Selectivity in Catalysis by Alloys

J. K. A. CLARKE

Department of Chemistry, University College, Dublin 4, Ireland

Contents

I. Introduction. Scope of Review

There has been in recent years a measure of progress, although somewhat uneven, in understanding the action of alloy catalysts. The advance has been most marked for the class of VIII-IB alloys, but main conclusions reached may turn out to hold for other binary alloy catalysts comprising a group VIII element and a metallic element from groups IB to IVB. This situation has come about through a better appreciation of the electronic structure of these metals and their mixtures. For other types of alloy of catalytic interest, particularly d-metal/d-metal combinations, more refined information than yet seems available for metal solutions appears to be needed for the treatment of catalytic action. Indeed, there is not yet agreement as to the most appropriate experimental parameters for interpreting fine structure of catalytic action in such cases in which the activities of the individual elements often differ only *in degree*. Discussions are consequently at a more exploratory level. In at least one case where the elements differ decisively in activity (section III.A.2), a semiempirical approach can be of help: we direct our attention away from the rationalization of catalysis in terms of atomic electron structure and turn rather toward the consequences of the physical dilution of the atoms of active metal. Overall, an important outgrowth of this whole body of research has been a fuller recognition of some of the properties of alloys which may promote selectivity in catalytic reactions. In the author's

view, an interim review of both progress and problems for future attention seems timely. The account is not intended as a compendium of recipes (see ref 1 and 2). Rather, the object will be to examine the main origins of the types of catalytic specificity mentioned. In this spirit, account has been taken of published literature recorded in *Chemical Abstracts* to the end of 1973.

Firstly, in what follows, a short account is given of recent developments in the electronic structure of a historically prominent alloy type, namely the VIII₃-IB group, for which it seems that useful catalytic conclusions can be drawn from a very simplified level of information. Specifically, this will allow to be introduced that means of effecting selectivity which depends on the number of contiguous active surface sites. Examples of application to alloy catalysts for the rearrangement and for the marginal oxidation of hydrocarbons are discussed in detail. The effect of surface blockage of a single metal on its catalytic selectivity is examined, with examples, on account of the close conceptual relationship of this to the foregoing even though the matter is not strictly covered by our title. Secondly, the electronic influence of one alloy component on another is considered. So far in the account it will have been ignored or at least deemphasized, but it can play an important role in selectivity in some catalyses. In the cases of interest reaction selectivity is not primarily affected by the geometry of the surface site distribution but on the electronic fine structure. Demands from theory being more exacting here, progress has been less dramatic. Several current lines of enquiry are discussed.

II. Electronic Structure of VIII₃-IB Alloys and Their Catalytic Action

The transition elements are notable for their activity for hydrogenations, C–H bond breaking, and similar reactions. Most opinion associates this with the presence of d-vacancies although there is now a disinclination to insist on the associated density of electron states or its gradient as the most directly determining parameters. One approach much used by investigators of catalytic fundamentals has been to search for a relationship between observed activity patterns within a series of binary VIII₃-IB alloy catalysts (good–poor catalyst pair) and some electronic characteristic of the metal; comprehensive reviews of such studies and of the problems they raised may be found in the scholarly textbook of Bond.[3] An obstacle to progress has been the inadequacy of information on the electronic structure of alloys. Difficulties associated with the measurement of electronic spectra of metals have only recently been overcome. Alloy spectra now reveal quite clearly that the concept of a rigid d-band, implicit in the conception of the general class of catalytic studies referred to, is so incorrect as to set severe limits on the potential of such studies. In the fol-
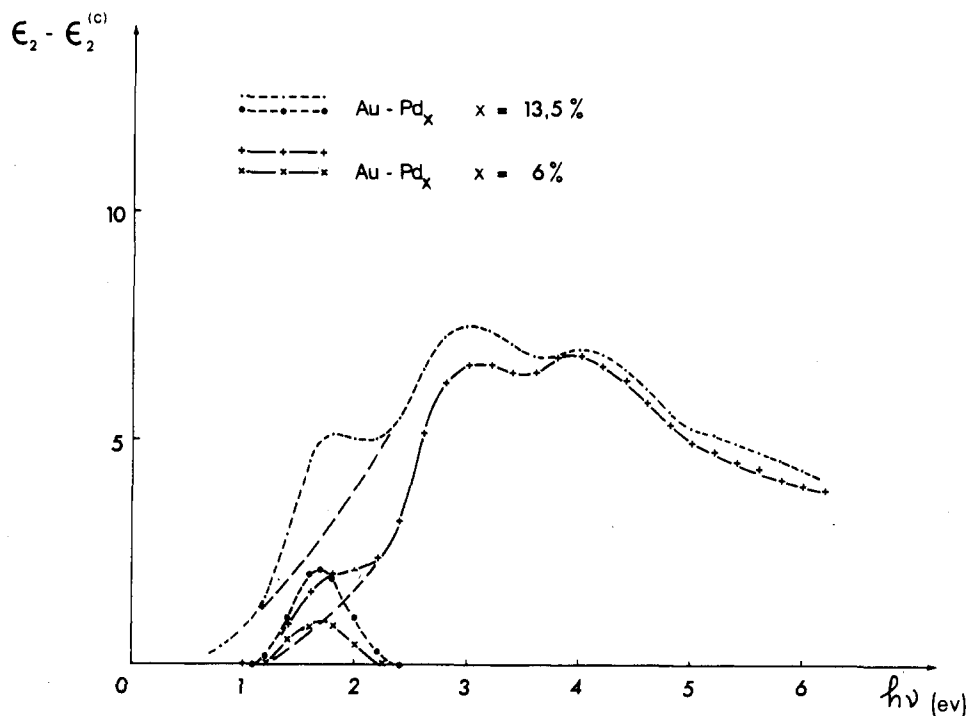
Figure 1. Supplementary absorption band due to Pd electronic states in two Pd–Au alloy samples. x is atom % Pd (reproduced with permission from ref 4).
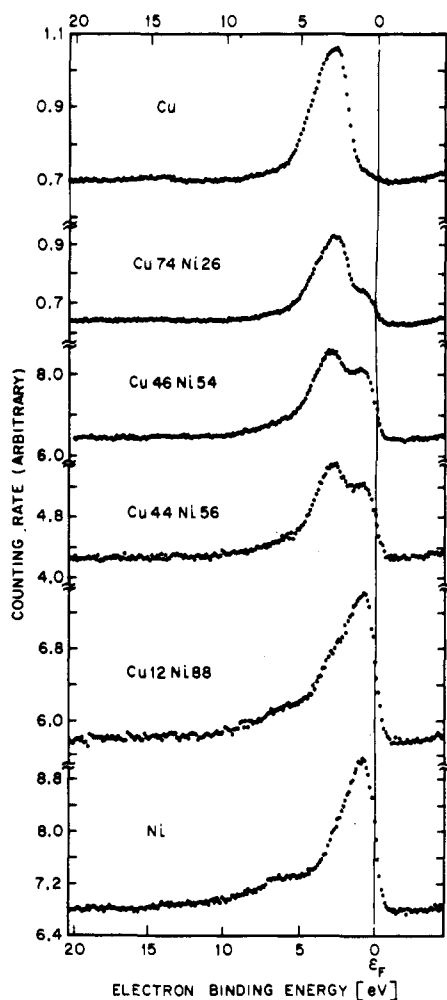

Figure 2. X-Ray photoemission valence-band spectra for Ni–Cu alloys. The Fermi energy (ϵ) was determined, with a Au sample, as the position where the 6s band is down to half its height (reproduced with permission from ref 9a).

lowing paragraphs the terminology of the collective-electron approach for metals will be retained without, however, implying that approach to have special suitability for analysis of catalytic action. While historical justification could be invoked, the choice is really one of convenience. Alloy spectroscopists are generally physicists, and the macroscopic properties of interest to the physicist are commonly related to spectra in band-theory terms.

It is now known that binary alloys of elements in the long periods can have separate d-bands associated with the component elements.[4] The band of higher energy is, in general, that derived from the element of smaller atomic number. For example, in Pd–Au and Pd–Ag the top of the Pd d-band is reported[5] to be higher by 1 and by 3 eV, respectively, than that of the Au(Ag) (Figure 1). d-Holes, present in metallic Pd, cease to exist at the Pd atoms when more than ~50 atom % Au is incorporated, and this has been attributed variously to descreening of the lower Pd nuclear charge by a reduction in the s–p electrons in the Pd cell[6] decrease in the width of the Pd d-band with increase in the average distance between Pd atoms[7] or, least probably,[8] donation of Au electrons to the Pd d-band. Although they represent a formally similar system, it has recently been argued that Pd–Ag alloys may have d-holes at all compositions.[7,7a] The Ni–Cu system appears more clear-cut as follows. The 2-eV-wide Ni d-band does not appear to alter significantly in energy or shape with % Ni (Figure 2).[9] It traverses the Fermi energy level at all compositions so that there are always d-holes at the Ni atoms.[10] Indeed, there is now a general impression that the Cu atoms have little influence electronically on their Ni neighbors. For mechanistically simple reactions, monotonic relationships between activity and % Ni and even constant activation energies are familiar findings,[11,12] most clearly apparent when the complication of phase separation in Ni–Cu alloys[13] is recognized. Even for Pd–Au, a linear relationship has been found[14a] between carbon monoxide chemisorption capacity and atom % Pd. The nature of the chemisorption

bond may change through the alloy series, as appears[15] to be the case for Pd-Ag. Because catalytic reaction rates and chemisorption bond properties may be differently determined by the characteristics of the surface, we restrict ourselves to the comment that these adsorption results illustrate the essential role of the Pd atoms in both phenomena.

For the description of bulk properties of binary alloys of the kind under discussion, a band model with d-bands which may be separate in energy is currently favored by solid-state physicists; for the surface properties of adsorption and catalysis, an analogous surface-band model would be of value. While the experimental and theoretical advances needed to achieve such a description are awaited, an interim working model applicable to $VIII_3$-IB surfaces has been suggested by Dowden.[16] In this the electronic configuration of a $VIII_3$ surface atom is taken to be determined by the proportion of its nearest neighbors which are IB atoms, and so the number of Pd atoms having d-vacancies on the whole surface can be calculated on a simple probability basis with an assumed size of atom "ensemble", taken as a count of the Pd site plus its nearest neighbors (Figure 3).[16a] On spectroscopic and general grounds it is accepted that where d-vacancies exist they are located at the $VIII_3$ atoms.

Evidently, from the foregoing, a theoretical vindication exists in the specific case of Ni-Cu alloys for the "individual atom" viewpoint,[11,19] which ascribes activity in hydrogenations and the like to the Ni atoms and regards the atoms of the B-subgroup component mainly as a diluent. Even for Pd-Ag and Pd-Au alloys hydrogenation activity can safely be identified with the Pd sites although there may be ranges of alloy composition where activity is much reduced because of the absence, or near absence, of d-vacancies. Of added importance, good evidence will be cited later that the different kinds of elemental component in a VIII-IB alloy retain their chemical individuality as shown by the products of catalytic transformation of certain hydrocarbons. In the section which follows a number of instances of selectivity of alloys from the even larger class of VIII/B-subgroup combinations will be given which can be rationalized on the basis of the simple level of description of the electronic structure of the alloy we have outlined.

III. Classification of Catalytic Reactions on the Basis of Site-Number Requirements

Bond, Dowden, and Mackenzie[20] have distinguished between the mechanistic and thermodynamic factors in catalytic selectivity. The first, for which we now examine possibilities for alloys, concerns whether the catalyst is inherently capable of converting certain only of the potential reactants or, in other words, whether the rate constants for their conversion differ appreciably. The second factor depends on there being a substantial difference in free energy of adsorption for the several competing reactants resulting in a large difference in coverage by each and so in their conversion rates; we shall return briefly to a possible alloy example at a later stage.

Interesting possibilities for selectivity control emerge when a reaction can follow alternative courses requiring a differing number of contiguous active sites. For this reason a preliminary classification of some catalytic processes on the basis of site-number requirements is attempted in Table I. In this, unparenthesized citations refer mainly to experimental observations and the parenthesized to overall mechanistic deductions although clearly such a division cannot be a sharp one. Suggestive information from homogeneous catalysis lies to hand in a
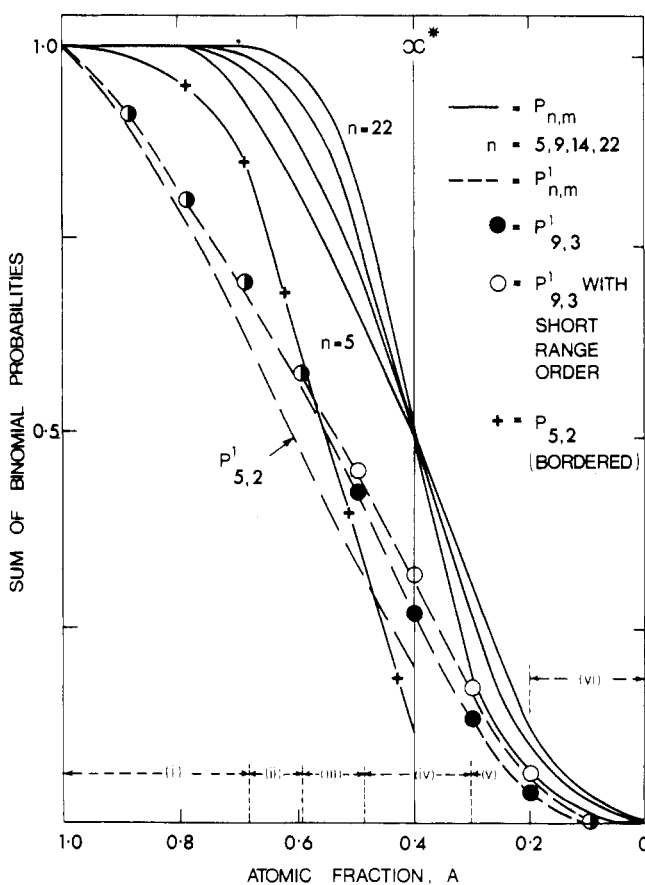

Figure 3. Values of P_n and $P^1{}_{n,m}$ at various compositions of a random $VIII_3$-IB alloy A_xB_{1-x} of ccp structure (for $P_{n,m}m \geq 0.4n$) $P_{n,m}$ is the probability of finding m or more atoms of A in a n-atom ensemble, $P^1{}_{n,m}$ is the probability that a given atom will be of type A and that it will have $\geq m$ nearest neighbors of the same kind in a n-ensemble (reproduced with permission from ref 16).

number of instances although it must be accepted that metal surfaces present more complex situations than mono- or binuclear molecular complexes. For example, a crystal surface can sustain adsorbed species in several states of bonding and, in the general case, catalytic reactions can proceed along different pathways to the same product. Our classification is necessarily tentative in some instances owing to the incomplete state of present information. Finally, we ignore the question as to whether a reaction requires one, two, or three, etc., coordination positions on a site atom, although recognizing that the position in the table of some examples may depend on the answer. For the following discussion what is important is the *relative* position in the table of alternative routes open to the reactant(s). Specific items arising from Table I will now be examined under sections A.1 and A.2 below and a further related topic discussed in section A.3.

