all temperatures. At low temperatures (20–150°C) the alloys were less active (per meter squared total surface area) than nickel, whereas at temperatures at which cracking also occurs (above 220°C) the alloys are more active than nickel. Apparently at high temperatures, alloying results in a decrease in self-poisoning due to coke formation, whereas at low temperatures no such effect occurs.

The hydrogenolysis of ethane has been demonstrated to be structure sensitive (*95a, 95b*). Figure 9 shows that alloying of nickel with 10% Cu decreases the specific activity for the hydrogenolysis of ethane by a factor of 1000 (*63*). Use was made of Ni–Cu alloys prepared by coprecipitation of the metals as carbonates, followed by calcination and reduction of the coprecipitate. The strong initial decrease in ethane hydrogenolysis could not be explained by the decrease in number of active sites as measured by the volume of strongly adsorbed H_2. One of the explanations given is the extensive dissociation of carbon–hydrogen bonds, leading to a highly unsaturated dicarbon surface residue as the reaction intermediate (*96*). It seems likely

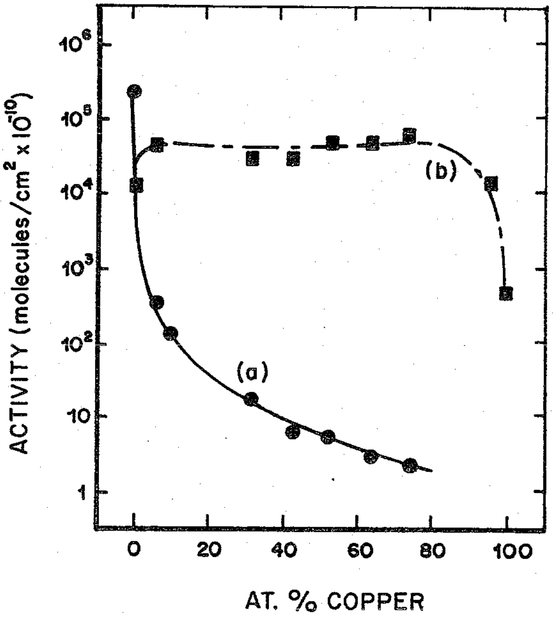


FIG. 9. Specific activities of Ni–Cu alloy catalysts for hydrogenolysis of (a) ethane to methane and (b) dehydrogenation of cyclohexane to benzene at 316°C. ●, Ethane hydrogenolysis at ethane and hydrogen partial pressures of 0.030 and 0.20 atm, respectively; ■, cyclohexane dehydrogenation at cyclohexane and hydrogen pressures of 0.17 and 0.83 atm, respectively. From Sinfelt *et al.* (*63*).

that such an intermediate would form a multiple bond with the surface metal atoms. The amount of intermediate is probably very sensitive to restrictions in the number of multiple nickel atoms available. This explanation is supported by the fact that a sharp decrease in preexponential factor is found, while the activation energy remains relatively constant.

Figure 9 also shows the activity of cyclohexane dehydrogenation. Remarkable is the dependence on copper concentration. Initially, a small enhancement in activity is found and then a sharp drop in activity when the copper concentration becomes 80%. This increase in specific activity could be due to a low steady-state concentration of carbonaceous residues on the surface of Ni–Cu alloys as compared to nickel. Except for the small initial enhancement, a similar behavior had been reported in 1939 by Rienäcker and Bommel (*86*) for the hydrogenation of ethylene. The sharp decrease at 80% Cu reported by these authors and by Sinfelt for the cyclohexane dehydrogenation coincides with the boundary of the miscibility gap of the Ni–Cu system. Sinfelt, *et al.* (*63a*) ascribe the initial enhancement to a decrease in heat of adsorption of benzene. However, results have been reported that contradict the hypothesis that desorption of benzene is the rate-limiting step. According to Paal and Tétényi (*97*) a decrease in H_2 concentration on the surface increases the yield of benzene. The rapid decline at 80% Cu has to be ascribed to a change in the rate-limiting step involving more than one nickel atom. Sinfelt (*98*) reports similar results for alloy clusters of Ru–Cu and Os–Cu on a support.

The study of the H_2–D_2 exchange with propane (*107*) over nickel and Ni–Cu alloys has led to the conclusion that the enhanced activity due to alloying was actually a decrease in self-poisoning. At −40°C the addition of copper to nickel resulted in a decrease in the activity from about 10^{13} to 10^{12} moles/cm^2 sec for alloys containing up to 40% copper. The rate on copper was less than 10^{10} moles/cm^2 sec, and distributions obtained from the alloy experiment were indistinguishable from those observed on nickel at −40°C. The situation was entirely different at 50°C: at this temperature the nickel films were rapidly inactivated by self-poisoning, so that hardly any exchange was found to take place, whereas the rate on copper was higher than that on nickel. The initial rate at 50°C proved to be higher for some alloys than for copper and nickel. This suggests that maxima and increases in the activity pattern as discussed earlier (e.g., cyclohexane dehydrogenation) can be caused by self-poisoning, i.e., are expected to be absent if no self-poisoning occurs. The observation was made that the maximum in the "activity pattern" was accompanied by a minimum in multiplicity. The results at 50°C seem to indicate that alloying with copper decreases the tendency of nickel to self-poisoning and multiple exchange.

The cyclopropane molecule offers a possibility to study the changes in selectivity upon alloying with respect to two parallel reactions (*99a–99*d).

$$\text{cyclo-}C_3H_6 + H_2 \rightarrow C_3H_8 \tag{I}$$

$$\text{cyclo-}C_3H_6 + 2H_2 \rightarrow C_2H_6 + CH_4 \tag{II}$$

At higher temperatures cyclopropane decomposes to methane by the overall reaction

$$\text{cyclo-}C_3H_6 + 3H_2 \rightarrow 3CH_4 \tag{III}$$

Whereas the hydrogenolysis of hexane and other alkanes (*60, 62, 100, 101*) can be observed only at temperatures slightly above the temperatures closing the miscibility gap in Ni–Cu alloys, reaction (II) occurs at substantially lower temperature, where separated phases (if present) are thermodynamically stable.

Reactions (I) and (II) were studied (*102*) on alloys prepared by thermal decomposition (at 400°C) in air of coprecipitated Ni–Cu carbonates, followed by reduction with hydrogen (at 300 to 400°C).

The results, presented in Fig. 10, are very similar to those already discussed for ethylene and ethane. Reaction (I), the hydrogenation of cyclopropane, has been shown earlier to be structure insensitive (*103a, 103b*). The activity pattern of this reaction is reminiscent of cyclohexane dehydrogenation (*63*). Initially, a small increase in activity is found, followed at 80% Cu by a rapid decline. These results show that reaction (II) is of the hydrogenolysis type and that reaction (I) is hydrogenation of an unsaturated bond.

