JOURNAL REVIEW

Progress Toward the a Priori Determination of Catalytic Properties

JOHN B. BUTT

Department of Chemical Engineering
and
Ipatieff Catalytic Laboratory
Northwestern University
Evanston, Illinois, 60201

SCOPE

The ultimate achievement in catalysis would be the ability to determine without experimentation the optimum catalyst for a given chemical reaction. Fortunately, we are assured of a certain degree of job security, for this feat is certainly not possible at present, nor does it seem likely for at least some time to come. What we can do, however, is to make use of the accumulated wisdom and experience resulting from decades of research in catalysis through development of correlations which can provide some norms for catalytic behavior.

The present review considers a number of these correlations, both old and new, with concern as to the progress which has been made over the years towards the ultimate achievement. In general, the concepts of the active site and surface complexes are viewed as ingredients more or less common to all correlations. Questions which should be addressed are the nature (chemical, geometric) of the active site and its relationship to surface structure, the density of active sites, chemistry of surface reactions at active sites, and the influence of electronic factors on the nature of active sites. Many correlations have an extensive history, as will become apparent, so the review presents an interesting combination of old and new in representative, if not comprehensive, form.

CONCLUSIONS AND SIGNIFICANCE

There is a wide variation in the degree of understanding of different types of catalysts. This depends on both the catalytic system and who is trying to understand it. Since this review ranges all the way from quantum mechanical calculations of chemisorption on metals to ex post facto correlations of coke deposition on silica-alumina. And one general observation can be made concerning the correlations considered here: they all work, sort of.

Chemisorption/titration methods have provided a significant amount of information regarding the nature of acid oxide and supported metal surfaces. In the latter case, it is found that rather simple geometric concepts may provide quite effective means of activity correlation, particularly for very highly dispersed metals with accompanying small crystallite dimension. Electronic theories, in and out of favor over the past 30 years return with deeper insight due to recently developed capabilities in quantum chemical calculations. The relationship between strength of chemisorption and activity seems firmly established on both metals and oxides, at least for the few systems for which sufficient experimental information exists.

Correlations in catalysts seem to remain an experiment first, theory second matter; however, there appears to be some progress in the understanding of relationships once thought to be strictly empirical. Examples in this review deal with the compensation effect, catalyst deactivation, and alloy catalysts.

To those readers actively engaged in catalysis research, apologies are offered for the presumption implied by the title of this review. Perhaps it should be "Has There Been Progress Toward the a Priori Determination of Catalytic Properties?" Probably one would admit that there has been progress of some sort, and the purpose of the present discussion would be to define a proper modifier for the noun *progress*, to wit: *appreciable, little, slight, large, discernable, substantial, considerable, distinguishable, vast, moderate, distinct, minimal, marked, enormous, miniscule, unexpected, atrocious, uncommon, unbelievable, noticeable, interesting, subtle, minute, gross, significant, or imperceptible.*[*]

To start at the beginning, let us recall the original writing of Berzelius (1836) on the subject (Robertson, 1975):

> "It is, then, proved that several simple or compound bodies, soluble and insoluble, have the property of exercising on other bodies an action very different from chemical affinity. By means of this action they produce, in these bodies, decompositions of their elements and different recombinations of these same elements to which they remain indifferent."

This is still a pretty good phenomenological description of catalysis. However, a priori determination of catalytic properties means that we must know to some level *how* these "decompositions . . . and different recombinations . . ." occur as far down on the molecular scale as possible. Now it is an historical fact that research in catalysis has been primarily experimentally oriented, and attempts to organize information concerning the general aspects of

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[*] The reader may be misled into thinking there is some substantive difference in the measures cited here. In fact, the list was culled from undergraduate unit operations lab reports over a 7 yr. period at Yale University. At issue was the description of about a 50% difference between laminar flow theory and experimentally measured heat transfer coefficients for a heat exchanger operated in transition flow.

TABLE 1. SOME CORRELATION IN CATALYSIS OVER THE YEARS SINCE 1900

Date	Major concepts	Some associated names
∼1910	Unstable surface Intermediate compounds	Sabatier
∼1920	Lattice imperfections	Many
∼1925	Surface active sites	Taylor
∼1930	Geometric properties of the surface	Balandin, Beeck
∼1950	Electronic properties Metals Semiconductors	 Boudart, Beeck Hauffe, Volkenstein
∼1960	Unstable surface Intermediates and surface Active sites	Sabatier, Taylor

catalytic reaction systems would more properly be termed correlations rather than theories in the strictest sense of that term. It is thus appropriate to first take a brief look at the history of various correlations in heterogeneous catalysis over the years.