A. Examples of Application

1. Alkane Conversion Reactions and Self-Poisoning by Carbonaceous Residues

There is agreement between three groups of workers that alloying Ni with small percentages of Cu leads to a sharp fall in activity for alkane hydrogenolysis.[36-38,49] Because all groups carried out measurements at temperatures above 320°, the alloy catalysts in these studies can be taken to be unambiguously single phased. The conclusion has been that at least two contiguous Ni

TABLE I. Number of Contiguous Sites Required for Selected Metal-Catalyzed Reactions (Schematic)

1	Olefin metathesis	(Dessing, Ponec, and Sachtler, 1972[21])
	Alkane isomerization: {cyclic	(Gault, 1963, 1973)[22,23]
	Esso 1969[25] {bond-shift	(McKervey et al., 1973[24])
	Olefin hydrogenation	(Wilkinson, 1966[26])
	Olefin isomerization	(Cramer, 1966[27])
	Acetylene hydrogenation: Rushford and Whan, 1971[40]	(Wilkinson, 1969[28])
	Aromatization of cyclohexane: Sinfelt, 1972[36]	
	1,2- and 1,4-cis hydrogenation of conjugated diene	(Kwiatek, 1965;[29] Bond and Wells, 1965[30])
	1,4-Trans hydrogenation of conjugated diene: π-allyl intermediate:	
	Joice et al., 1966[31]	(Kwiatek, 1965[29])
	Ethylene oxidation (Ag) → ethylene oxide	(Margolis, 1963[32])
	Oligomerization of acetylene, norbornadiene	(Schrauzer, 1966[33])
	Rosenmund reduction	(Affrossman and Thomson, 1962[34])
2	Aromatization of cyclohexane: Gryaznov, Polyakova et al., 1970[35]	
	Alkane hydrogenolysis	(Sinfelt, 1972;[36] Plunkett and Clarke, 1972;[37b]
		Ponec and Sachtler, 1972a[38])
	Olefin isomerization	(Kovács, 1970[39])
	[Acetylene hydrogenation	(Morgan and Somorjai, 1969[41])]
	1,4-Trans hydrogenation of conjugated diene: "classical"	
	mechanism	(Bond and Wells, 1965[30])
	Ethylene oxidation (Ag) → acetaldehyde, CO_2: Flank and	
	Beachell, 1967[42]	(Margolis, 1964[32])
	Oligomerization of acetylene, norbornadiene—stereospecific	(Schrauzer, 1966[33])
	Self-poisoning of catalyst (high temp.) with carbon	(Lobo and Trimm, 1972[43])
	Methanation of CO_2: Cratty and Russell, 1958[44]	
	Ammonia synthesis	(Carrà and Ugo, 1969[45])
≥3	Self-poisoning of catalyst with "acetylenic" residues: Dow Corp.,	
	1957;[46] Dowden, Mackenzie, and Bond, 1958;[20] Inami, Wood,	
	and Wise, 1969[47]	
	"Total" hydrogenolysis of alkanes: Swift, Lutinski, and Kehl, 1965[48]	

atoms are necessary in this reaction with most probably a restriction on their geometry.

Ponec and Sachtler have found in their later work[49] with *n*-hexane reactant that isomerization proceeds in preference to hydrogenolysis at Cu contents in excess of 20–30% (Figure 4). They interpret this result by pointing out that at least one of the two contemporary mechanisms of paraffin isomerization requires only single-atom sites. Thus, for platinum, Gault and his coworkers found that isomerization through a C_5-ring intermediate was promoted by using smaller metal crystallites, and for this reason as well as from bonding arguments they have favored a single metal atom reaction site.[23] The isomerization products found by Ponec and Sachtler[49] appear to have resulted from a cyclic intermediate so that these workers were led to propose that the rapid fall in fraction of multiple sites at low[49a] nickel content causes the selectivity for isomerization relative to hydrogenolysis to increase markedly. (It may be that the immediate cause of the selectivity change lies in the altered surface concentration of hydrogen.[50]) If platinum and nickel are found to behave similarly, this will represent an impressive vindication of the insight of Ponec and Sachtler. Recent work[24] suggests strongly that the alternative "bond-shift" mechanism with platinum also involves a single metal atom so that their proposal could have an even more general applicability.

The important predictive principle introduced is that alloying an active metal with an inert one alters the ratio of products arising from pathways requiring differing numbers of contiguous active site atoms.[50a] A further feature—relevant in hydrocarbon reactions—is self-poisoning of catalysts with polymerized acetylenic residues (coking) which may be associated with larger contiguous-site arrays designated "≥3" in Table I. By the same principle as before, such self-poisoning is discouraged by alloying with an inert element. Extensive or total hydroge-

nolysis of alkanes containing several carbon atoms may be linked with a formally similar site availability judging by results[48] for "deep" hydrogenolysis of *n*-octane on Ni–Cu alloys.

a. Cyclization/Aromatization of Alkanes

i. Alloy Catalyst Examples. The two foregoing bases of design have consciously or unconsciously been built into catalysts used for several years by the petroleum industry. Reforming catalysts are for the most part dual-functional so that, apart from optimizing the physical characteristics of the reactor, a suitable balance of dehydrogenation (metal) and acidic (alumina) activity has to be aimed at for the desired process.[51,52a] By alloying active with inactive metal, the dehydrogenating role of the metal function can be emphasized relative to its hydrogenolyzing effect. This is an especially desirable aim with the lighter paraffin[53a] and in "hydrocracking" operations (high temperatures; see section III.A.1.b) where the production of unwanted light paraffins by hydrogenolysis on the metal can be suppressed in favor of the more selective C–C scission on the acidic component. Although Pt alloyed with Co or other transition metal and supported on silica or alumina was already finding use for reforming in the late 1950's, being considered more resistant to sintering than the more usual platinum catalyst,[54] there appears in the last few years to have been a marked intensification of development work on alloyed platinum and palladium for hydrocarbon conversions. Much of this recent interest derives from the quest for lead-free gasoline and the resulting need for reforming catalysts which have acceptable yield stability at the higher temperatures (partly offset by higher hydrogen pressures) used to boost aromatics content. By way of a general illustration, a British patent[55] describes the better resistance to coking of alloyed palladium catalysts (nickel, rhodium, or silver as
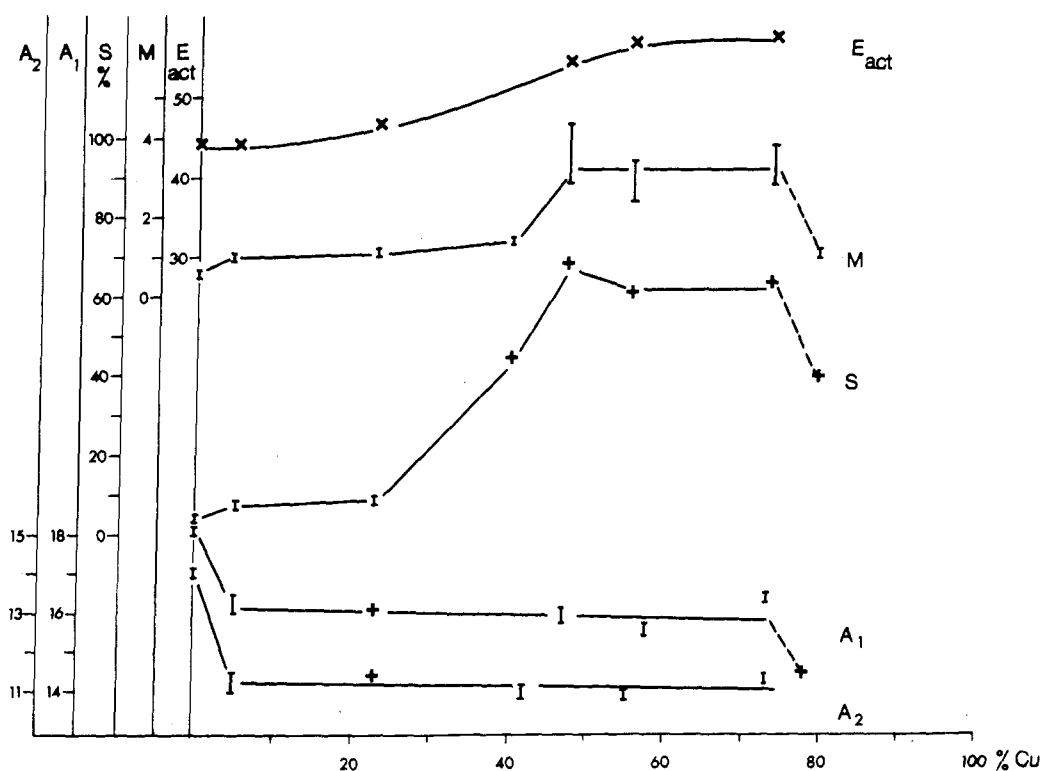
Figure 4. Reaction parameters of n-hexane conversion by Ni and Ni–Cu alloys as a function of alloy composition. $A_1 = \log r_w$ at 330°, where r_w is the rate of overall reaction per gram of catalyst; $A_2 = \log r_s$ at 330°, where r_s is the rate per cm^2 of total surface; S, a selectivity parameter, is the % of product mass which comprises C_6 isomers; fission parameter M is a measure of the ratio of nonterminal to terminal fission so that $M \leq 1$ if methane is predominant and $M > 1$ when methane production is minor (reproduced with permission from ref 49).

second metallic constituent) relative to unalloyed palladium either in alkane dehydrogenation or in alkane dehydrocyclization at 400–600°. This is said to allow the desired reaction to proceed at lower temperature and so more cleanly.

Recent catalysts for dehydrocyclizations[56] and aromatics production[57,58] have emphasized the use of Pt–Sn or[59] Pt–Sn–Re. The Re incorporation has the main effect of decisively increasing the stability of the catalyst under severe dehydrogenating conditions and, in newer versions, of its activity.[60,61] Pt–Pb systems are effective in aromatizations[62] as is Pt_3Cu.[57] Pt–Ge catalysts have been developed for paraffin dehydrogenation accompanied by a minimum of cracking (see section III.A.1.b) for reforming[63] and even for "hydrocracking" operations;[64] there is some question whether the germanium is not present as oxide in these cases.[65] Sinfelt and coworkers at Esso laboratories have explored noble metals other than platinum alloyed with copper, silver, or gold as isomerization/reforming catalysts. A noteworthy development here has been the use of supported alloys of high dispersion wherein the additional surface free energy can be exploited[66] to yield otherwise unavailable ranges of surface composition: (i) with Ru–Cu, Ru–Ag, and Os–Cu, hydrogenolysis is considerably suppressed compared to isomerization;[67] (ii) a patent[68] reports Ir–Au (preferred), Ir–Ag, or Ir–Cu on high-area alumina for hydroforming of paraffins and cycloalkanes with scope for procuring a large aromatics yield at >500°; (iii) the performance of a reforming catalyst KX-130 which is rather more active than conventional Pt or Pt–Re catalysts and is especially effective in paraffin aromatizations has been given,[69] information otherwise being confined to its being multimetallic and dual functional.

ii. Background and Interim Interpretations of Alloy Action. Because of the current heightened increase in the

conversion of alkanes to more highly branched isomers and particularly to aromatics, more detailed comments are offered as a contribution to interpreting the distinctive behavior of certain alloy reforming catalysts. Remarks will be restricted to monofunctional (metal) action. As indicated, two main modes of skeletal rearrangement of paraffins are currently under discussion.[70] The first mode is the bond-shift mechanism which appears to participate to an appreciable extent on low index faces[71] and which can occur with the second of the two mechanisms during a single hydrocarbon residence time. Opinion is not yet unanimous as to whether one site or several sites[70] are required for this process. We note that formation of products through bond-shift should be enhanced by alloying by a diminution of hydrogenolysis as treated earlier and, perhaps, by lessened coking. The second mode of skeletal rearrangement is by cyclization through a C_5- or C_6-ring intermediate; in either case the product may be cycloalkane or an isomeric alkane resulting from hydrogenolysis of the ring or, in the case of the C_6 ring, a benzenoid product resulting from further dehydrogenation. C_5- (the preferred course) and C_6-cyclization may be parallel processes in the case of paraffin reactants having a six-carbon chain.[72,73] For paraffins having only a five-carbon chain, C_5-cyclization may be followed in the same sojourn at the surface by ring expansion at the metal sites to yield a C_6 cycle[74-76] or by ring opening to a straight-six-carbon-chain hydrocarbon which undergoes C_6-cyclization.[72] At temperatures above about 350°, conversion of a C_6 ring to "benzene" is so favorable thermodynamically that the only cyclization pathway to isomerized alkanes is by a C_5-ring intermediate. A further possible route to benzene production is by cyclization of hexatriene intermediates;[72,77] Anderson[70] is of the view that this pathway is of relatively small importance save under extreme dehydrogenating conditions. In the following

paragraph we examine the information on dehydrogenated residues in chemisorbed benzene on metals and then proceed to attempt useful conclusions as to the possible effects of such residues on the reaction routes just described with particular attention to the action of alloy catalysts.