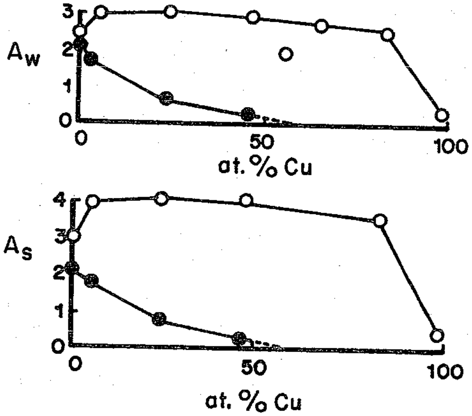


FIG. 10. Activity parameters A_w and A_s as a function of alloy composition (at. % Cu). Upper curves A_w and A_s are for cyclopropane at 90°C; lower curves A_w and A_s are for propane at 320°C. $A_w = \log(\alpha/w)$; $A_s = \log(\alpha/sw)$; α is conversion, s specific surface area of catalyst, w weight of catalyst. From Beelen *et al.* (*102*).

The feature that a reaction needing multiple bonding is more influenced by alloying than a reaction needing less bonds with the surface atoms has also been found in a study of the hydrogenation of 1,3-butadiene on Ni–Cu alloys (*104*). The rate of hydrogenation as a function of alloy composition proved to be two orders of magnitude lower than that for pure nickel. The 1-butene/2-butene ratio tended to increase with increasing copper content. This agrees well with the structure sensitivity of these reactions reported by Oliver and Wells (*105*). Earlier (*106*) it had been shown that the product distribution of 1,3-butadiene hydrogenated over palladium and Pd–Au alloys is relatively insensitive to alloying. This is considered proof of the fact that in this case hydrogenation occurs via a π-allylic complex.

In a series of papers, studies have been reported of the exchange of deuterium in, and the deuteration of, benzene (*101*, *40*), the exchange of deuterium in cyclopentane (*62*), and the reactivity of hexane (*60*) and methylcyclopentane (*100*) over nickel and Ni–Cu alloys.

The constancy of the activity for benzene hydrogenation over a wide range of overall concentrations of copper and nickel was shown to be indeed due to a surface phase of constant concentration, in accord with the cherry model.

Initial rates on films were also measured. After an initial drop, these rates remained constant as a function of alloy composition, as illustrated in Fig. 11.

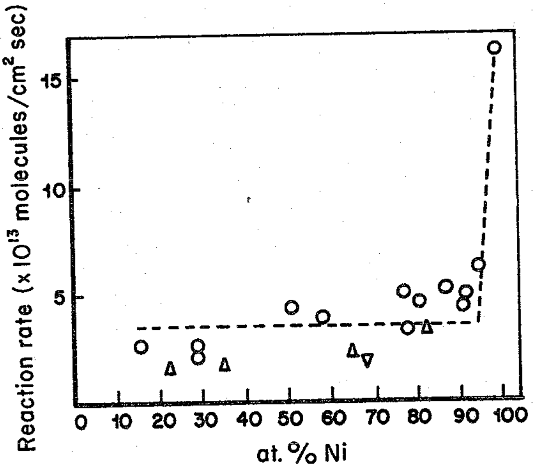


FIG. 11. Activity pattern for benzene hydrogenation at 150°C. p_{H_2} = 322 Torr; p_{benz} = 5.8 Torr. ○, Nickel deposited on top of copper, films sintered at 200°C for 18 to 20 hours; △, copper deposited on top of nickel, films sintered at 200°C for 18 to 20 hours; ▽, copper deposited on top of nickel, films sintered at 300°C for 14 hours. From van der Plank and Sachtler (*101*).

The activation energy is roughly twice as large for the alloys as for pure nickel. Lyubarski (*108*) was the first to show that the specific activity of benzene hydrogenation decreases upon alloying of nickel with copper. He found, however, an initial rise in activity on plotting the activity as a function of weight of the catalysts.

The H/D exchange between D_2 and benzene was found to have a rate exceeding that of benzene deuteration by several orders of magnitude. This result shows that exchange and hydrogenation reactions follow different reaction paths. The exchange parameters were also found to be independent of the overall alloy composition.

Cadenhead and Masse (*109*) report similar results for the benzene hydrogenation. They stress the importance of measuring specific activities because plots of the surface areas versus alloy composition show a maximum (*108*). For Pd–Cu and Pd–Au samples it is concluded (*109*) that the catalytic behavior found indicates the formation of ternary transition metal–group IB metal–hydrogen systems.

Cinneide and Clarke (*110*) have studied the activity of Pd–Au films for the deuteration and exchange of benzene and the hydrogenation of *p*-xylene. The authors report that the activity for the exchange reaction between benzene and deuterium persists to the palladium-lean compositions, which is in agreement with results obtained by Honex *et al.* (*111*) in a study of the exchange of toluene over alloys of the same kind. The rates are much reduced (by 10^2 to 10^3) compared to those found with palladium-rich films.

The hydrogenation of benzene over supported Pd–Au catalysts initially exhibits a rise in activity as gold is added to the catalyst, but further addition brings about a pronounced activity decrease (*112*). The same authors find a marked increase in catalytic hydrogenation activity for Pd–Au alloy microspheres containing up to 60 at.% gold as compared with that measured for palladium.

Cyclopentane–deuterium exchange has been followed on nickel and some Ni–Cu alloy films in the temperature range 200–430 K (*62*). Over the entire ranges, the reaction is accompanied by self-poisoning, and on Ni at 340 to 430 K also by hydrogenolysis. The catalytic effect of alloying has been found to be most pronounced on hydrogenolysis and self-poisoning, but is rather small with respect to multiple exchange.

In having a low activity with respect to C–C bond fission and in promoting isomerization, the Ni–Cu alloys are more reminiscent of platinum than nickel. The explanation given is similar to that proposed for the suppression of ethane hydrogenolysis. Hydrogenolysis requires multicenter adsorption and is therefore more sensitive to alloying than reactions needing fewer centers. This was examined in detail by Ponec *et al.* (*60*) in a study of the