CORRELATIONS IN CATALYSIS—A SHORT HISTORY

Table 1 gives a summary of a number of concepts which have been used since the beginning of this century to correlate catalytic properties. The list is not exhaustive, and perhaps the chronology is not as well defined as it might be, but the variety of factors which people have thought to be important in catalysis provides a clue as to the wide latitude possible in approaches to the problem. The table also indicates some periodicity as to the relative favor in which the various correlations have been viewed. This is true to some extent, but in most cases there is considerable overlap between the different approaches, and it would be incorrect to attempt a sharp distinction between them. For example, the idea that lattice imperfections might be important in heterogeneous catalysis has been around almost since the beginnings of x-ray crystallography, when it became clear that real crystals were not the geometrically neat things that artists' drawings tend to show. In metal crystals there can exist edge and screw dislocations, Schottky and Frenkel defects—any of which can introduce substantial changes in the geometry of the surface and simultaneously alter its microscopic electronic properties. Thus, geometric properties, electronic properties, and lattice imperfections are all involved in this type of correlation. Similarly, the defect structure of semiconductor oxides plays a large role in the electronic theory of the catalytic properties of those materials. Some references to representative studies which have attempted to relate catalytic activity to defect structure are given in Table 2, and the matter has been thoroughly reviewed by Thomas and Thomas (1967).

In what follows we shall discuss representative examples of correlations from the literature, classified along the lines given in Table 1. However, we have just commented upon the dangers associated with unnecessarily sharp distinctions between these correlations. As a unifying theme, then, we shall use the concepts of surface intermediates and surface active sites; each of the approaches given in Table 1 plays a slightly different role in such a view of the catalytic event.

The basis for this viewpoint was established a number of years ago in an excellent summary by Boudart (1961), which should be required reading for those interested in the topic.

TABLE 2. LATTICE IMPERFECTIONS AND CATALYTIC ACTIVITY

Reference	Description
1. Duell and Robertson, *Trans. Faraday Soc.*, **57**, 1416 (1954).	Cu and Ni wire in formic acid decomposition; flash at high temperature to freeze defect structure into surface.
2. Farnsworth and Woodcock, *Advan. Catalysis*, **9**, 123 (1957).	Enhancement of activity of Ni and Pt for ethylene hydrogenation after ion bombardment of surface.
3. Sosnovsky, *J. Phys. Chem. Solids*, **10**, 304 (1959).	Enhancement of activity of Ag, 100, 110, and 111 faces, for formic acid decomposition after bombardment with Ar.
4. Uhara et al., *Nature, Lond.*, **192**, 867 (1961).	Activity changes for cold worked metals (Cu, Pt, Ni) for ethanol dehydrogenation and o-p H_2 conversion.
5. Hall and Rase, *Nature, Lond.*, **199**, 585 (1963).	Ethanol dehydrogenation on defect structures of LiF.
6. Krauss, *Z. Elektrochem.*, **53**, 320 (1940).	Ammonia oxidation vs. oxygen stoichiometry in MnO, CoO, NiO and Fe_2O_3.

CRITICAL FACTORS IN DETERMINATION OF CATALYTIC PROPERTIES

To an important extent, the nature of the surface intermediate compound, and thus the course of the surface reaction, is established by the nature of the active site on the surface. There are a number of questions which need to be answered concerning the active site before we can attain any significant understanding of a given catalytic reaction. Important among these would be such questions as:

1. What is the nature (chemical, geometric) of the active site and how is it related to surface structure?
2. How many active sites are there per unit area?
3. What is the area?
4. What is the chemistry of the reactions at the active site?
5. Are there specific properties of the site which will permit investigation independent of a particular reaction?

Certainly, if one had available answers to all these questions for a sufficient number of related catalysts and related reactions, then at least a reliable extrapolation to other similar catalysts and reactions would be within the realm of reasonable possibility. Whether this represents an a priori determination can be argued, but these questions certainly establish a logical starting point.

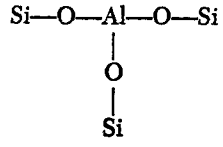
In the following we will be concerned with correlations and comparisons based on various measures of catalytic activity. Such measures include the temperature required for a given conversion, the space velocity required for set conversion at a given temperature, the conversion at set temperature, and the reaction rate at set temperature and reaction mixture composition. Some of these are rather inaccurate measures of activity, and caution must be exercised in making quantitative judgments; it will be seen that in many cases, while trends can be identified, definitive conclusions cannot be made.