Most information on chemisorption of hydrocarbons is available for nickel catalysts. Selwood[78] reported from measurements by the ac permeameter method of the changes in magnetization in nickel samples caused by benzene chemisorption at 120° that the number of "bonds" formed between hydrocarbon and metal was about 6 and that the number of such bonds increased rapidly to about 18 at 200°. There is evidence that cyclohexane chemisorption on nickel leads to substantial hydrogenolysis to adsorbed C_1 units, such hydrogenolysis being much less marked with cyclohexene or benzene.[79] Benzene chemisorbed at room temperature on nickel seems to require hydrogen treatment at temperatures in excess of 300° to remove it.[80] LEED studies,[80a] particularly since about 1969, have shown that layers formed by benzene adsorption on the three principal faces of nickel in the range 175–375° show extensively dehydrogenated polymers which appear also to have suffered C–C bond rearrangement (Figure 5). Higher temperature annealing (375–425°) produced partly disoriented layers of graphite which, under still more severe conditions, break down and carbon diffuses into the bulk of the crystal. There is a quantity of evidence, some of it circumstantial, pointing to a preferential formation or attachment of carbonaceous residues on rougher regions of nickel, platinum, or tungsten.[81-84] LEED experiments on the dehydrocyclization of n-heptane[84a] showed that residues formed on certain stepped regions of a platinum surface still allowed reaction (250–350°) to proceed there with high activity and without self-poisoning. Finally, we note that platinum chemisorbs only about one-third the amount of benzene chemisorbed by nickel under comparable conditions.[86]

We may conveniently, in what follows, examine separately production of aromatic hydrocarbon (i) by dehydrogenation of a cyclohexane and (ii) by dehydrocyclization of alkane followed by dehydrogenation.

(i) Aromatization is favored above about 300°. Boudart has cited experimental evidence that the reaction on platinum is not surface-structure sensitive,[85] and this result is as might be expected irrespective of whether the slow step is the initial chemisorption,[86] a dehydrogenation stage in the chemisorbed layer,[87] or desorption of the benzenoid product,[36] for none of which are there grounds for supposing the need for special sites. Aromatization of cyclohexane is denoted "two-site" in Table I as one possibility to take cognizance of spatial needs[52b] of the intermediates and not to denote pair sites having a special geometric relationship such as probably needed for hydrogenolysis.

In the light of the foregoing, alloying the catalytically active metal with a diluent metal would be expected to lead to a lessening of both hydrogenolysis and coke formation. Sinfelt, Carter, and Yates[36] report that, in fact, the specific activity of copper–nickel powders for this aromatization was not sensitive to the percentage copper content ($P_{cyclohexane}$, 0.83 atm; P_{H_2}, 0.17 atm). There was a slight increase in activity, perhaps by about a factor of 5, on first copper addition; then the activity remained constant for most of the composition range (6–74% Cu) and fell by less than one order of magnitude in the interval from 80 to 95% Cu. We note that these alloys were well characterized and that reactions were conducted in the single-phase region of temperature. Because these workers came to the view that the copper

component of the alloys influenced the nickel component electronically from an evaluation of the pattern of activity of their catalysts for ethane hydrogenolysis, also measured, they took the position that the rate-determining step in the cyclohexane dehydrogenation reaction changed with composition because of the same electronic influence. Sinfelt has subsequently reported[67] that the activity of highly dispersed Ru–Cu and Os–Cu alloys for dehydrogenation of cyclohexane (316°) followed a similar pattern with alloy composition to that found with Ni–Cu. Activity for hydrogenolysis of cyclohexane on the former alloys, also measured at 316°, fell by two orders of magnitude over the range of $VIII_1$ metal content. This fall was not, however, as pronounced as that found in ethane hydrogenolysis for which activities with the same catalyst fell by nearly four orders of magnitude. In addition to their finding that the selectivity for dehydrogenation relative to hydrogenolysis increased by about a factor of 10 through the range of increasing copper content for the cyclohexane reaction, there are indications from their results that the $VIII_1$ metal catalyst is more prone to self-poisoning by carbonaceous residues than are its alloys with copper in the case of cyclohexane hydrogenolysis. The first part of this finding is in agreement with the earlier results for Ni–Cu of Sinfelt's group and others, already discussed; the latter finding suggests that, at least in the case of cyclohexane reaction, there is relief from poisoning residues from use of the alloy. A substantial decrease in cyclohexane dehydrogenation activity has been reported[35] for a series of Pd–Ag alloys for which no characterization is, however, available.

(ii) Dehydrocyclization of paraffins includes at least one additional slow step, namely, the cyclization itself. Anderson[70] has argued that this and any subsequent ring hydrogenolysis are the two (comparably) slow processes. The cyclization stage would seem to require step sites. This follows firstly from experimental evidence. Gault and his coworkers[23] have found that high-dispersion platinum catalysts favor cyclization. Joyner et al.[84a] showed that a high index face with (111) terraces and (100) steps was ten times more active for dehydrocyclization of n-heptane than a flat (111) plane; this finding must be seen alongside the near certainty that carbon or carbonaceous residues from hydrocarbon dehydrogenation tend to form at this type of step preferentially. Further, on the basis that several coordination positions are required to accommodate the relevant "ligands" on the reaction site (see ref 23 and 88), a site of low coordination ("rough" region) seems necessary. Ring expansion[74] or C_5-ring opening to yield a six-carbon-chain hydrocarbon precursor for C_6-cyclization[72] may, in either case, likewise be expected to be demanding, and for the same reason. Stepwise removal of hydrogen atoms by reversal of the steps in benzene hydrogenation should, by contrast, be fast and (see section (i)) facile. Some consequences of employing alloy catalysts containing diluent metallic atoms at the surface appear now to emerge on account, inter alia, of the presence of residues on both low- and high-index regions, noted above. (a) The average degree of dehydrogenation of hydrocarbon species should be substantially less and cyclization sites should be correspondingly more available. Most notably, catalyst life appears generally to be increased as seen from the various published examples cited earlier. (b) Surface migration of species between low-index and higher index surface regions[89] would presumably be enhanced relative to desorption as interim product so that the nature of the product distribution should be more "mixed" (both cyclic and bond-shift isomerization occurring in a single sojourn; for a test by C^{13}-labeling, see Corolleur[87a]). At above about 350°,

however, such is the position of the surface equilibria that cyclic species tend largely to convert to aromatics. Aromatic products are then favored at the expense of products from bond-shift isomerization sites.[89a]

There are several ways by which the surface concentration of adsorbed hydrogen may exert kinetic influence (or control) over the character of the reaction, and these may be relevant in the adoption of alloy catalysts. (i) The selectivity for hydrogenolysis relative to rearrangement reactions will depend, in part, on the surface concentration of hydrogen and this, as pointed out by Anderson,[50] will certainly be dependent on the alloy composition. (ii) Paál and Tétényi[90] have shown that diminution of surface concentration of hydrogen in the conversion of n-hexane on platinum black favors benzene production for kinetic reasons. Essentially it is argued that C_5-cyclization becomes unimportant. (iii) If hexadiene structures prove to play a significant part under reforming conditions, subsequent work by the same authors[77] implies a kinetic need for some hydrogen, to make possible geometrical isomerization of trans hexadiene to the cis form which can cyclize relatively rapidly to benzene by intramolecular bonding; an inadequate hydrogen pressure leaves the trans diene to aggregate to surface polymer by formation of analogous intermolecular bonds. A low concentration of surface hydrogen will therefore favor coking rather than benzene production. If, as has been argued,[77] these steps are heterogeneous, that is, catalyzed by active surface sites, alloying with a diluent metal would certainly be expected to further inhibit the extent of polymerization on spatial grounds. For application of items (i)–(iii) to practical cases there is a need for reliable experimental information on the variation of surface adsorbed hydrogen with diluent metal content of the alloy catalyst: at present it is not clear how far means (i) and (iii) may be in conflict in maximizing "benzene" production.

b. Other Alkane Reactions. Dehydrogenation and "Hydrocracking"

Returning to applications of the classification in Table I, we may examine dehydrogenation procedures in their own right. Dehydrogenation of alkanes to alkenes, like the reverse change, appears to be a single-site process but, as temperatures of 500° or higher are required to give useful yields of alkene, formation of carbonaceous deposits on single-metal catalysts (multisite process: Table I) is inevitable. Binary alloy catalysts for practical application have been developed which contain an inert metal and show extended life. Pt–Sn is now quite fully documented for this application.[91] Other alloys used have been Pt–Ge[92] (which brings about a minimum of cracking) and Pt or Ir with In or Ga.[93] An Ir–Au on a relatively nonporous support has been patented[94] for the oxidative dehydrogenation of hydrocarbons (see section III.A.2).

A final example of the use of alloys in reactions of paraffin with hydrogen may be mentioned. When reduction in mean molecular size is to be effected in oil processing, designers arrange that this takes place on the acidic function of a dual-functional catalyst. More-or-less-central scission of the alkanes results. This is loosely termed a "hydrocracking" process. Suppression of hydrogenolysis on the metal component, which otherwise tends to give an indiscriminate breaking of C–C bonds leading to products of all possible carbon numbers, can be effected by using a suitable alloy for the metal function. Pd–Sn catalysts have been suggested[95] as also have alloys of Au with a metal chosen from the noble group VIII elements.[96] Supported Ge–Re–VIII (noble metal) catalysts have been reported for hydrocracking uses and are
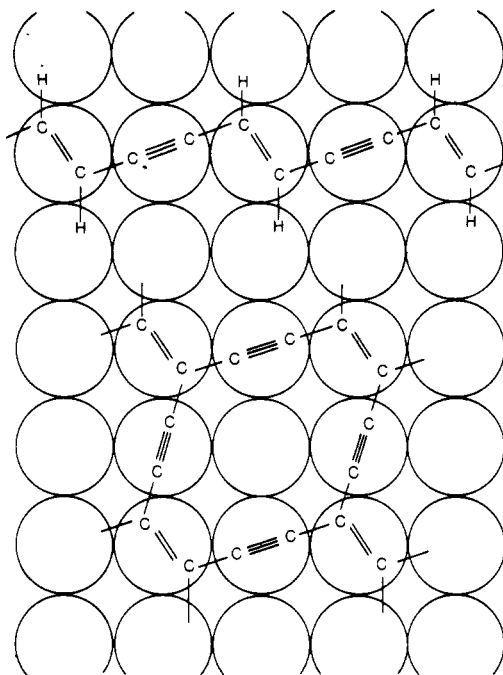
Figure 5. Surface polymers proposed in interpretation of LEED patterns for benzene adsorbed on Ni(110) at 175–375° (due to J. J. McCarroll, T. Edmonds, and R. C. Pitkethly; reproduced with permission from ref 80a).

claimed to show extended life.[97]

In the foregoing, as well as in examples of alloy catalysts which will follow, there is usually an uncertainty as to the surface composition of the metal. In strict terms fundamental interpretation of catalytic behavior should be delayed until an examination has been carried out on the system(s) of interest by X-ray diffractometry[98,99] (to give homogeneity ranges, if necessary measured on more massive forms of catalyst; from these a rough estimate of surface composition is possible) or, more satisfactorily, by newer surface probes such as Auger electron spectroscopy (yielding the composition of the outermost surface layers directly).[100,101a] Fortunately, even when such information is not available or is incomplete, a qualitative assessment of these factors is possible, certainly for the commoner alloy combinations. Firstly, data on heat of mixing, when available, allow a determination of the nominal composition range in which phase separation is thermodynamically to be expected. Secondly, in a two-phased binary alloy prepared at typical temperatures it is to be expected that the phase rich in the metallic element of lower sublimation energy (and so of generally greater surface migration rate) should envelop the second phase.[102] Thirdly, there is the quite general Gibbs enrichment of the surface atomic layers of an alloy[102a] which manifests as an enrichment in the elemental component of lower sublimation energy on account of its lower surface energy: Auger studies of the surface of Ni–Cu, Pd–Ag, and Pt–Sn samples having typical thermal histories reveal little, moderate, and extreme B-group-metal enrichment, respectively.[101] Differences between surface and bulk compositions arising in these or other ways may modify basic trends in selectivity within an alloy series.
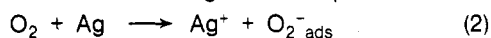
2. Oxidation of Ethylene and of Cumene on Silver-Based Catalysts and Related Examples