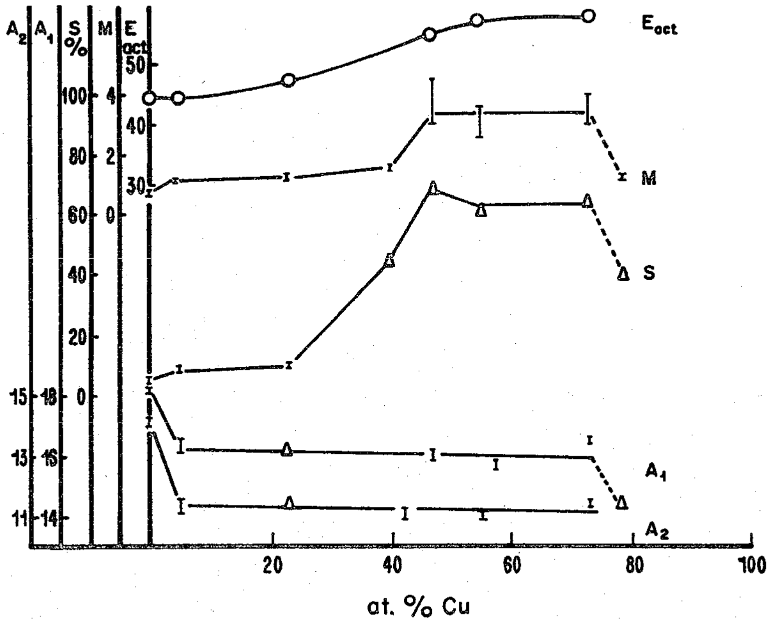


FIG. 12. Reaction parameters of *n*-hexane conversion by nickel and Ni–Cu alloys. $A_1 = \log r_w$ at 330°C, $A_2 = \log r_s$ at 330°C, activation energy of the overall reaction E_{act}, fission parameter M, selectivity parameter S; all as a function of alloy composition (in at. % Cu). r_s is rate per cm^2, r_w rate per gram catalyst. From Ponec and Sachtler (*14*).

reactivity by *n*-hexane of nickel and Ni–Cu powders. The results are presented in Fig. 12. It is worth noting that:

(1) Between 0 and 23% Cu the activity parameters A_1 and A_2 decrease sharply, and this decrease is accompanied by an increase of the selectivity parameter S to values previously found for extremely thin nickel films (*113*); S is the selectivity in producing other C$_6$-hydrocarbons:

$$S = 600 \sum_{j, j \neq k} C_6^{(j)} \Big/ \sum_{j, j \neq k} \sum_{i=1}^{6} i C_i^{(j)},$$

where the subscript k denotes the hydrocarbon in the feed.

(2) A much more pronounced increase in S and the fission parameter M is observed at 40 to 73% Cu, where S reaches values common for platinum; in this region the A parameters change only little. The fission parameter M is defined as

$$M = \sum_{j} \sum_{i=2}^{5} (6 - i) C_i^{(j)} \Big/ (C_1)_{\text{meas}}$$

The temperatures adopted during catalyst preparation and subsequent reaction were chosen above the temperatures closing the miscibility gap of Ni–Cu alloys (*25*).

These results confirm the different influences of alloying upon destructive and nondestructive reactions. The reaction rate per surface nickel atom remains essentially the same on alloying with copper.

In alloys with 0–23% Cu the activation energy of the total conversion of *n*-hexane is only marginally influenced and the observed effects are consequently connected with the preexponential factors. Since the selectivity of nickel diluted with copper is near the value found by Anderson *et al.* (*113*) for highly dispersed films, considering a common cause is suggested (*60*). Anderson assumes that with a large fraction of surface atoms in very small crystals the "isolated" corner atoms favor the formation of carbocyclic intermediates of isomerization, whereas hydrogenolysis requires two or more adjacent platinum atoms in a crystal plane.

An effect other than this ensemble effect has to be invoked in order to explain the increase in M and S for the alloys with 40–70% Cu. Although the origin of this apparent energetic effect is not clear, the effect could be due to differences in size of the nickel clusters in the surface caused by differences in bulk concentration of the alloy, or to adsorption-induced enrichments of nickel in the surface. The latter can also depend on the bulk concentration of the alloys.

The temperature at which the reactivity of *n*-hexane has been studied is very near the temperature of demixing of the Ni–Cu alloys. Therefore, the surface phase will be reminiscent of the phase expected for lower temperatures, except that the transition to the solid solution has already started, which can explain the slight dependence on bulk composition.

Reman *et al.* (*114*) found essentially the same change in product distribution with alloying, when investigating the conversion of *n*-hexane on alloys.

Methylcyclopentane (MCP) (*100*) shows much stronger self-poisoning than *n*-hexane or cyclopentane. The activity and the selectivity pattern is essentially the same as that already discussed for the other reactants. Alloying nickel films with copper lowers the activity for the overall conversion of MCP and leads to a higher selectivity for C_6-hydrocarbons (slowing down hydrogenolytic cracking reactions) and to a higher activation energy. Simultaneously, the 2-methyl/3-methylpentane ratio and the contribution of random splitting show an increase. This pattern resembles that of platinum.

It has been reported (*115*) that *n*-heptane and *n*-octane dehydrocyclize upon alloying of palladium with silver. The dehydrocyclization products are to a considerable degree dealkylated.

The most thoroughly studied alloy system is Ni–Cu, because of the original suggestion by Dowden (*116a*) and Reynolds (*116b*) that d-band vacancies are essential for alloys to be active as catalysts and the ignorance of the existence of a miscibility gap in these alloys. From the present discussion it is seen that surface enrichment dominates the catalytic behavior of Ni–Cu alloys. Pd–Ag and Pd–Au alloys have also been the subject of many catalytic studies (*61*). The interpretation of the experiments is, however, hampered by the dissolution of H_2 in palladium. d-Band filling (*78*, *80*) has been thought to be responsible for the characteristic catalytic behavior of these alloys.

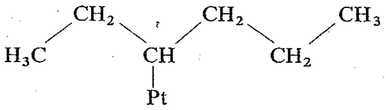
In the next section experimental and theoretical approaches will be discussed to settle the dispute about the relevance of the electronic factor (*117*) to catalysis.

IV. Ensemble and Ligand Effects

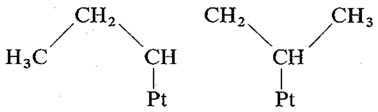
Crucial to the understanding of the selectivity patterns discussed in the previous section is the concept of an ensemble of surface metal atoms.

Inasmuch as parallel catalytic reactions differ in the number of adjacent surface atoms of the active metal that are required for forming the respective chemisorption complexes, it is clear that the reaction requiring the largest ensemble of these atoms will be the most sensitive to alloying with a second metal unable to form such chemisorption bonds (*62*, *63*, *85*) as illustrated by the following considerations.

In every catalytic reaction involving a hydrocarbon molecule, an important intermediate is the monoadsorbed complex, e.g., for *n*-hexane on a surface containing platinum atoms, the complex

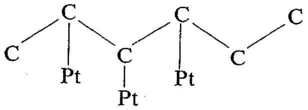


will be formed. This intermediate can either be desorbed or undergo a chemical reaction, e.g., a dehydrogenation or a H/D exchange. A second possibility is that it becomes diadsorbed, e.g.,



In practice this will occur at high temperature, resulting in a complex that according to Anderson (*118*) is a necessary prerequisite for skeletal isomerization.

Another possibility is to become triadsorbed, e.g.,

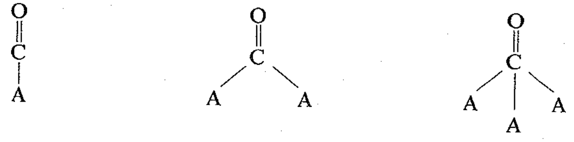


From this state, nondestructive desorption might be difficult, so that hydrogenolysis (metal cracking) might become the preferred way to regenerate the free sites of the catalyst.

From this example it is clear that the selectivity for (a) dehydrogenation, (b) isomerization, and (c) cracking is likely to be related to the relative concentrations of mono-, di-, and tri-adsorbed complexes, etc. More generally, the selectivity of a catalytic reaction will depend on the relative chance for a molecule adsorbed on *n*-surface atoms either to desorb or become adsorbed on $(n + 1)$ surface atoms. This idea easily permits us to understand that dilution of an element A, capable of forming chemisorption bonds with a given molecule, with an inert element B will lower the ratio of poly- to monoadsorbed molecules and have an effect on catalytic selectivity. We will call this concept the *primary ensemble effect*.

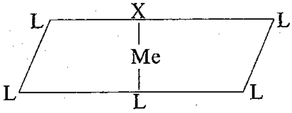
Simple examples where this geometric effect might be operating are the oxidation of ethylene to ethylene oxide and of cumene to cumene hydroperoxide (*119*) on Ag–Au alloys. In these processes the monoadsorbed O_2^- ion is decisive for the selectivity (*120*). While on silver these ions can further dissociate to form O^{2-} ions, this dissociation is less important on Ag–Au surfaces with, as a result, an enhanced selectivity. However, for possible reasons to reject the ensemble effect as the decisive cause of the selectivity pattern of these examples, the reader is referred to Van Santen and Boersma (*36*).

The geometry of the ensembles of A atoms in the surface can, however, influence the adsorption complexes not only by changing the number of single bonds to different atoms of the adsorbed molecule, as illustrated above: a second type of ensemble effect can be visualized for any given atom of the adsorbate. Taking the adsorption complexes of CO on a transition metal as an example, we can discern "linear," "bridged," and "multisite" complexes:



Again, it is predictable that with increasing dilution of the A atoms the concentration of the multisite complexes will decrease more strongly than that of the single-site complex and, again, the different complexes can be defined by the ensembles A_n they require. Dilution of the surface with an inert element will thus change not only the probability of formation of adsorbates in which more than one atom is connected with the surface, but also the average coordination of the adsorbate atoms with surface atoms. In this review we shall call the latter effect of alloying the *secondary ensemble effect*. It is a possible cause of changes in heat of chemisorption.

Alloying A with B involves, however, not only changes in geometry, i.e., the concentration of the A_n ensembles in the surface. Even if a well-defined bond of an atom X in the adsorbed molecule and, e.g., one A atom of the surface is considered, the X–A bond strength may be expected to depend on the nature of the electronic interaction of the A atom with its neighbors in and below the surface; it is therefore changed if these neighbors are changed by alloying. This effect of alloying on the adsorption is called the *ligand effect*. This term has been chosen (*41*) because in complex chemistry it is a well-established fact that the strength of the bond between a metal atom Me and another atom X depends on all other ligands L of the same metal atom:



Replacing some of the ligands L by other ligands L′ will influence the strength of the Me–X bond and, e.g., the position of the IR band caused by the Me–X vibration. In the same manner, it is of great importance for the adsorption bond between, e.g., an organic molecule and a platinum atom whether the atoms adjacent to that atom are also platinum atoms, as in the case of a platinum crystal, or, e.g., tin atoms, as in the surface of a Pt–Sn alloy. Figure 13 shows temperature-programmed desorption spectra for the desorption of chemisorbed CO from two different Pt–Sn alloys, Pt_3Sn and PtSn (*14*). The spectra clearly indicate that a higher temperature is required to remove CO from Pt_3Sn than from PtSn. As the adsorption of CO is known to be non-activated for either alloy, it is safe to conclude that the heat of adsorption for CO is larger on Pt_3Sn than on PtSn. Changes in specific catalytic activity (i.e., per A atom exposed) and changes in selectivity due to alloying can thus be caused by the chemical interaction of the alloy partners, resulting in, e.g., an increase in the number of d-electrons on the atoms active in the catalytic reaction considered.

It is clear that the ensemble effects and the ligand effect will often occur together and concomitantly contribute to the changes in the nature and the concentration of the adsorbed complexes caused by alloying, and, hence, to the changes in catalytic performance. If the ligand effect and the secondary ensemble effect were truly independent of each other, the change in bond strength would be the product of the changes caused by each effect separately.

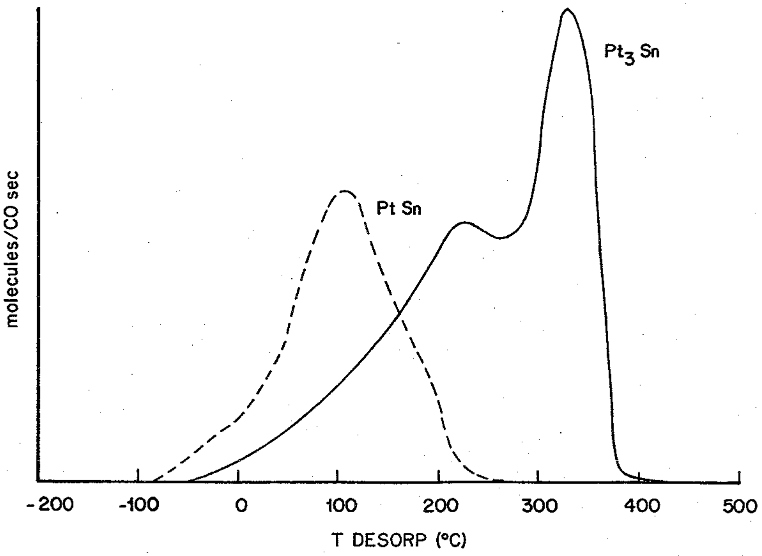


FIG. 13. Temperature-programmed desorption spectra for CO on two Pt–Sn alloys. Only gas desorbed below 500°C is recorded. Adsorption temperature, 28°C; cooling temperature, −78°C; heating rate, 145°C/min. From Verbeek and Sachtler (*14*).

It would be of considerable interest to demonstrate the importance of the ligand effect in a catalytic reaction. Unfortunately, the experimental conditions have to be rather severe in order to ensure that no artifacts are introduced by changes in impurity level or poisoning. The ideal experiment to establish a pure ligand effect unequivocally would involve a comparison of alloys having the same group VIII metal but containing second metals of different electronegativity, which are inactive to the gases used in the experiment. If such alloys with identical surface composition and structure show a different catalytic behavior under equal conditions these differences would characterize a pure ligand effect.