Silver is unique among the metals in its ability to convert ethylene to ethylene oxide, and there is a consensus that this property derives from the ability of this metal to
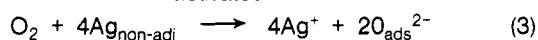
SCHEME I. Adsorption of Oxygen on Silver (Following Kilty, Rol, and Sachtler[107])

$$O_2 + 4Ag_{adj} \longrightarrow 4Ag_{adj}^+ + 2O_{ads}^{2-} \qquad (1)$$

nonactivated in initial stages of adsorption

$$O_2 + Ag \longrightarrow Ag^+ + O_2^-_{ads} \qquad (2)$$

activated

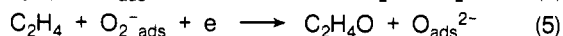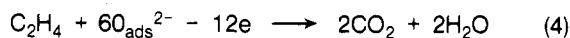$$O_2 + 4Ag_{non\text{-}adj} \longrightarrow 4Ag^+ + 2O_{ads}^{2-} \qquad (3)$$

at higher temperatures if the 4 × Ag

ensembles have to be formed by activated migration

SCHEME II. Distinctive Reaction Paths of Ethylene with Oxygen Adatoms and Admolecules on Silver

$$C_2H_4 + 6O_{ads}^{2-} - 12e \longrightarrow 2CO_2 + 2H_2O \qquad (4)$$

$$C_2H_4 + O_2^-_{ads} + e \longrightarrow C_2H_4O + O_{ads}^{2-} \qquad (5)$$

chemisorb oxygen nondissociatively: the diatomic oxygen species is held on a single silver atom, a normal peroxidic configuration[103] being one possibility. Dissociative adsorption of oxygen takes place, in addition, on silver as has long been clear from isotopic exchange measurements with labeled oxygen.[104-107] Mobility of oxygen atoms on silver seems to set in about 100°:[106] clearly, both pressure and temperature determine the relative amounts of oxygen admolecules and adatoms under conditions of catalytic interest. Ethylene reacts with the peroxidic silver entity to give ethylene oxide and an oxygen adatom (Schemes I and II) as has now been elegantly established by Kilty, Rol, and Sachtler,[107] who showed the disappearance of infrared absorption bands due to the peroxy complex and the emergence of bands identical with those obtained upon adsorbing ethylene oxide. Monoatomic oxygen, so resulting or from primary dissociative adsorption, reacts with ethylene to give CO_2 and H_2O.

Clearly, when all peroxidic oxygen has reacted (to give ethylene oxide) the surface will be covered with oxygen atoms. Total combustion of further ethylene to give CO_2 and H_2O is necessary to make bare some silver atoms for continued peroxide formation. If such bare Ag atoms diffuse apart and form O_2 admolecules, this will tend to lead to an upper limit to selectivity expressed as ratio of ethylene oxide to carbon dioxide produced of about 6/7 because of the stoichiometry of these processes.[111]

While selectivity is generally high, it is sensitive to moderators added either unintentionally or deliberately. Some remarks on this effect are in order to set in proper context the effect of alloying silver described later. Voge and Adams[108] suggested that moderators (such as chlorine) may act by decreasing $O_{(ads)}$ relative to $O_{2(ads)}$ by giving a larger fraction of isolated sites. Kilty et al.[107] found that (i) only one-fourth of the Ag sites were taken up at 100° by dissociative oxygen adsorption, further adsorption being nondissociative, and (ii) the nonactivated adsorption of oxygen (eq I in Scheme I) was prevented by a precoverage of about, or greater than, one Cl atom on four Ag atoms. From the first of these experimental observations they concluded that ensembles of four contiguous silver atoms are required to produce adatoms of oxygen in primary adsorption (Scheme I, eq 1). Thus, the overall effect of adsorbed chlorine on the catalytic selectivity is explained in its destroying these quartets of silver atoms, and so favoring the process in eq 2 over that in eq 1. Electrostatic repulsion between the Cl^- ions causing a rather regular spreading of these is proposed to account for the magnitude of their influence on the nature of the oxygen adsorption.[107] It must be added that some opinion[32,109] interprets the influence of moderators on

silver in terms of an alteration in its work function. Thus if the latter is decreased, chemisorption of atomic oxygen species is favored and selectivity is reduced (and vice versa).

In the light of the foregoing, alloying silver with a proportion of gold, which only chemisorbs oxygen weakly,[110] might be expected to increase selectivity for ethylene oxide production by producing a higher ratio of diatomic to monoatomic adsorbed oxygen, on account of the greater fraction of isolated silver sites. Flank and Beachell,[42] working with powders, and (as they admitted) not under reactor conditions which would lead to optimization of ethylene oxide production, found that selectivity approximately doubled on passing from silver powders to 5-25 atom % Au alloys, and then decreased rapidly for higher gold contents (Figure 6). There is support for the first of these two effects from measurements on silver and a silver-gold film catalyst having, in the latter case, "a composition giving maximum isolation of the surface silver atoms".[111] If the absolute magnitude of the selectivity for the alloy given in this work (namely, 100%) is accepted, however, there appears to be a need for the assumption that peroxy species on silver can form by an efficient recombination of oxygen adatoms.[112] Such recombination has been proposed from a comparative study of oxidations of ethylene and of ethylene oxide on silver.[113] However, it is unclear how the gold constituent can enhance such a process so as to allow an increase in selectivity from the inherent upper limit of about 85% to a value of 100%. Certainly there are indications[42] that oxygen attachment is of greater binding energy at higher Au content so that electronic influences between the metallic components[113a] may still be moot. Also, Cha and Parravano[114] report measurable activity in the range 200-350° for oxygen transfer on gold surfaces, which may be greater than that corresponding to the interaction of gold surfaces with molecular oxygen. There is clearly scope for further study of this system.

A further example of the improved action of Ag-Au alloys is the selective oxidation of cumene to cumene hydroperoxide:[115]
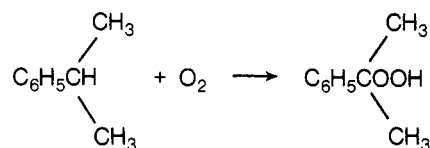
Here insertion of a pair of oxygen atoms in one step is required,[116] and the rate of reaction increases markedly on passing from silver to silver-gold alloys with a maximum at about 10% Au.

Gerberich, Cant, and Hall[14] have reported that the selectivity of oxidation of ethylene to acetic acid, acetaldehyde, and acetic anhydride compared to carbon dioxide and water is maximal to 80 atom % Au at 70-100°. They have suggested that the palladium atoms are isolated, leading to less (or less extensive) dissociative chemisorption of ethylene. There is disagreement as to the effect of palladium addition to silver in promoting ethylene oxide production from ethylene and oxygen, patents[117] suggesting improved selectivity, other work reporting decreased selectivity through decreased C_2H_4O production alongside rather constant CO_2 yield.[118] There are, however, complications due to "dealloying" and to dissolution of hydrogen under reaction conditions[118] which must complicate detailed interpretations. Adventitious addition of moderators is possible in the industrial operation.

A number of patents describe oxidative dehydrogenation of alkanes to alkenes,[94] n-butenes to butadiene, and

methanol to formaldehyde[119] by use of Pt–Au and Pd–Au alloy catalysts. Because gold additions are always substantial (at least 40–50%), these reports suggest once again some kind of isolation of chemisorbed oxygen species, perhaps O_2 units, which are especially effective for the desired process. Butene-1 and oxygen give a butadiene/CO_2 mole ratio at 40 atom % Au enhanced by 2.5–3.0 at 300°, and by about 1.3 at 400°; that is, the specificity is clearly enhanced by the presence of gold.[47]

Concurrence between the optimal alloy concentrations for the several reactions in this section is not obvious. The need for analyses of alloy surface composition is most severe for these catalysts, and a full assessment of mechanistic details must await these. However, the hydrocarbon oxidation studies are at least suggestive that selectivity derives primarily from isolation of active surface site atoms.

3. Modification of Catalyst Selectivity by "Blocking" the Surface

Three decades ago Herington and Rideal[120] treated by a simple mathematical approach the influence of a neutral poison on the rates of catalytic reactions having different site-multiplicity requirements. If the reaction rate could be assumed to be proportional to the surface concentration of reactant, it was shown to be proportional to θ^n for a reaction requiring an isolated group of n centers, where the poison occupies one active site per poison molecule and leaves a fraction θ of the active sites bare; the good measure of agreement with the then available experimental results on poisoning of heterogeneous catalysts led the authors to prefer a picture of uniform availability of reaction sites to the concept of active patches for hydrogenations, etc. While the Herington–Rideal treatment is a better approximation, the nearer the reaction kinetics approach zero order in the main reactant (e.g., hydrocarbon), alteration of product distributions in parallel or successive reactions by such poisoning is to be expected for various reactions. (It is at present realized that, as well, blocking of specific crystal faces may frequently be responsible for a selectivity change:[121] for possible role of surface-structure sensitivity in alloy selectivity patterns, see section V). It is clear that the Herington–Rideal poisoning model is closely related to our general theme and some specific examples follow.

(i) It appears from a recent report[21] that a common catalytic characteristic, as follows, is shown by (a) alloys containing roughly equal amounts of Pt and Au and (b) platinum surfaces largely covered with carbonaceous residues from a preliminary cracking reaction. Thus olefin metathesis (a one-site process) has been inferred to occur when either type of catalyst surface is exposed to a n-butane/hydrogen feed at above about 300° because n-pentane is produced in addition to hydrogenolyzed material. It seems possible, therefore, to extend our earlier deduction and say that hydrogenolysis (a pair- or multi-site process) is suppressed relative to methathesis (a one-site process) by the presence of either an inactive alloy component within the surface or residues on the surface.

(ii) The sulfur "activation" of platinum catalysts for reforming, effected the H_2/H_2S mixtures, appears to operate largely by suppression of hydrogenolysis events (compare Weisz[53b]). By contrast, it is likely that the thiophene poisoning of supported platinum catalysts, brought about by trace amounts of thiophene in reactant alkane and which depresses cyclization activity relative to dehydrogenation,[122] represents a selective poisoning of surface regions required[23,84a] for cyclization. An alternative viewpoint, which has been suggested as a general proposition for surface-structure sensitive reactions, is that sul-
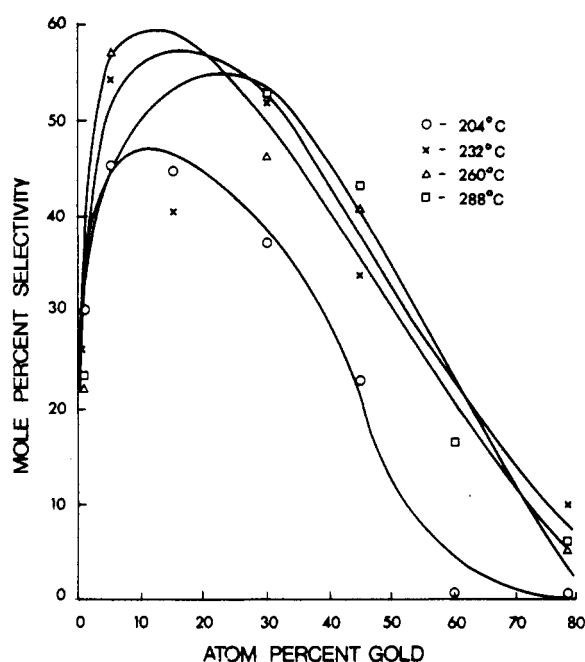

Figure 6. Ethylene oxidation on Ag–Au alloys: mole percent selectivity vs. alloy composition (reproduced with permission from ref 42).

fur poisoning (as H_2S) operates by causing surface reconstruction to a less active metal site arrangement.[122a]

(iii) The role of nonmetallic moderators such as sulfur or chlorine on silver catalysts for ethylene oxidation to improve epoxidation selectivity, which has been referred to in section III.A.2, may be analogous to that suggested for gold alloying although there appears to be some evidence of an electronic factor as well in the action of the former.[32]

(iv) The Rosenmund reduction of acyl chlorides to aldehydes using supported palladium is conducted in the presence of sulfur-containing poisons such as thiourea and tetramethylthiourea. Elemental sulfur is also effective. Production of alcohol by further reaction is thereby inhibited, and this has been attributed for the most part to the need for a larger number of contiguous sites for the second reaction than for the first.[34]

IV. Role of Electronic Influences between Alloy Components

Advances in the knowledge of electronic structure of the type of alloys so far discussed have clearly justified a deemphasis for catalysis of the idea of electronic influences of one alloy component on another. It would be over-rigid, however, even from a practical standpoint, always to assume that the inactive components of an alloy catalyst act merely as diluents. The approximation seems to be a close one for Ni–Cu alloys, may or may not be for homogeneous Pd–Ag alloys (as noted earlier) and certainly needs qualification for catalysis on Pd–Au alloys. The latter examples, in consequence indeed of the breakdown in the diluent approximation, furnish examples of selective action which are discussed in the following paragraph. It is a truism that alloy components can have a significant electronic influence on one another when a wide definition of alloy is adopted. For the purposes of the present review we artificially restrict our definition so as to exclude consideration of interstitial solid solutions (where the nonmetal component more obviously plays the part of a ligand such as in an organometallic compound: see ref 123 and 125), intermetallic compounds and the influence of oxidation state of the metal on catalysis.[126]
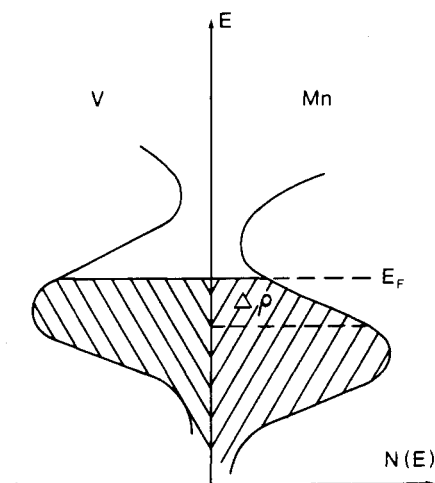
3-d ELECTRON BANDS FOR DILUTE Mn IN V

Figure 7. Schematic illustration of the solute- and solvent-band relationship (and occupancy) for dilute Mn in V. The occupation of the Mn band exceeds that of the V band by $\Delta\rho$ (reproduced with permission from ref 133).