A. THE LIGAND EFFECT

Whereas in the older literature (*78*, *80*, *116*) no clear distinction was made between surface properties and bulk properties, it is now generally accepted that the catalytic properties of the surface atoms are primarily determined by their immediate environment (*3*). The term "ligand effect" (*41*) stresses that the influence on an adsorbing atom by its neighbors in and below the surface decreases steeply with their distance, the greatest contribution coming from the direct neighbors of the metal atom considered.

Our view that in chemisorption and catalysis one has to look at the properties of the individual atoms at the surface rather than at parameters of the continuum (*3*) has received decisive support from recent advances in solid state physics.

Experimental results from ultraviolet photoelectron spectroscopy (*121a–121d*, *122*) and from ESCA (*123*) clearly show that the shape of the d-bands of metals of group VIII and group IB is greatly changed upon alloying. This demonstrates that the rigid-band model (*124*) or the virtual-crystal approximation (*125*), which assumes that band shapes do not alter upon alloying, is not applicable to the alloys of interest here. This necessitates a thorough revision of all those conclusions which had been based in the past on the assumption that the rigid-band approximation is a permissible basis for discussing catalysis by alloys (*80*). The other extreme is the minimum polarity model (*126*), which has been applied successfully to the Ni–Cu alloy. According to this approximation the electronic configuration of each component in its pure state is carried over into the alloy. In other words, the individual properties of the atoms are retained in the alloy. This is in accord with the point of view taken in van der Plank and Sachtler (*101*, *40*). The ensemble effect interprets the catalytic properties of the alloy solely in terms of the minimum polarity model.

If the active metal becomes highly diluted the minimum polarity model leads to the virtual bound-state model (*127*, *128*, *129*). This model has also been applied to highly diluted Ni–Cu alloys (*121a*). The nickel d-states are then found to form not a common band with the copper d-states but narrow virtual levels between the copper d-states and the Fermi level. The levels are in resonance with the s,p-band of the metal.

The coherent potential approximation (*1*, *2*) is a consistent theoretical frame, which unifies the different alloy models. In order to account for changes in the electronic nature of the atoms, the coherent potential approximation for a disordered alloy appears at present to be the best. It has been applied to single- and two-band systems (*130a–130c*).

Two parameters of interest on a site active in chemisorption and thus in catalysis are (1) local energy density of states, and (2) local electron density of states. The energy density of states determines among other things the energies involved in the transfer of an electron between adsorbate and substrate; the electron density in a particular orbital then contributes to the probability of transfers back and forth between substrate and metal.

Theoretically and experimentally, large decreases in the d-band widths have been observed. For instance, a decrease by a factor of 5 in the d-band width of Pd–Ag has been reported (*121b*, *122*). One also expects changes in the relative positions of the bands, but these are found to be small, at least in the Ni–Cu and Ag–Pd alloys (*122*).

This implies that the interaction of the d-electrons with their electronic environment is in general found to decrease. In highly diluted alloys the interaction with other d-electrons is nearly absent and broadening of the levels is then caused by interaction with the s,p-band. It should be noted that according to modern metal theory (*131*) in the pure metals this interaction is very small compared with d–d interactions. In contrast to earlier ideas (*132a*, *132b*) hybridization is only of secondary importance in these metals. The valence electrons are considered to fill a narrow d-band overlapped by a broad s,p-band, which weakly interact with each other. The percentage of d-character of the metallic bond, although giving some correlation with catalytic activity (*63*, *132a*, *132b*), is not based on a correct theory of metals. Therefore, we will use a theory of chemisorption based on modern concepts of transition metals.

Before the advent of ultraviolet photoelectron spectroscopy and ESCA, experimental evidence on the energy density was mainly available from static magnetic susceptibility and specific heat measurements (*134*). These provide information on the density of states at the Fermi level and it is impossible to base any conclusions on such experimental information with regard to the shapes of the d-bands in the alloys. It is currently believed that there is very little transfer of d-electrons between the atoms. If an increase in the number of d-electrons on a particular atom does occur, it is due to transfer of electrons from the s,p-band to the lower d-band. This is, of course, related to the difference in electronegativity of the alloying components (*135a*, *135b*).

There is very little conclusive evidence regarding d-band filling. According to Seib and Spicer (*121a*) no appreciable electron transfer takes place in Ni–Cu alloys. Gelatt and Ehrenreich (*130b*) estimate a transfer from copper to nickel that is less than 0.1 electron per atom for dilute nickel in copper. At present there are no experimental techniques available to measure electron transfers with such precision. Norris and Myers (*121b*) propose that the number of d-band holes of palladium in Pd–Ag alloys is zero at a silver concentration of 60%. However, if the concentration of silver increases, the number of d-band holes in palladium increases again; at very high dilutions it is similar to that in pure palladium.

Hardy and Linnett (*26*) have compared the recombination of hydrogen atoms on Pd–Ag and Ni–Cu alloys under conditions where the surface composition is nearly equal to that of the bulk. In both cases they observe a maximum in activity, as shown in Fig. 14. The maximum is at 40% Ag in the Ag–Pd alloy, but at 60% Cu in the Ni–Cu alloy. Since the final decrease in activity is probably the result of a decrease in rate of adsorption, the rapid decline in the Pd–Ag alloys compared with that in the Ni–Cu alloys could be due to the loss of holes at 60% Ag. Another contribution to the lower rate can be the solution of hydrogen or deuterium in the Pd–Ag alloy.

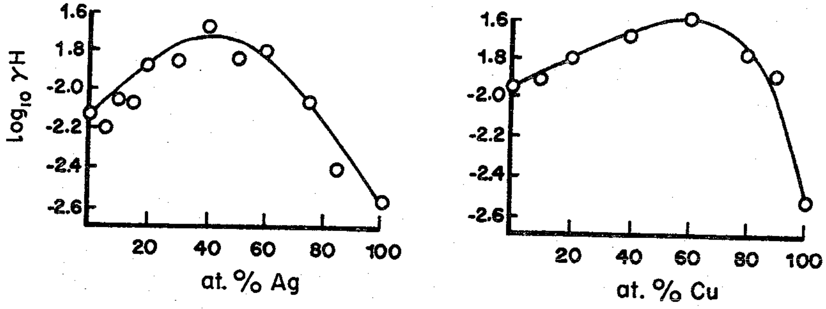


FIG. 14. Dependence of $\log_{10} \gamma_H$ on bulk composition for Pd–Ag and Ni–Cu alloys. γ_H is the recombination coefficient of hydrogen atoms. From Hardy and Linnett (*26*).

B. HEAT OF ADSORPTION ON ALLOYS

This section deals with changes in the heat of chemisorption caused by the secondary ensemble effect and the ligand effect, which are used to determine the factors governing the changes in bond strength upon alloying.