A. Palladium/B-Subgroup Combinations

On both Pd-Au[127] and Pd-Ag[128] activity for alkene hydrogenation ceases at atom % Pd < ~40. Because alkyne hydrogenation proceeds even at lower palladium contents than this, the product under such conditions is clearly alkene irrespective of the conversion level.[128a] Such palladium-lean alloys have uses, therefore, either for this selective hydrogenation per se or for the selective removal of alkynes from alkene streams.[20,46] Zinc and lead are other well-known additives to palladium which promote this object.[2] The gold (certainly), silver (at low temperatures at least[130]), and the zinc or lead (probably) act by producing surfaces having no d-holes[130a] which are then unable to catalyze hydrogenation of alkenes but, owing to a strong influence of the reactant on the electron density at the surface palladium atoms alluded to by several authors (e.g., ref 31), can hydrogenate alkynes to the alkene stage. It is consistent with the foregoing that mercury poisoning of palladium leads to loss of its ability to hydrogenate ethylene while deactivation with respect to acetylene hydrogenation is much less severe.[132] It is worth noting that addition of silver to palladium in the foregoing applications gives a longer lived catalyst[20,46] due, as in the examples discussed in section III.A.1, to a lesser formation of carbonaceous residues than found with 100% Pd.

B. Binary Alloys between d-Metals

With a view to completeness in this account, current viewpoints on the electronic structure of d-metal/d-metal alloys will first be examined.

In most cases of interest the Fermi energy level E_F appears to lie below the tops of the d-bands of both components. Electron donation between the two types of atom may well take place (see below), and descriptions of the resultant electronic structure tend to employ a "similar-but-displaced-band" picture[133] (Figure 7) rather than the cruder rigid d-band. Whether component (partial) d-bands merge energy-wise depends[134] inter alia on the strength of the random scattering in the lattice. Development of virtual bound states for one component is a possibility for some alloys;[135] e.g., VIA-VIII combinations of catalytic interest may approach this kind of electronic structure. There is, in fact, a useful rule[136] that for neigh-

boring elements in the same transition series, or, seemingly, if the elements belong to the same column, the collective band—with screening of the "impurity" atoms—is satisfactory, but if from a different row and different column a virtual bound state may need to be considered.

For discussion of microscopic properties of alloys such as in the interpretation of magnetic moments of solute atoms, use of the parameter of partial density of states (at E_F) associated with a particular type of atomic component, but modified locally[135,137] by the other partner, is being favored currently by physicists. Brief reference will be made to this again in concluding remarks. For the present we note that electron donation between the two kinds of atom is a general possibility but as well as leading to net fractional charges on atomic centers increase/decrease in local density of states will also occur because of the modified electron population of the partial bands. As the property of catalytic activity also may still turn out to be dependent on parameters such as the density of states or its gradient,[137a] this consideration may supplement usefully deductions made on the basis primarily of electron shifts.

Severe difficulties await attempts at applying the ideas just described to catalysis by alloys of d-metals. Over-facile assumptions as to the shape of the partial band of one alloy component can lead to difficulty as has been found[138] in attempted interpretations of the solid solution chemistry of group VIII elements. A simpler and more hopeful approach is to try to infer the direction, and ideally the extent, of electron shift between the alloy constituents. Experience with homogeneous hydrogenation catalysts[139] suggests that in homolytic activation of hydrogen, other factors remaining constant, the greater the electron density at the metal atom because of the presence of appropriate ligands the greater its ability to activate hydrogen. Relative electronegativities of the elements may furnish indication of electron drift in binary alloys, but clearly experimental deductions are to be preferred. Information may be obtained from studies of molecular compounds containing metal–metal bonds[140] in their pattern of reactions at the metal–metal bond,[141] infrared spectra,[142] or other spectroscopic methods;[143] some caution may be necessary in extrapolating conclusions from one type of molecular system to another or from molecular systems to bulk metals.[144]

One instance in which the concept of an inductive influence may be helpful is to explain part of the function of rhenium incorporated in platinum catalysts for hydrocarbon isomerization,[60,145] namely the enhancement of the intrinsic activity of the platinum sites. Of the two principal pathways for isomerization discussed earlier, the bond-shift route, at least, is by a carbonium-ion-type mechanism,[24] and one mechanistic version[23] of the second appears in essence also to proceed with electron drift toward the metal site (Figure 8). It seems reasonable to argue that these processes are enhanced by electron abstraction from the platinum atoms by the rhenium. Although residual doubt must exist prior to direct experimental measurement whether a particular d-metal component, such as rhenium, donates or abstracts charge in a mixture with another later element such as platinum, experience with other metal pairs[133] suggests for this case a drift in the sense $Re^{\delta-}-Pt^{\delta+}$.

In practice, a significant degree of synergism in catalytic activity is common for alloys formed from among the group VIII metals.[2,146,147] It is rarely, however, a really dramatic phenomenon even though a nonmonotonic change with alloy composition of a quantity such as density of states is, in principle, quite possible on account of
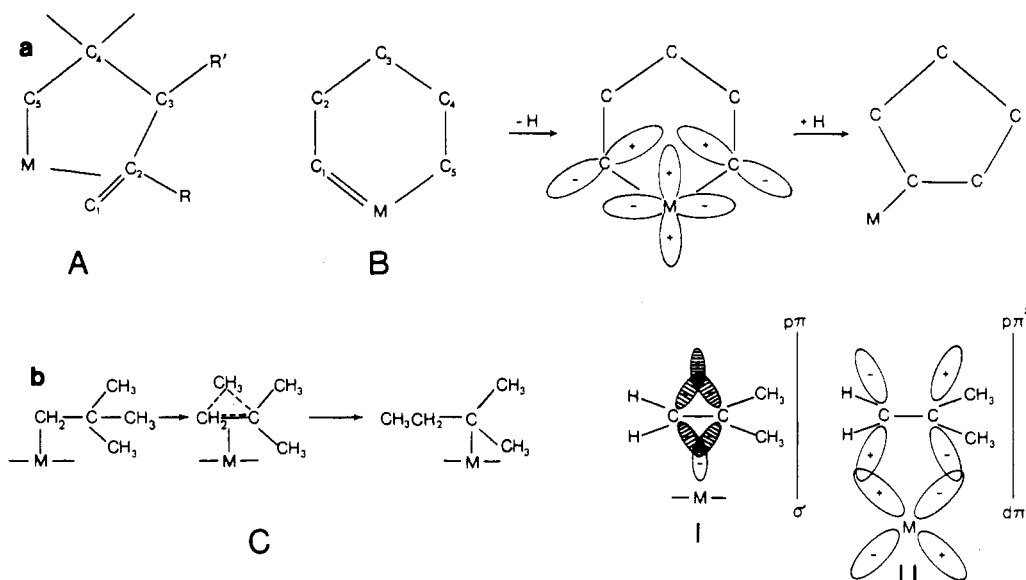
Figure 8. (a) Dehydrocyclization intermediates for palladium and platinum catalysts. A is appropriate for palladium whereas B is preferred for platinum on the basis of experiments with model compounds. Also shown is an orbital scheme suggested for the latter intermediate (adapted from ref 23). (b) Mechanism proposed by McKervey et al. for isomerization of neopentane. The intermediate C has carbonium ion character: bonding and antibonding orbitals are shown in I and II, respectively (reproduced with permission from ref 24).

TABLE II. Activity of Ternary Ni–Ru–Pt "Mixed Oxides" for Hydrogenation of Nitrobenzene[a] (Ref 146b)

Wt % Ni	Activity	Wt % Ni	Activity
0	158	5	45
2.5	67	25	20

[a] Ru:Pt. 1:2 atomic.

irregular band shape. Nevertheless, the existence of activity maxima at certain alloy compositions serves to emphasize that there exists an optimal amount of one metallic component in the other. Bond and Webster[146b] have adduced evidence that activity in nitrobenzene hydrogenation is determined mainly by electronic factors. Ru–Pt alloys were found to have maximum activity at 20 wt % Ru. Addition of nickel to this optimal alloy depressed the activity (Table II). However, these authors draw the clear conclusion that, for example, the properties of rhodium cannot be reproduced by blending equiatomic parts of ruthenium and palladium, even though such an alloy would have closely the same concentration of d-electron holes as rhodium; activity maxima for hydrogenation tend to exist even in the *individual* alloy series Ru–Rh and Rh–Pd (Figure 9). The elements, therefore, exert their own chemical individuality, in an intriguing but elusive way. Significantly for our theme, Bond and Webster[146b] draw attention to the fact that in the Ru–Pt system the rate maxima for hydrogenation of olefins occur when the d-electron hole per atom ratio is about 1.5, and for hydrogenation of acetylenic bonds when it is about 0.7. Thus there are grounds for believing that for each type of catalytic process there is an optimum number of d-electron holes per atom for most efficient catalysis: tentatively, they propose that the bond order of the function being reduced may determine this number of d-holes.

The foregoing may be linked to our main theme. Selectivity under preparative chemistry conditions can result from synergic improvement of a desired reaction route to the relative exclusion of an undesired one. An example from Rylander and his group may serve as an illustration, viz., the hydrogenation of diphenyl ether over Adams-type Pt–Rh.[148] Aryl–oxygen bonds hydrogenolyze rather readily under hydrogenation conditions. Experimentally dicyclohexyl ether and phenyl cyclohexyl ether appeared in
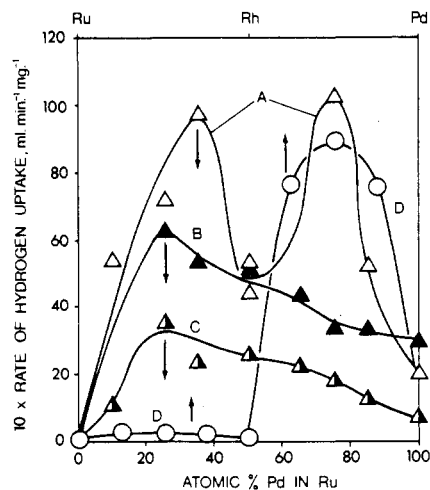

Figure 9. Rates of hydrogenation of methylbutenol (A and D), of maleic acid (B), and of 1-octene (C) using Ru–Pd "oxides" (triangles) and Ru–Rh and Rh–Pd "oxides" (circles) (reproduced with permission from ref 146b).

maximum yield at a nominal composition of about 70% Rh/30% Pt where hydrogenolysis was a minimum (Figure 10). Present information is that an alloy of this composition can form a single solid solution at relevant temperatures. Anderson and Kemball[149] have given evidence that once the benzene ring is hydrogenated in anisole the C–O bonds become less susceptible to hydrogenolysis. They suggested that the lower rate of C–O breaking with anisole over platinum was due to the more rapid conversion of anisole to the less reactive cyclohexyl methyl ether. There are indeed indications[150] that among various noble metal alloy pairs Pt–Rh showed maximum efficiency for hydrogenating xylenes. The basic property of the Pt–Rh alloy system which causes it to hydrogenate an aromatic ring with high activity makes it as a result a selective catalyst which avoids C–O scission during this process.

Attention will now be drawn to alloy catalysis examples which seem to require the development of more refined theoretical models perhaps coupled with reliable measurements of physical properties of the alloys.

Workers at Gulf Laboratories[151] have reported that
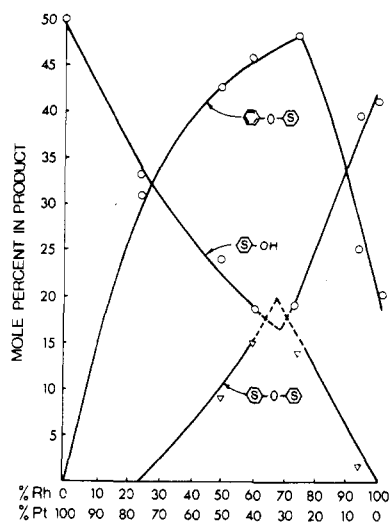
Figure 10. Hydrogenation of diphenyl ether over Pt–Rh "oxides" in cyclohexane. Effect of catalyst composition (reproduced with permission from ref 148).

tungsten or molybdenum addition to nickel promotes in a most dramatic way conversion of *n*-octane to butanes and pentanes at the expense of "total" hydrogenolysis (found with 100% Ni), the conditions being 400°, 1 atm, H_2/n-octane equal to 1.5. It is probable that the surface composition is very low in tungsten or molybdenum on the basis of both phase stability and likely Gibbs enrichment. This finding is sufficiently impressive to merit explanation on any acceptable theory of catalysis by d-metal/d-metal alloys. The Mo (or W) atoms at the surface appear to have a specific active role; that is, they are not inert "spacer" atoms in the manner of copper in the Ni–Cu system. The action may be one of hydrogenolysis on Mo (W) single-atom sites occurring more rapidly than on Ni pair or multiplet sites, and recalls Anderson's suggestion[50] that quasi-isolated metal atoms may well be active in hydrogenolysis. Further, the action of the VIA atoms may be related to special electronic structures (virtual bound d-states) associated with dilute solutions of A subgroup metals in group VIII metal matrices[152] which can even in some extreme examples[153] leave d-vacancies on the solute atoms only. Certainly electron donation to the nickel would be expected to cause lessened hydrogenolysis activity at the Ni atoms, from Sinfelt's[154] type of correlation of activity and group number. This result, if it is confirmed using nonchemically prepared alloys (such as metal films), particularly with characterization of the surface by modern techniques, would encourage exploration of catalysis at isolated atoms of group IIIA to perhaps VIA or VIIA in group VIII matrices.

The second example selected to spotlight the need for theoretical advance is taken from a thoroughly fundamental investigation. McKee has reported[155] results for the exchange reaction between methane and deuterium on Rh–Pd alloys the surface phase in which is ∼10% Rh.[156] In these catalysts the Pd atoms dominate the catalytic activity as shown by simple (d_1) rather than multiple (d_2–d_4) exchange. On an atom fraction basis the rhodium would be expected to be at least as active a component. Further, rhodium gives multiple exchange with methane.[157] It may be that the effect of site volume (smaller in Rh) is to promote d-vacancies in the Pd (the opposite effect to an Au matrix), but this inference gives no information on the total electron density on each kind of atom. Any electron shift is more likely to be from palladium to rhodium atoms.[157a] Such a shift might produce something like the catalytic result found even for this essentially homolytic bond breaking process: on the sim-

plest approach, the Fermi level of Pd lies on the high-energy side of a maximum in $N(E)$ vs. E so that the Rh atoms would depopulate somewhat the Pd band and move E_F to an energy level at which $N(E)$ is larger. The density of states gradient may also, of course, be changed. This example of alloy catalysis serves as a caution in our search for simple chemical/"individual atom" explanations of alloy catalytic action. The direction of enquiry suggested is forced on us because the effect is the opposite to that mentioned earlier from homogeneous catalysis[139] of hydrogen activation and the reaction is homolytic.

The direction of future thinking is likely to be rather as has been described for d-metal/B-metal combinations. There is certainly a realization[17,158] that averaged properties of an alloy (such as, e.g., electronic specific heat), which result in effect from a summation over the various atom clusters of the different possible A to B atomic ratio, are inappropriate for interpretation of catalysis—a phenomenon sensitive to local environment. A similar position has arisen in metal physics in the interpretation of magnetic moments, and of Mössbauer and NMR shifts (e.g., ref 137). It still seems useful to regard the concept of a local density of states in an alloy as providing a link to the chemical or "individual atom" standpoint[11,31] on catalytic action. The catalytic chemist will follow with interest exploration of microscopic rather than macroscopic properties[17] in the search for his rationalizations.

V. Surface-Structure Sensitivity

Occasional reference has been made in this review to the distinction between reactions which are surface-structure sensitive ("demanding"[85]) and others—perhaps the majority—which are not ("facile"). The possibility is very real that formation of an alloy of a catalytically active d-metal by incorporating a metal having a different specific surface energy, for example, one from a B subgroup where melting points are lower and sublimation energies smaller, could lead to alteration of the fraction of rougher regions of atoms on the surface as compared to the d-metal catalyst itself; variations in mode of preparation and other previous history of the catalyst prevent a unique end result. Clearly, since there are reactions which proceed with different rate on different crystal faces and there can be in consequence an artificial variation in activity with alloy composition[159] (Figure 11), selectivity changes arising out of this surface-structure dependence of one of several alternative routes are to be expected on occasions. Hydrocarbon hydrogenolysis is possibly such a case[160] so that it cannot at present be excluded with certainty that the influence of alloying nickel with copper in suppressing hydrocarbon hydrogenolysis more than isomerization is due to partial elimination of special rough regions which are more necessary for the former reaction than for the latter.[161] It is pertinent to this question that quasi-isolated site atoms may act as hydrogenolysis centers on some metals.[50] A more subtle effect, namely the influence of grain boundaries where alloy phases meet at the surface, may be of importance as with platinum alloys.[162] While evaluation of influences of surface structure on selectivity of alloy catalysts is still at a primitive stage, answers are important to obtain so that catalyst design may be less empirical. This as well as a variety of other problems arising with alloy surfaces can be expected to be substantially resolved by means of LEED and Auger spectroscopy of alloy single crystals.[100,163]
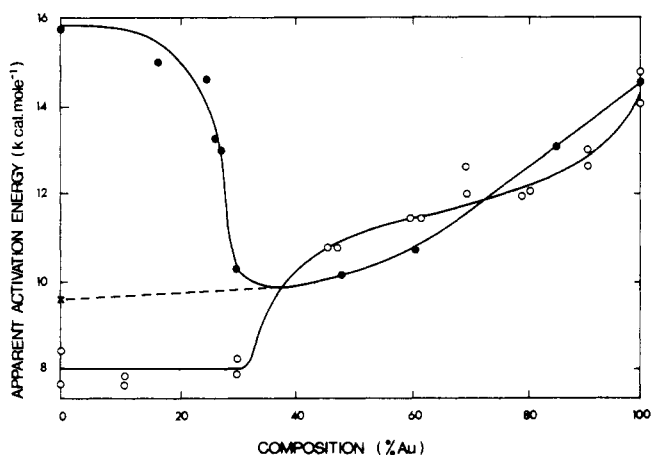
Figure 11. The apparent activation energy for formic acid decomposition on Pd–Au alloys: (O) wires,[164] (●) evaporated films,[159] and (X) randomly sintered Pd film.[159] The formation of the alloy films leads to changing relative extent of exposed crystal faces with alloy composition.[159]

VI. Addendum

A further number of pertinent papers have appeared. Comparison of product distributions in reactions of *n*-hexane and *n*-pentane on supported Pt–Au alloy catalysts shows that, at a sufficient dilution of the platinum atoms (1–12.5 atom % Pt) at least, selectivity for nondestructive reactions was increased.[165] The selectivity for benzene formation from *n*-hexane at *ca.* 300° has been found to be greater on Ir–Au than on Ir films essentially because of a tenfold difference in specific hydrogenolysis rate.[166] Pt–Sn alloy films behave similarly.[167] Rhodium films have been found to effect 1,6- but not 1,5-cyclization of *n*-hexane whereas a 92% Rh, 8% Sn film gives predominantly 1,5-cyclization (280–310°).[167] An increase in hydrogen pressure causes a sharp but equivalent increase in hydrogenolysis selectivity for methylcyclopentane reaction on Re and on Re–Au, so that the selectivity decrease of about one order of magnitude consequent on gold incorporation is still found.[168] An appreciable effect of hydrogen pressure on selectivity with other alloy combinations remains possible following the findings of Paál and Tétényi for platinum black,[169] and a fuller study with several alloy series is now clearly called for.

The role of multimetallic catalysts in reforming processes has been surveyed.[169a]

Infrared spectra of carbon monoxide adsorbed on Pd–Ag and Ni–Cu alloys support the idea that the second elemental constituent has little effect electronically on the Pd and Ni site atoms in these systems.[170] There is evidence, however, from the same study for a geometric "ensemble" effect in chemisorption which accordingly tends to support this concept for catalysis intermediates (section III.A.1).

van Santen and Boersma, using a regular solution model, have estimated that only 10–20% gold appears in the surface of Ag–Au alloys at 250° even at a bulk concentration of gold of 70%.[171] If it is assumed that gold has an equivalent influence to chlorine on the selectivity in ethylene oxidation (section III.A.2), the optimum yield of ethylene oxide would be expected at ~25 atom % Au. Because this surface composition would only be attained at very high bulk gold content, these authors conclude that the experimentally observed influence of gold content on selectivity[42,111] is the result of several as yet undetermined factors rather than simply a geometric effect. In view of this argument the finding[14] of a maximum in selectivity of oxidation of ethylene to acetic acid, acetaldehyde, and acetic anhydride at 80 atom % Au (section III.A.2) assumes a

particular interest.

For the preparation of supported alloy catalysts suitable for fundamental work, low metal loading,[172] use of a high-area silica support,[172] and hydrazine as a reducing agent for the mixed noble-metal salts[173] have been suggested.

The applicability of the available techniques for estimating charge shift in alloys has been more clearly appreciated. Systems studied include some of prominent catalytic interest. The Ag Knight shift in Pd–Ag alloys undergoes a nonlinear decrease with increase in palladium content, and it has been inferred that there is some movement of s-electron charge from silver to palladium sites.[174] Both Mössbauer shift[175] and NMR measurements[176] point to an s-electron donation from tin to platinum atoms in Pt–Sn alloys. The s-electron shift here does not therefore appear to be in the sense expected from electronegativities. This is in contrast with a previous rather striking correlation of this type for binary alloys of gold with 16 metallic elements in turn.[177] Watson, Perlman, and coworkers have argued that s charge transfers between the constituents in an alloy can be accompanied by a compensating d charge transfer.[178,179] For the Ag–Au system, in which an atomic size difference is not a complication, isomer shift determinations suggest an s charge transfer from silver to gold atoms of the order of 0.15 e. Thus, from XPS (which can be used to furnish estimates of changes in the bulk charge around an atomic site) it is concluded that the ratio of d-depletion, i.e., gold to silver, to conduction electron gain is 0.6 ± 0.2 in the case of $Au_{0.5}Ag_{0.5}$.[179] In a discussion of Au–Sn alloys the same group[180] suggest that the supposedly strong electronegativity of gold as manifested by conduction electron flow onto it (Mössbauer shift) reflects merely the screening of the d charge depletion due to hybridization. In any case, charge neutrality according to the Pauling electroneutrality principle is maintained in both these alloy systems and a similar situation may well obtain for Pt–Sn, already referred to.

A development in X-ray spectroscopy of solids is of considerable potential interest. It involves high resolution examination in the neighborhood of a characteristic absorption edge for each atomic species. Fourier analysis of the absorption fine structure gives a measure of the radial environment of each type of atom. Application to a Cr–Cu catalyst has been illustrated.[181]

VII. References and Notes

(1) R. L. Augustine, "Catalytic Hydrogenation," Marcel Dekker, New York, N.Y., 1965.
(2) P. N. Rylander, "Catalytic Hydrogenation on Platinum Metals," Academic Press, New York, N.Y., 1967.
(3) G. C. Bond, "Catalysis by Metals," Academic Press, New York, N.Y., 1962.
(4) F. Abelès, "Optical Properties and Electronic Structure of Metals and Alloys," North-Holland Publishing Co., Amsterdam, 1966, pp 553, 596.
(5) A. Karlsson, H. P. Myers, and L. Wallden, *Solid State Commun.*, 5, 971 (1967).
(6) H. Montgomery, G. P. Pells, and E. M. Wray, *Proc. Roy. Soc., Ser. A*, 301, 261 (1967).
(7) C. Norris and H. P. Myers, *J. Phys. F*, 1, 62 (1971) (UPS).
(7a) S. Hüfner, G. K. Wertheim, J. Wernick, and A. Melera, *Solid State Commun.*, 11, 259 (1972); V. V. Nemoshkalenko, *Dokl. Akad. Nauk SSSR*, 211, 1089 (1973), argues that Ag atoms are electron withdrawing in Pd–Ag (XPS).
(8) L. D. Roberts, D. O. Patterson, J. O. Thomson, and R. P. Levy, *Phys. Rev.*, 179, 656 (1969), and references therein; see, however, G. Longworth, *J. Phys. C*, 1, S81 (1970).
(9) (a) S. Hüfner, G. K. Wertheim, R. L. Cohen, and J. H. Wernick, *Phys. Rev. Lett.*, 28, 488 (1972); (b) D. H. Seib and W. E. Spicer, *ibid.*, 20, 1441 (1968).
(10) D. H. Seib and W. E. Spicer, *Phys. Rev. B*, 2, 1676 (1970).
(11) W. M. H. Sachtler and P. van der Plank, *Surface Sci.*, 18, 62 (1969).
(12) J. J. Byrne, P. F. Carr, and J. K. A. Clarke, *J. Catal.*, 20, 412 (1971).
(13) W. M. H. Sachtler and R. Jongepier, *J. Catal.*, 4, 654 (1965).
(14) (a) H. R. Gerberich, N. W. Cant, and W. K. Hall, *J. Catal.*, 16, 204 (1970); (b) H. R. Gerberich and W. K. Hall (Gulf Research and Development Co.), U.S. Patent 3,534,093 (1970); *Chem.*

Abstr., **73**, 130605u (1970).

(15) L. Whalley, D. H. Thomas, and R. L. Moss, *J. Catal.*, **22**, 302 (1971).

(16) D. A. Dowden, "Proceedings of the Fifth International Congress on Catalysis, 1972," North-Holland Publishing Co., Amsterdam, 1973, Paper 41, p 621.

(16a) This approach is in line with a recent trend in alloy physics when local electronic properties are under discussion,[17,18] and the concept, at least, seems important more generally for interpretation of alloy catalysis.

(17) V. Jaccarino, *J. Appl. Phys.*, **39**, 1166 (1968).

(18) C. G. Robbins, H. Claus, and P. A. Beck, *Phys. Rev. Lett.*, **22**, 1307 (1969).

(19) K. N. Zhavoronkova, G. K. Boreskov, and V. N. Nekipelov, *Dokl. Akad. Nauk SSSR*, **177**, 1124 (1967).

(20) G. C. Bond, D. A. Dowden, and N. Mackenzie, *Trans. Farad. Soc.*, **54**, 1537 (1958).

(21) R. P. Dessing, V. Ponec, and W. M. H. Sachtler, *Chem. Commun.*, 880 (1972).

(22) Y. Barron, G. Maire, D. Cornet, and F. G. Gault, *J. Catal.*, **2**, 152 (1963).