Recently, a simple theory dealing with the ligand effect has been developed (*136*). Differences in chemisorption on transition metals are thought to be mainly due to changes in the d-band widths and electron occupation in different metals. Assuming that the distance between adsorbate and metal atom is the same for single bonding as for different kinds of multiple bonding, changes in heat of chemisorption have been computed for a hydrogen atom using simple models. The results are shown in Table III. The heat of adsorption of complexes with Z coordinating atoms compared with the single bonded case is given as a function of the parameter μ, which is a measure of the bond strength and is the quotient of the exchange integral between one metal atom and a hydrogen atom and the exchange integral between the metal atoms. The latter is proportional to the d-band width of the transi-

TABLE III

The Ensemble Effect: Comparison of Relative Adsorption Energies

	μ														
Z	0.5	0.6	0.7	0.8	0.9	1	2	3	4	5	6	7	8	9	10
6	5.62	5.56	5.48	5.40	5.33	5.27	4.74	4.31	3.93	3.64	3.41	3.24	3.12	3.02	2.94
5	4.73	4.69	4.63	4.56	4.52	4.46	4.06	3.71	3.41	3.16	2.98	2.84	2.73	2.65	2.59
4	3.82	3.80	3.76	3.71	3.67	3.64	3.34	3.07	2.84	2.65	2.51	2.40	2.32	2.25	2.20
3	2.90	2.88	2.86	2.83	2.81	2.78	2.58	2.39	2.22	2.09	1.99	1.91	1.85	1.81	1.77

tion metal. The larger μ, the stronger the interaction will be between metal atom and adsorbate. If adsorption is strong, changes in heat of chemisorption due to the secondary ensemble effect will be proportional to the square root of the number of coordinating atoms Z. If adsorption becomes weaker it will change in proportion to the number of coordinating atoms. The fact that the dependence of the heat of chemisorption on the number of coordinating atoms is weaker for strong adsorbates than for weak adsorbates is due to the stronger competition between the coordinating metal atoms to bind the hydrogen electron if adsorption is strong.

Weak adsorption is understood to be chemisorption simply determined by charge transfer, in Mulliken's sense (*137*); for instance, adsorption of xenon to transition metals (*138*) as compared to physical adsorption determined by dispersion forces. In terms of this secondary ensemble effect the influence of alloying is smaller for strong adsorbates than for weak adsorbates, if adsorption on the same sites is considered.

Since these results have been derived for initial heats of adsorption, extension of these results to the case with a finite surface coverage should be done with care. If the interaction between adsorbates were important, one could imagine that the increase in average distance of the adsorbates because of surface dilution would lead to a decrease in interaction energy at continuing coverage of the surface. If the interaction were repulsive, the decrease in heat of adsorption upon adsorption would be smaller on an alloy than on a nonalloyed metal. Interaction between adsorbates is expected to be larger for multiply bonded species than for singly bonded species, because in the latter case adsorbates do not have to compete with each other for binding to the same surface atom.

Christmann and Ertl (*59*) have measured the heats of CO adsorption on the (100) planes of palladium and a few of its alloys with silver (Fig. 15). Increasing the surface coverage results in a decline of the heat of adsorption,

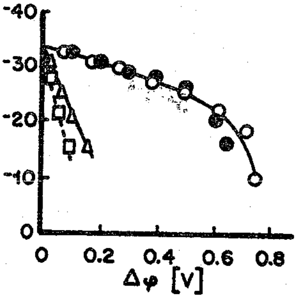


FIG. 15. Heats of CO adsorption on different (100) planes as a function of $\Delta\phi$. ○, Compact crystal (*139*); ●, 100% Pd; △, 82% Pd; □, 62% Pd. From Christmann and Ertl (*59*).

which is steeper according as the concentration of silver is higher. Therefore, the difference between the curves cannot be ascribed to a difference between the interactions of the adsorbates.

Figure 16 shows some curves of the calculated heats of chemisorption for nonlocalized strong adsorption at different degrees of alloying. In the case of the pure metal A the adsorbates are assumed to be coordinated with four A atoms. Dowden (*140*) has published analogous results assuming proportionality of the heat of adsorption with the number of coordinating atoms. Interaction between the adsorbates is neglected. Also the alloying metal atoms are supposed not to contribute to the bonding of the adsorbates to the substrate. θ is the number of adsorbates divided by the total number of metal atoms present. The temperature is assumed to be so low and the pressure so high that even at very high dilutions complete coverage is possible. The curves in Fig. 16 for low coverage show a striking similarity with the

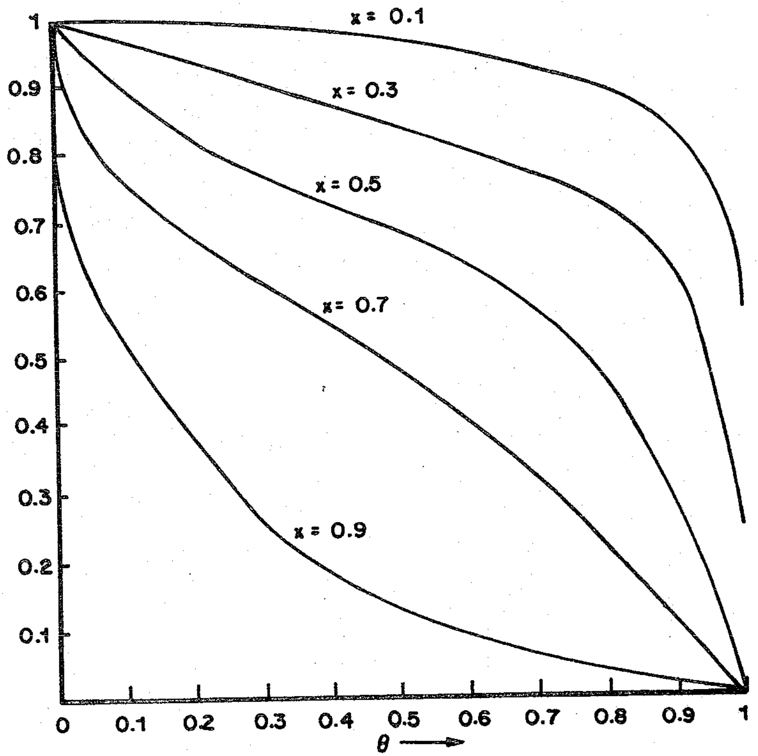


FIG. 16. Heat of adsorption as a function of surface coverage θ for a particular x (concentration of inert atoms) on a (100) face of an fcc crystal for nonlocalized adsorption.

curves found by Christmann and Ertl (Fig. 15). $\Delta\phi$ is a measure of the coverage. However, the dependence on the silver concentration found is much stronger than that computed. Two explanations are possible: one is enrichment of the surface in silver, and the other is that filling of the palladium d-band by electrons out of the s,p-band upon alloying with silver causes an additional decrease in heat of chemisorption. Observe, however, that the secondary ensemble effect already goes a long way toward accounting for the decrease in heat of adsorption.