(23) J. M. Muller and F. G. Gault, *J. Catal.*, **24**, 361 (1972).

(24) M. A. McKervey, N. G. Samman, and J. J. Rooney, *J. Catal.*, **30**, 330 (1973).

(25) J. H. Sinfelt, A. E. Barnett, and G. W. Dembinski (Esso Research and Engineering Co.), U.S. Patent 3,442,973 (1969); *Chem. Abstr.*, **71**, 41018w (1969).

(26) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).

(27) R. Cramer and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **88**, 3534 (1966).

(28) P. Legzdins, G. L. Rempel, and G. Wilkinson, *Chem. Commun.*, 825 (1969).

(29) J. Kwiatek and J. K. Seyler, *J. Organometal. Chem.*, **3**, 421 (1965).

(30) G. C. Bond, G. Webb, P. B. Wells, and J. M. Winterbottom, *J. Chem. Soc.*, 3218 (1965).

(31) B. J. Joice, J. J. Rooney, P. B. Wells, and G. R. Wilson, *Discuss. Farad. Soc.*, **41**, 223 (1966).

(32) L. Ya Margolis, *Adv. Catal.*, **14**, 429 (1963).

(33) G. N. Schrauzer, *Adv. Catal.*, **18**, 373 (1968).

(34) S. Affrossman and S. J. Thomson, *J. Chem. Soc.*, 2024 (1962).

(35) V. M. Gryaznov, V. P. Polyakova, E. M. Savitskia, L. Frades, E. V. Khrapova, E. Khuares, and G. V. Shkola, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (11) 2520 (1970).

(36) J. H. Sinfelt, J. L. Carter, and D. J. C. Yates, *J. Catal.*, **24**, 283 (1972).

(37) (a) E. McMahon, P. F. Carr, and J. K. A. Clarke, *J. Chem. Soc. A*, 2012 (1971); (b) T. J. Plunkett and J. K. A. Clarke, *J. Chem. Soc., Farad. Trans. 1*, **68**, 600 (1972).

(38) V. Ponec and W. M. H. Sachtler, *J. Catal.*, **24**, 250 (1972).

(39) J. Kovács, G. Speier, and L. Markó, *Inorg. Chim. Acta*, **4**, 412 (1970).

(40) H. G. Rushford and D. A. Whan, *Trans. Farad. Soc.*, **67**, 3577 (1971).

(41) A. E. Morgan and G. A. Somorjai, *J. Chem. Phys.*, **51**, 3309 (1969).

(42) W. H. Flank and H. C. Beachell, *J. Catal.*, **8**, 316 (1967).

(43) L. S. Lobo, D. L. Trimm, and J. L. Figueiredo in ref 16, Paper 82, p 1159.

(44) L. E. Cratty, Jr., and W. W. Russell, *J. Am. Chem. Soc.*, **80**, 767 (1958).

(45) S. Carrà nd R. Ugo, *J. Catal.*, **15**, 435 (1969).

(46) L. K. Frevel and L. J. Kressley (Dow Chemical Co.), U.S. Patent 2,802,889 (1957); *Chem. Abstr.*, **51**, P17025i (1957) (Pd–Ag, Pd–Au, Pd–Cu). J. S. Elkins (British Petroleum Co., Ltd.) finds 80% selectivity in isopentene production from isoprene using 10–30% Pt alloys with Cu: British Patent 1,328,532 (1973); *Chem. Abstr.*, **79**, 136465u (1973).

(47) S. H. Inami, B. J. Wood, and H. Wise, *J. Catal.*, **13**, 397 (1969).

(48) H. E. Swift, F. E. Lutinski, and W. L. Kehl, *J. Phys. Chem.*, **69**, 3268 (1965).

(49) V. Ponec and W. M. H. Sachtler, ref 16, Paper 43, p 645.

(49a) No nickel pair sites would remain at less than 6–7 atom % Ni (see, e.g., K. C. Campbell and S. J. Thomson, *Trans. Farad. Soc.*, **55**, 306 (1959)).

(50) J. R. Anderson, ref 16, comments on Paper 43, p 655.

(50a) By corollary, constancy of product distribution, as found for diene hydrogenation on Pd–Au,[31] can be interpreted to mean that the same number of sites is needed to bond the respective intermediates providing that these do not significantly interconvert at reaction temperatures. A similar conclusion is possible for alkyne hydrogenation where products from but-2-yne do not vary significantly with % Pd in Pd–Au,[40] and therefore mono- and diadsorption on the acetylenic function[41] do not apparently lead to different products.

(51) J. M. Thomas and W. J. Thomas, "Introduction to the Physical Principles of Heterogeneous Catalysis," Academic Press, London, 1967, p 339.

(52) J. E. Germain, "Catalytic Conversion of Hydrocarbons," Academic Press, London, 1969: (a) pp 49, 103; (b) p 108.

(53) (a) P. B. Weisz, *Adv. Catal.*, **13**, 137 (1962); (b) ibid., **13**, 168, 174 (1962).

(54) J. W. Myers and F. A. Prange (Phillips Petroleum Co.), U.S. Patent 2,911,357 (1959); *Chem. Abstr.*, **54**, 23301a (1960).

(55) Institut Neftekhimicheskogo Sinteza An SSSR, British Patent 1,199,683 (1970).

(56) F. M. Dautzenberg (Shell Internationale Research Maatschappij

N. V.), German Offen., 2,121,765 (1971); *Chem. Abstr.*, **76**, 37875j (1972).

(57) E. E. Davies, J. S. Elkins, and R. C. Pitkethly (British Petroleum Co.), German Offen. 2,117,651 (1971); *Chem. Abstr.*, **76**, 37876k (1972).

(58) F. M. Dautzenberg and H. W. Kouwenhoven (Shell Internationale Maatschappij N. V.), German Offen. 2,153,891 (1972); *Chem. Abstr.*, **77**, 61513f (1972).

(59) R. E. Rausch (Universal Oil Products Co.), German Offen. 2,104,428 (1972); *Chem. Abstr.*, **77**, 166970f (1972).

(60) E. L. Pollitzer, *Platinum Met. Rev.*, **16**, 42 (1972).

(61) J. E. Weisang and P. Engelhard (Compagnie Francaise de Raffinage), German Offen. 2,139,069 (1972); *Chem. Abstr.*, **76**, 143167q (1972).

(62) N. Kominami, T. Iwaisako, and K. Ohki (Asahi Chemical Industry Co.), German Offen. 2,123,606 (1971); 2,127,348 (1971); 2,141,420 (1972); *Chem. Abstr.*, **76**, 74539y (1972); **76**, 48041k (1972); **77**, 77586t (1972).

(63) T. P. McCallister and K. R. O'Neal (Universal Oil Products Co.), German Offen. 2,104,429 (1971); *Chem. Abstr.*, **76**, 37870d (1972).

(64) J. C. Hayes (Universal Oil Products Co.), U.S. Patent 3,617,510 (1971); *Chem. Abstr.*, **76**, 35993x (1972).

(65) Cf. H. E. Swift and J. E. Bozik, *J. Catal.*, **12**, 5 (1968).

(66) D. F. Ollis, *J. Catal.*, **23**, 131 (1971); D. W. Hoffman, *J. Catal.*, **27**, 374 (1972). The latter author argues for a kinetic basis for this phenomenon.

(67) J. H. Sinfelt, ref 16, comment on Paper 43, p 653; *J. Catal.*, **29**, 308 (1973).

(68) J. H. Sinfelt and A. E. Barnett (Esso Research and Engineering Co.), U.S. Patent 3,567,625 (1971).

(69) R. R. Cecil, W. S. Kmak, J. H. Sinfelt, and L. W. Chambers, *Oil Gas J.*, 50 (Aug 7, 1972).

(70) J. R. Anderson, *Adv. Catal.*, **23**, 1 (1973).

(71) J. R. Anderson, ref 16, p 752.

(72) F. M. Dautzenberg and J. C. Platteeuw, *J. Catal.*, **19**, 41 (1970).

(73) B. H. Davis, *J. Catal.*, **23**, 340 (1971).

(74) Y. Barron, G. Maire, J. M. Muller, and F. G. Gault, *J. Catal.*, **5**, 428 (1966).

(75) B. A. Kazanskii, V. S. Fadeev, and I. V. Gostunskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 677 (1971).

(76) G. R. Lester, *J. Catal.*, **13**, 187 (1969).

(77) Z. Paál and P. Tétényi, *J. Catal.*, **30**, 350 (1973).

(78) P. W. Selwood, "Actes du Deuxième Congrès International de Catalyse, 1960, Paris," Vol. 2, Technip, Paris, 1961, p 1810.

(79) A. K. Galwey, *Proc. Roy. Soc., Ser. A*, **271**, 218 (1963).

(80) D. Shopov, A. Palazov, and A. Andreev, Proceedings of the Fourth International Congress on Catalysis, Moscow, 1968, Paper No. 30, p 528.

(80a) R. B. Moyes and P. B. Wells, *Adv. Catal.*, **23**, 121 (1973).

(81) R. E. Cunningham and A. T. Gwathmey, *Adv. Catal.*, **9**, 25 (1957).

(82) A. J. Melmed, "Molecular Processes on Solid Surfaces," E. Drauglis, R. D. Gretz, and R. I. Jaffe, Ed., McGraw-Hill, New York, N.Y., 1969, p 105.

(83) L Whalley, B. J. Davis, and R. L. Moss, *Trans. Farad. Soc.*, **66**, 3143 (1970).

(84) J. R. Anderson and R. J. Macdonald, *J. Catal.*, **13**, 345 (1969).

(84a) R. W. Joyner, B. Lang, and G. A. Somorjai, *J. Catal.*, **27**, 405 (1972).

(85) M. Boudart, *Adv. Catal.*, **20**, 153 (1969).

(86) P. Tétényi and L. Babernics, *J. Catal.*, **8**, 215 (1967); **17**, 35 (1970).

(87) R. W. Maatman, P. Mahaffy, P. Hoekstra, and C. Addink, *J. Catal.*, **23**, 105 (1971).

(87a) C. Corolleur, D. Tomanova, and F. G. Gault, *J. Catal.*, **24**, 401 (1972).

(88) F. E. Shephard and J. J. Rooney, *J. Catal.*, **3**, 129 (1964).

(89) J. R. Anderson, ref 16, p 752.

(89a) This effect would be expected to be more striking with catalysts having moderate metal dispersion where, as for platinum, cyclic isomerization has only about the same rate as (or less than) that of bond shift.[70] We note also that interruption of the surface network of active metal atoms begins at atom % of that element less than about 70 and the effect of further dilution with the inactive metal will be to begin to affect the benefit of reduced residues by restricting the migration of chemisorbed reactant. No striking trends of a similar kind are likely for high-dispersion catalysts where cyclic isomerization can already represent 80% or more of the total rearrangement.[70] In summary, the result for selectivity in aromatics production of the presence of a diluent alloy component, for other than the smallest metal crystallites, is expected to be beneficial, at any rate up to a surface content of diluent metal of ca. 30 atom %; the benefit described may be reversed, however, at percentages much higher than this, but the exact turn-around point is hazardous to estimate because of our present ignorance as to the decrease in extent of carbonaceous polymer with alloy composition. Clearly, although it is possible to relate in a superficial way with deduction (ii) the increase in aromatics yield reported from the use of alloy-reforming catalysts, further more systematic comparisons between such alloys will be needed to test these more detailed inferences. Tests needed would include ^{13}C labeling[87a] and, particularly, determination of alloy surface composition.

(90) Z. Paál and P. Tétényi, *J. Catal.*, **29**, 176 (1973).

(91) E.g., E. O. Box, L. E. Drehman, and F. Farha, Jr. (Phillips Petroleum Co.), German Offen. 2,127,353 (1971); *Chem. Abstr.*, **76**, 37879p (1971).