These results clarify the conditions of applicability of chemisorptive titration. It is clear that if a large contribution to chemisorption stems from multiply adsorbed species, chemisorptive titration cannot be used to determine the surface concentration because the surface coverage of adsorbate will be much less influenced than the surface concentration of active metal atoms. From these considerations, the conclusion already mentioned in Section II can be derived, that chemisorptive titration can be employed if

$$\begin{aligned} |\Delta H_{\mathrm{ads}}| &\gg RT \qquad \text{as long as} \quad \theta \leq x, \\ &\sim 0 \qquad \text{if} \quad \theta > x. \end{aligned}$$

We have assumed in this section that multiple bonding gives a larger binding energy than single bonding (*136*, *141*). This assumption will be valid only if the distance between the metal atoms coordinated with the hydrogen atom is so small that the increase in coordination is not canceled by a much larger increase in repulsive forces. Indeed, Doyen and Ertl (*142*) have published calculations, accounting for the Pauli repulsion, that show that the heat of adsorption of multiply adsorbed species is comparable to that of singly bonded species.

The ligand effect can also be discussed (*136*) using current theoretical concepts on chemisorption (*143a*, *143b*). The effects expected will be illustrated with some results of cluster calculations. Table IV gives for different

TABLE IV

The Ligand Effect: Comparison of Relative Adsorption Energies

	μ					
Cluster	5	6	7	8	9	10
B	1.12	1.11	1.10	1.09	1.08	1.07
C	0.878	0.791	0.703	0.660	0.627	0.591
D	0.858	0.760	0.701	0.654	0.620	0.587

clusters (see Fig. 17) the calculated heat of adsorption relative to the heat of adsorption of a chosen standard cluster A. In cluster A a hydrogen atom is supposed to be bound to one metal atom, which in its turn has 6 neighbors. The assumptions involved in the quantum-chemical calculations on these clusters are similar to those made in the Anderson model (*128a*). Within these assumptions, the heat of chemisorption can be calculated exactly. Each metal atom is represented by one orbital, characterized by the valence state ionization potential α_m. The interaction between the metals is represented by the exchange integral β. The hydrogen atom has an interaction β' with the metal atom to which it is bound. One electron on the hydrogen atom has the energy α_H, and two electrons on the hydrogen atom have energy $2\alpha_H + \lambda$, where λ is the repulsion integral between two electrons.

The calculations have been performed for fixed α_H, α_m, β', and λ, but also with varying values of the parameter μ, which is a measure of the bonding strength and is represented by

$$\mu = \beta'/\beta.$$

For cluster A, where each metal atom is supposed to contain one electron, the heat of adsorption as a function of μ is given in Fig. 18. The values calculated are found to be less than $1.33\beta'$, which is the heat of formation of the MeH molecule. The largest decrease is found for the lowest values of μ. The large

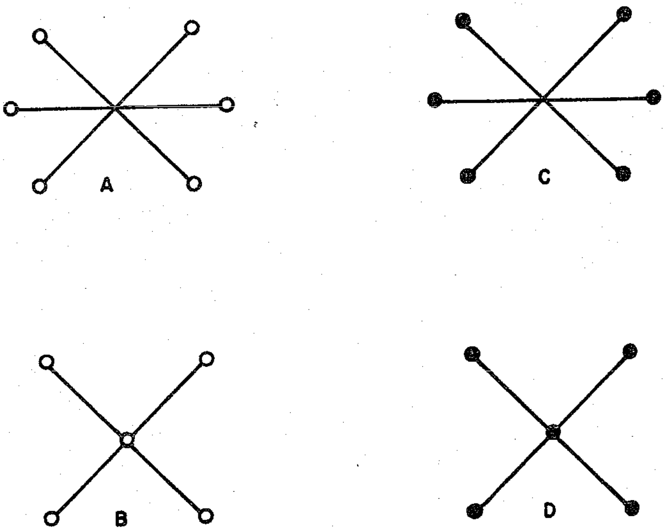


FIG. 17. Metal clusters. ○, Singly occupied orbital; ●, doubly occupied orbital.

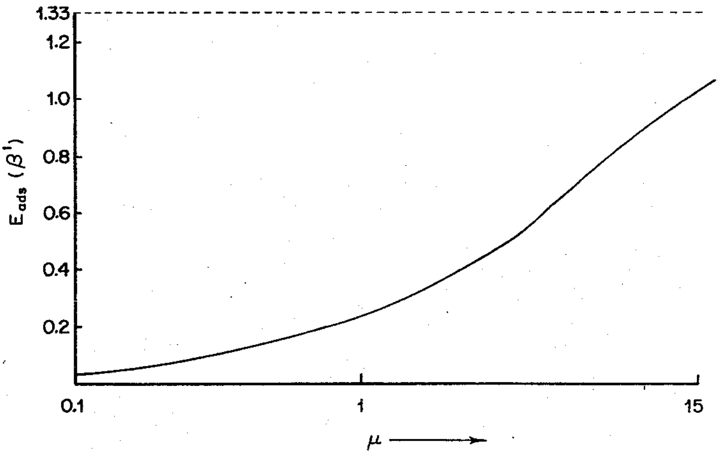


FIG. 18. Heat of adsorption E_{ads} as a function of μ.

difference in heat of chemisorption as a function of μ explains why it is found (*144*) that the bond strength of a CuH molecule is larger than that of NiH, whereas the heat of dissociative adsorption of hydrogen is less on copper than on nickel (*145*).

The effect of alloying is studied in the model clusters (see Fig. 17) by letting the metal orbitals simulate a d-band in a true transition metal cluster.

As already discussed, alloying narrows the d-band of transition metal atoms. In our model this can be represented by a decrease of the number of neighbors of the metal atom active in bonding. As illustrated in Fig. 17 in cluster B this number is decreased from six to four. As with the secondary ensemble effect, the largest contribution is found for the lowest values of μ, the reason being that for lower values of μ the metal–metal interaction becomes more important than the Me–H interaction. It is actually a ligand effect because the extent of narrowing will depend on the metal used for alloying.

In cluster C the number of neighbors of the bonding metal is again six, but now the metal orbitals are doubly filled. The largest decrease is now found for the highest values of μ. The decrease in heat of chemisorption becomes smaller for lower values of μ and the heat of chemisorption can even be found to increase for low values of μ. The behavior of the heat of chemisorption as a function of μ is opposite to that found for cluster A. The negative ion of the MeH molecule gives here the best zero-order approximation to the binding energy, even for low values of μ, because the localization energy for two electrons on a metal atom is zero in this case. The stronger the metal–metal interaction, the more energy is gained by rebonding. The large increase for low values of μ is due to this increasing probability of the formation of negative ions. Prior to adsorption, charge transfer is already favorable and chemisorption becomes ionosorption.