(92) K. D. Vesely and H. D. Gass (Universal Oil Products Co.), Ger-

man Offen. 2,128,603 (1971); *Chem. Abstr.*, **76**, 35962m (1972).
(93) D. W. Walker, E. O. Box, Jr., and F. Farha, Jr. (Phillips Petroleum Co.), German Offen. 2,136,487 (1972); *Chem. Abstr.*, **76**, 104363f (1972).
(94) W. E. Armstrong (Shell Oil Co.), U.S. Patent 3,156,735 (1964); Belgian Patent 611,379 (1962); *Chem. Abstr.*, **57**, 14933f (1962).
(95) J. R. Kittrell (Chevron Research Co.), U.S. Patent 3,632,501 (1971); *Chem. Abstr.*, **76**, 74532r (1972).
(96) S. M. Csicsery (Chevron Research Co.), U.S. Patent 3,617,489 (1971); *Chem. Abstr.*, **76**, 26967q (1972).
(97) J. C. Hayes (Universal Oil Products Co.), U.S. Patent 3,617,510 (1971); *Chem. Abstr.*, **76**, 35993x (1971).
(98) J. J. Byrne and J. K. A. Clarke, *J. Catal.*, **9**, 166 (1967).
(99) R. L. Moss and D. H. Thomas, *Trans. Farad. Soc.*, **60**, 1110 (1964).
(100) F. L. Williams and M. Boudart, *J. Catal.*, **30**, 438 (1973).
(101) R. Bouwman, L. H. Toneman, and A. A. Holscher, *Surface Sci.*, **35**, 8 (1973).
(101a) D. P. Smith, *Surface Sci.*, **25**, 171 (1971) (low-energy ion-beam scattering); B. F. Phillips, *J. Vac. Sci. Technol.*, **11**, 1093 (1974) (secondary-ion mass analysis).
(102) W. M. H. Sachtler and G. J. H. Dorgelo, *J. Catal.*, **4**, 654 (1966).
(102a) On thermodynamic grounds this is greater for smaller crystallites.
(103) J. V. Valentine, *Chem. Rev.*, **73**, 235 (1973).
(104) G. K. Boreskov, *Adv. Catal.*, **15**, 286 (1964).
(105) T. B. Gruenwald and G. Gordon, *J. Catal.*, **6**, 220 (1966).
(106) A. W. Czanderna, *J. Phys. Chem.*, **68**, 2765 (1964).
(107) P. A. Kilty, N. C. Rol, and W. M. H. Sachtler, ref 16, p 929.
(108) H. H. Voge and C. R. Adams, *Adv. Catal.*, **17**, 151 (1967).
(109) H. T. Spath and K. Torkar, *J. Catal.*, **26**, 163 (1972).
(110) B. M. W. Trapnell, *Trans. Farad. Soc.*, **52**, 1618 (1956).
(111) F. G. Young, ref 16, p 938.
(112) W. M. H. Sachtler, ref 16, p 938.
(113) R. E. Kenson and M. Lapkin, *J. Phys. Chem.*, **74**, 1493 (1970).
(113a) F. Abélès, J. Rivory, and M. L. Theye, "Optical Investigation of the Electronic Structure of Binary Alloys," Final Report, Laboratoire d'Optique, University of Paris, Jan 1973, and references therein; V. V. Nemoshkalenko, A. I. Senkevich, V. G. Aleshin, and V. V. Gorskii, *Phys. Status Solidi B*, **58**, K125–K127 (1973).
(114) D. Y. Cha and G. Parravano, *J. Catal.*, **18**, 200 (1970); cf. R. R. Ford and J. Pritchard, *Chem. Commun.*, 362 (1968).
(115) N. H. A. van Ham, B. E. Nieuwenhuys, and W. M. H. Sachtler, *J. Catal.*, **20**, 408 (1971).
(116) J. H. de Boer, *Adv. Catal.*, **8**, 17 (1956).
(117) B. Calcagno, N. Ferlazzo, and M. Ghirga (Societa Italiana Resine S.p.A.), German Offen. 1,958,586 (1970); 1,958,597 (1970); 1,958,596 (1971); *Chem. Abstr.*, **74**, 35158n, 35159p, 140884u (1971).
(118) R. L. Moss and D. H. Thomas, *J. Catal.*, **8**, 162 (1967).
(119) Shell International Research Maatschappij N. V., British Patent 940,710 (1963); W. E. Armstrong (Shell International Research Maatschappij N. V.), Belgian Patent 611,379 (1962); *Chem. Abstr.*, **57**, 14933f (1962).
(120) E. F. G. Herington and E. K. Rideal, *Trans. Farad. Soc.*, **40**, 405 (1944); E. K. Rideal, "Concepts in Catalysis," Academic Press, New York, N.Y., 1968, p 38.
(121) E.g., K. C. Campbell, *J. Catal.*, **27**, 7 (1972).
(122) E.g., A. J. Silvestri, P. A. Naro, and R. L. Smith, *J. Catal.*, **14**, 386 (1969).
(122a) G. A. Somorjai, *J. Catal.*, **27**, 452 (1972).
(123) J. Freel and A. K. Galwey, *J. Catal.*, **10**, 277 (1968) (nickel carbide); R. B. Levy and M. Boudart, *Science*, **181**, 547 (1973) (tungsten carbide). Hydrogenolysis activity is much less for both carbides than for the parent metals.
(124) (a) C. A. Brown, *J. Org. Chem.*, **35**, 190 (1970), and references therein; (b) P. Lenfant, C. Legras, and B. Kervella, *C. R. Acad. Sci.*, **260**, 1636 (1965) ("nickel boride").
(125) N. N. Greenwood, R. V. Parish, and P. Thornton, *Quart. Rev., Chem. Soc.*, **20**, 441 (1966) (borides: electronic structure).
(126) E.g., J. S. Brinen and A. Melera, *J. Phys. Chem.*, **76**, 2525 (1972).
(127) C. Horrex, R. B. Moyes, and R. C. Squire, ref 80, Paper 25, p 435.
(128) M. Kowaka, *J. Jpn. Inst. Metals*, **23**, 655 (1959).
(128a) The basis described is distinct in principle at least, from that referred to by Bond and Wells[129] for conditions of partial conversion on 100% Pd which originates in competitive adsorption of alkyne and alkene and which is an example of the thermodynamic factor in selectivity.
(129) G. C. Bond and P. B. Wells, *Adv. Catal.*, **15**, 91 (1964).
(130) B. R. Coles and J. C. Taylor, *Proc. Roy. Soc., Ser. A*, **267**, 139 (1962).
(130a) There are grounds[131] for believing that surface silver enrichment may be greater in extent in Pd–Ag than is gold-enrichment in Pd–Au of similar atom % Pd and under otherwise comparable conditions: the nominal atom % Ag at which surface d-holes disappear would then be less than anticipated from the bulk properties of Pd–Ag or those of a superficially similar alloy system.
(131) R. Bouwman, Thesis, Rijksuniversiteit, Leiden, 1970.
(132) G. C. Bond and P. B. Wells, ref 78, Vol. 1. p 1159.
(133) E. von Meerwall and D. S. Schreiber, *Phys. Rev. B*, **3**, 1 (1971).
(134) S. Kirkpatrick B. Velicky, and H. Ehrenreich, *Phys. Rev. B*, **1**, 3250 (1970).
(135) E.g., B. Window and G. Longworth, *J. Phys. F, Metal Phys.*, **1**, 718 (1971).
(136) B. R. Coles, *Phys. Lett.*, **8**, 243 (1964).
(137) A. J. Heeger, *Solid State Phys.*, **23**, 283 (1969).
(137a) D. A. Dowden, *J. Chem. Soc.*, 242 (1950).

(138) See G. Wolf and B. Baronowski, *Phys. Chem. Solids.* **32**, 1649 (1971), for the problem of the specific heat of nickel hydride.
(139) E.g., J. Kwiatek in "Transition Metals in Homogeneous Catalysis," G. N. Schrauzer, Ed., Marcel Dekker, New York, N.Y., 1971, p 15.
(140) C. E. Coffey, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1741 (1964); L. Brewer, "Transition Metal Alloys. Chemists' View," Proceedings of the Conference of the American Institute of Physics 1972, No. 10, "Magnetism and Magnetic Materials" (Part 1), pp 1–16, 1973.
(141) E.g., G. Dolcetti, M. Nicolini, M. Giustiniani, and U. Belluco, *J. Chem. Soc. A*, 1387 (1969).
(142) J. P. Collman, F. D. Vastine, and W. R. Roper, *J. Am. Chem. Soc.*, **90**, 2282 (1968).
(143) T. S. Cameron, C. K. Prout, G. V. Rees, M. L. H. Green, K. K. Joshi, G. R. Davies, B. T. Kilbourn, P. S. Braterman, and V. A. Wilson, *J. Chem. Soc., Chem. Commun.*, 14 (1971).
(144) C. G. Pitt, L. K. Monteith, L. F. Ballard, J. P. Collman, J. C. Morrow, W. R. Roper, and D. Ulkii, *J. Am. Chem. Soc.*, **88**, 4286 (1966).
(145) T. J. Gray, N. G. Masse, and H. G. Oswin, ref 78, p 1697; characteristics of recent Pt–Re based reforming catalysts are summarized in ref 60.
(146) (a) G. C. Bond and D. E. Webster, *Platinum Met. Rev.*, **9**, 12 (1965); (b) *Ann. N.Y. Acad. Sci.*, **158**, 540 (1969).
(147) N. I. Popov, D. V. Sokol'skii, F. B. Bizhanov, and Zh. G. Akchalov, *Russ. J. Phys. Chem.*, **46**, 363 (1972).
(148) P. N. Rylander and M. Kilroy, *Engelhard Ind. Tech. Bull.*, **9**, 14 (1968); cf. S. Nishimura, *Bull. Chem. Soc. Jpn.*, **34**, 1544 (1961).
(149) R. B. Anderson and C. Kemball, *J. Catal.*, **6**, 82 (1966).
(150) P. N. Rylander, L. Hasbrouck, S. G. Hindin, R. Iverson, I. Karpenko, and G. Pond, *Engelhard Ind. Tech. Bull.*, **8**, 93 (1967); K. Yoshida, *Shokubai*, **10**, 2 (1968).
(151) W. L. Kehl, F. E. Lutinski, and H. E. Swift (Gulf Research and Development Co.), U.S. Patent 3,639,647 (1972); *Chem. Abstr.*, **76**, 116974u (1972). A similar result appears to have been found for Cr or Mn addition to Pt or Pd by O. V. Andreeva and R. I. Ismailov, *Mater. Nauchn. Konf., Inst. Org. Fiz. Khim., Akad. Nauk SSSR*, *1969*, 130 (1970); *Chem. Abstr.*, 78, 60438u (1973).
(152) B. Window and G. Longworth, *J. Phys. F*, **1**, 718 (1971).
(153) E. Kudielka-Artner and B. B. Argent, *Proc. Phys. Soc., London.* **80**, 1143 (1962).
(154) J. H. Sinfelt, *Catal. Rev.*, **3**, 175 (1969).
(155) D. W. McKee and F. J. Norton, *J. Catal.*, **3**, 252 (1964).
(156) R. L. Moss and L. Whalley, *Adv. Catal.*, **22**, 115 (1972).
(157) C. Kemball, *Proc. Roy. Soc.. Ser. A*, **217**, 376 (1953).
(157a) J. Eggs and K. Ulmer, *Z. Phys.*, **213**, 293 (1968).
(158) D. A. Dowden, "Chemisorption and Catalysis," E. P. Hepple, Ed., Institute of Petroleum, London, 1970, p 1.
(159) J. K. A. Clarke and E. A. Rafter, *Z. Phys. Chem. (Frankfurt am Main)*, **67**, 169 (1969).
(159a) E. G. Allison and G. C. Bond, *Catal. Rev.*, **7**, 233 (1973).
(160) (a) A. D. O Cinneide and J. K. A. Clarke, *Catal. Rev.*, **7**, 213 (1973); (b) E. G. Schlosser, *Ber. Bunsenges. Phys. Chem.*, **75**, 358 (1969).
(161) J. R. Anderson and Y. Shimoyama, ref 16, p 695.
(162) R. Bouwman and W. M. H. Sachtler, *J. Catal.*, **26**, 63 (1972).
(163) K. Christmann and G. Ertl, *Surface Sci.*, **33**, 254 (1972); G. Ertl and J. Küppers, *J. Vac. Sci. Technol.*, **9**, 829 (1972) (Pd–Ag, Ni–Cu).
(164) D. D. Eley and P. Luetic, *Trans. Farad. Soc.*, **53**, 1483 (1957).
(165) J. R. H. van Schaik, R. P. Dessing, and V. Ponec, *J. Catal.*, in press.
(166) T. J. Plunkett and J. K. A. Clarke, *J. Catal.*, **35**, 330 (1974).
(167) Z. Karpiński and J. K. A. Clarke, *J. Chem. Soc.. Faraday Trans. 1.* **71**, 893 (1975).
(168) J. K. A. Clarke and J. F. Taylor, in course of publication.
(169) Z. Paál and P. Tétényi, *J. Catal.*, **29**, 176 (1973).
(169a) L. M. Lovell, T. M. Moore, and R. D. Petersen, ACS Division of Petroleum Chemistry Symposium. New York meeting, August 27, 1972.
(170) Y. Soma-Noto and W. M. H. Sachtler, *J. Catal.*, **32**, 315 (1974); **34**, 162 (1974).
(171) R. A. van Santen and M. A. M. Boersma. *J. Catal.*, **34**, 13 (1974).
(172) D. Cormack, D. H. Thomas, and R. L. Moss, *J. Catal.*, **32**, 492 (1974) (Pd–Ag).
(173) E. G. Allison and G. C. Bond, unpublished work (Pd–Au). See also citation 85 in ref 159a. Special attention to purity of reagents is implicit.[148]
(174) A. Narath, *J. Appl. Phys.*, **39**, 553 (1968); R. J. Snodgrass, *Phys. Rev.. B*, **1**, 3738 (1971).
(175) J. S. Charlton, M. Cordey-Hayes, and I. R. Harris, *J. Less Common Metals*, **20**, 105 (1970).
(176) H. T. Weaver, R. K. Quinn, R. J. Baughman, and R. C. Knauer, *J. Chem. Phys.*, **59**, 4961 (1973), and references therein.
(177) P. H. Barrett, R. W. Grant, M. Kaplan, D. A. Keller, and D. A. Shirley, *J. Chem. Phys.*, **39**, 1035 (1963). An opposite trend to this for Pt alloys is discussed by N. Benczer-Keller in "Platinum Group Metals and Compounds," *Adv. Chem. Ser.* **No. 98**, 135 (1971).
(178) L. H. Bennett and R. E. Watson, "Charge Transfer/Electronic Structure of Alloys," L. H. Bennett and R. H. Willens, Ed., Metallurgical Society of A.I.M.E., 1973. p 1; *Chem. Abstr.*, **81**, 18613j (1974).
(179) R. E. Watson. J. Hudis. and M. L. Perlman. *Phys. Rev.. B*, **4**, 4139 (1971).
(180) R. M. Friedman, J. Hudis, M. L. Perlman, and R. E. Watson, *Phys. Rev.*, **8**, 2433 (1973).
(181) F. W. Lytle, D. E. Sayers, and E. B. Moore. Jr., *Appl. Phys. Lett.*, **24**, 45 (1974).