If the number of neighbors decreases from six to four as in cluster D, the heat of adsorption is found to decrease rather than to increase, as it does in the case where the metal atom orbitals are half-filled.

It is seen that a decrease in heat of chemisorption due to filling of the band is counteracted by the changes in bandwidth.

From calculations on quasi-infinite lattices it was found that there is a distinct difference between initial changes in heat of chemisorption due to the presence of a surface layer of inactive atoms and changes induced by alloying in several outer layers (*136*).

In the first case changes in metal–adsorbate bond strength are very small; in the second case the effect of atom isolation is found to be comparable to band filling. Only with very large filling of the band does the heat of chemisorption decrease.

If one compares adsorbates on similar sites, our results allow of two generalizations:

(1) If the electron band contains enough holes, weak adsorption complexes are more affected than strong adsorption complexes.

(2) If the metal electron band is completely filled, the strength of the stronger chemical bond is more affected than that of the weaker bond.

If condition (1) is satisfied, the ligand effect is smaller than the secondary ensemble effect. Under condition (2) the two effects can become comparable.

According to the model the heat of adsorption is related to the cohesive energy. The latter is proportional to β. The cohesive energy of most of group VIII metals decreases with increasing number of band electrons, paralleling the behavior for the heats of adsorption.

Measurements of the infrared spectra of carbon monoxide on supported palladium and Pd–Ag atoms (*75a*) shed light on the relative importance of the ensemble and ligand effects. Three CO absorption bands were observed on palladium and its alloys at ~2060, 1960, and 1920 cm^{-1}.

As shown in Fig. 19, the most marked result is that the band frequency remains almost constant for palladium and Pd–Ag alloys, but the relative intensities change in a dramatic manner. The 2060 cm^{-1} band, which is ascribed to the linear CO complexes and is rather weak for CO on palladium, becomes the most important feature of the spectrum of CO on Pd–Ag alloys, where the bands characteristic of multicenter-adsorbed CO are very faint. Measurement on Cu–Ni alloys (*75b*) show an almost similar behavior.

Hence, it is found that the stronger adsorbates are more influenced by alloying than the weaker adsorbates. According to the theory just discussed

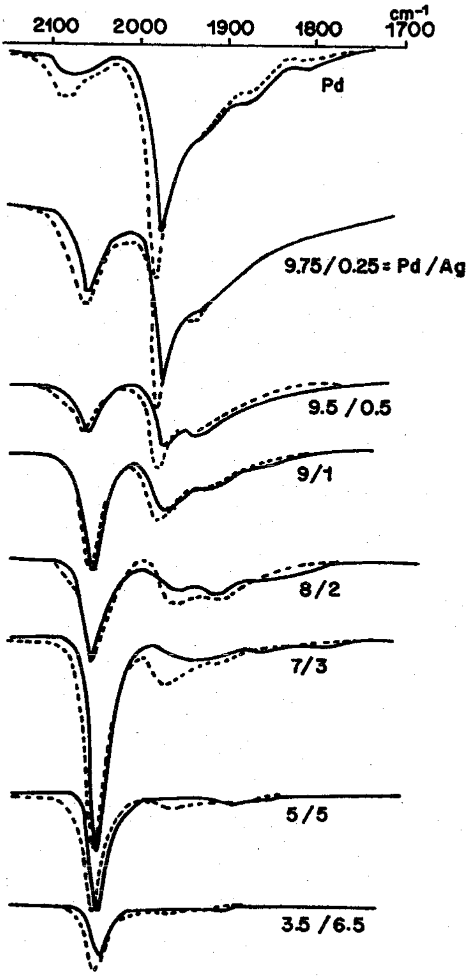


FIG. 19. Spectra of CO adsorbed on Pd–Ag alloys. ——; $p_{CO} = 0.01$ Torr, ---, $p_{CO} = 0.5$ Torr. From Soma-Nota and Sachtler (*75a*).

this is only possible if adsorption takes place on different sites, characterized by different ensembles.

Thermal desorption of hydrogen from platinum and Pt–Au films (*146*) results in a similar conclusion for these alloys. On average, hydrogen is more loosely bound to the alloys than to pure platinum. About 50% of the adsorbate is desorbed by pumping at 78 K from the alloys, while only a very small percentage is desorbed from platinum at this temperature.

After maximum coverage of platinum films upon hydrogen adsorption, three desorption peaks have been observed. The same peaks have been found for the alloys, but the relative populations of the various adsorption types were different. Here again, the peak corresponding to the larger heat of adsorption is most influenced, leading to the conclusion that it corresponds to hydrogen atoms bonded to several metal atoms.

V. Conclusions

Alloying of a catalytically active metal with an inert component changes the selectivity in hydrocarbon reactions such that C–C bond fission is suppressed compared with C–H bond breaking. Upon alloying, therefore, the selectivity for cracking reactions will decrease. In this review, we have shown that the surface composition of macroscopic alloys will often differ from the bulk composition and that the laws governing the actual surface composition are now reasonably well understood. We have further stressed that selectivity changes can often be understood in terms of the primary ensemble effect, i.e., dilution of the metal surface with inactive atoms diminishes the probability for metal–adsorbate complexes containing several neighboring metal atoms as required for cracking. The concept of an ensemble of metal atoms, crucial to the understanding of selectivity patterns on alloys, implies that the metal atoms in the surface of the alloy keep their individuality and are only influenced by their immediate environment. Indeed, the evidence from solid state physics that the rigid-band theory of an alloy, implying loss of individuality of the atoms, is not valid for alloys of group VIII metals with catalytically inactive metals is overwhelming.

In this paper we have introduced the secondary ensemble effect, which ascribes changes in heat of chemisorption of multiply bonded atoms to a decrease in the coordination of these atoms to the surface metal atoms. This effect will in general lead to a decrease in heat of adsorption upon alloying.

The heat of adsorption can, in principle, increase because of the ligand effect, which ascribes changes in adsorbate–metal bond strength to differences in electronic properties of the binding atoms induced by alloying. Although the ensemble effects primarily determine selectivity changes, they cannot explain all changes in reactivity induced by alloying. The ligand effect must then be invoked and can become important.

The ligand effect can influence the heat of adsorption in two ways. First, it can decrease the localization energy of the electrons needed for the formation of a chemical bond with the adsorbate. This would lead to an increase in heat of adsorption. Second, the heat of adsorption can decrease, if there is an increase of electrons in the d-band because of electron transfer from the alloying component to the transition metal. Theory shows that both effects can become of the same order of magnitude. Because adsorbates of different bond strengths are influenced in different ways by the ligand effect, this will influence selectivities. Since the specific activity depends primarily on the electronic properties of the active metal atoms, the ligand effect can become of great importance in the search for more stable catalysts.

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