NATURE OF ACTIVE SITES AND THEIR NUMBER

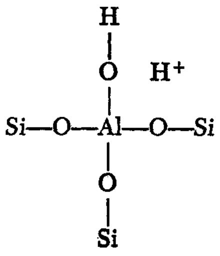
A considerable amount of information concerning the chemical nature of active sites and their number for several classes of catalysts has been developed by using chemical titration/chemisorption techniques. These are distinct from the physical adsorption methods which have been developed for measurement of total surface area and internal volume-area distribution which have been reviewed elsewhere (Innes, 1968; Gregg and Sing, 1967), since information obtained from the specific chemical nature of the chemisorption bond is used. Two types of catalysts, both of considerable technological importance as well as of scientific interest, have primarily been investigated by this method: metal oxides and supported transition metals.

Chemical Titration Methods for Acidic Oxide Surfaces

A number of oxides, used either as catalysts alone or in bifunctional formulations, have been shown to be acidic in nature. For example, in silica-alumina, it has been proposed (Tamele, 1950) that the presence of aluminum atoms in the surface of the silica structure leads to the development of acidity through formation of two types of sites:



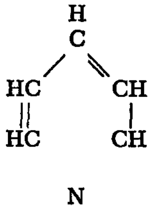
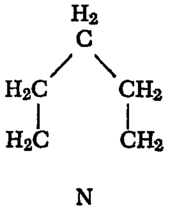
(A)



(B)

in which A acts as a Lewis acid (capable of accepting electrons) and B a Brønsted acid (capable of donating protons). The acidic nature of the hydrated surface of B is apparent; however, the development of Lewis acidity may not be so clear. This arises from the fact that the aluminum in the surface layer is incompletely coordinated, lacking one oxygen bond for formation of the stable eight valence electrons. It thus will accept a pair of electrons from a suitable donor species. There are, of course, many such species, as shown in Table 3, a number of which are well-known catalyst poisons (Butt, 1972).

TABLE 3. ELECTRONIC CONFIGURATION OF SOME TYPICAL DONOR SPECIES ENCOUNTERED IN CATALYSIS

Hydrogen sulfide	H S H
Phosphine	H P H H
Organic thiol	(R)C S H
Organic sulfide	(R)C S C(R)′
Pyridine	
Piperidine	
Ammonia	H H N H H

Whether one deals with Lewis or Brønsted acid sites, the possibility exists of strong and specific acid-base interactions with such compounds. In principle, this property of surface acidity should be characteristic of any oxide with coordinatively unsaturated metal atoms in the surface layer. Hence, one can use data on the chemisorption of basic compounds as some measure of surface acidity for a wide variety of oxides. Indeed, if we can envision stoichiometry such as illustrated in Figure 1 for pyridine on alumina, chemisorption data should provide information on the total number of sites.* Now, for this information to be of use in correlation of catalytic properties, acidity must play some role in the reactions for which such oxides are active catalysts. This is by now well established for reactions such as cracking or isomerization catalyzed by silica-alumina, to cite just one example.

The most widely employed method of chemical titration for oxides utilizes chemisorption from the gas phase of such organic bases as quinoline or pyridine. The total uptake at saturation is used as the measure of acidity, although there are some tricks in the interpretation of such data, as will be discussed subsequently. Some idea of the methods which can be employed and the information which can be obtained is provided by the classical early work of Mills et al. (1950). They studied a number of silica and silica-alumina cracking catalysts for activity in cumene cracking in a portion of their work, correlating loss of activity vs. uptake of various basic nitrogen compounds on the catalyst. Also, they compared the adsorption of quinoline on silica and silica-alumina, as shown in Figure 2*a*. It is seen that quinoline is completely reversibly adsorbed on silica, but is partially irreversibly adsorbed on the silica-alumina, immediate, direct evidence of the stronger acidity of silica-alumina. Partial poisoning studies on the silica-alumina are shown in Figure 2*b*; in each case the poisoning is highly selective, with activity approximately exponentially dependent on the total uptake. The effectiveness of these compounds in poisoning of cumene cracking is quinaldine > quinoline > pyrrole > piperidine > decylamine > aniline, which is not in the same order as their relative basic strengths. However, some of these compounds (notably piperidine) are also partially cracked under conditions of the experiments; when allowance is made for this cracking, there is excellent correlation between basic strength and effectiveness as a poison. In view of these results, it was proposed that the amount of chemisorption of a compound such as quinoline* "... thus measures a fundamental property of the catalyst which is related to its ability to act as a catalyst." The property measured we now know to be the surface acidity of the catalyst.

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* The figure indicates the existence of Brønsted acid sites on alumina. In fact this is disputed by many on the basis of accumulated infra-red data which gives no evidence of the existence of the pyridinium ion on the surface.

* Quinoline is often used as the reagent in chemisorption experiments because it is not difficult to handle, is chemically stable up to around 350°C, and is rapidly adsorbed.

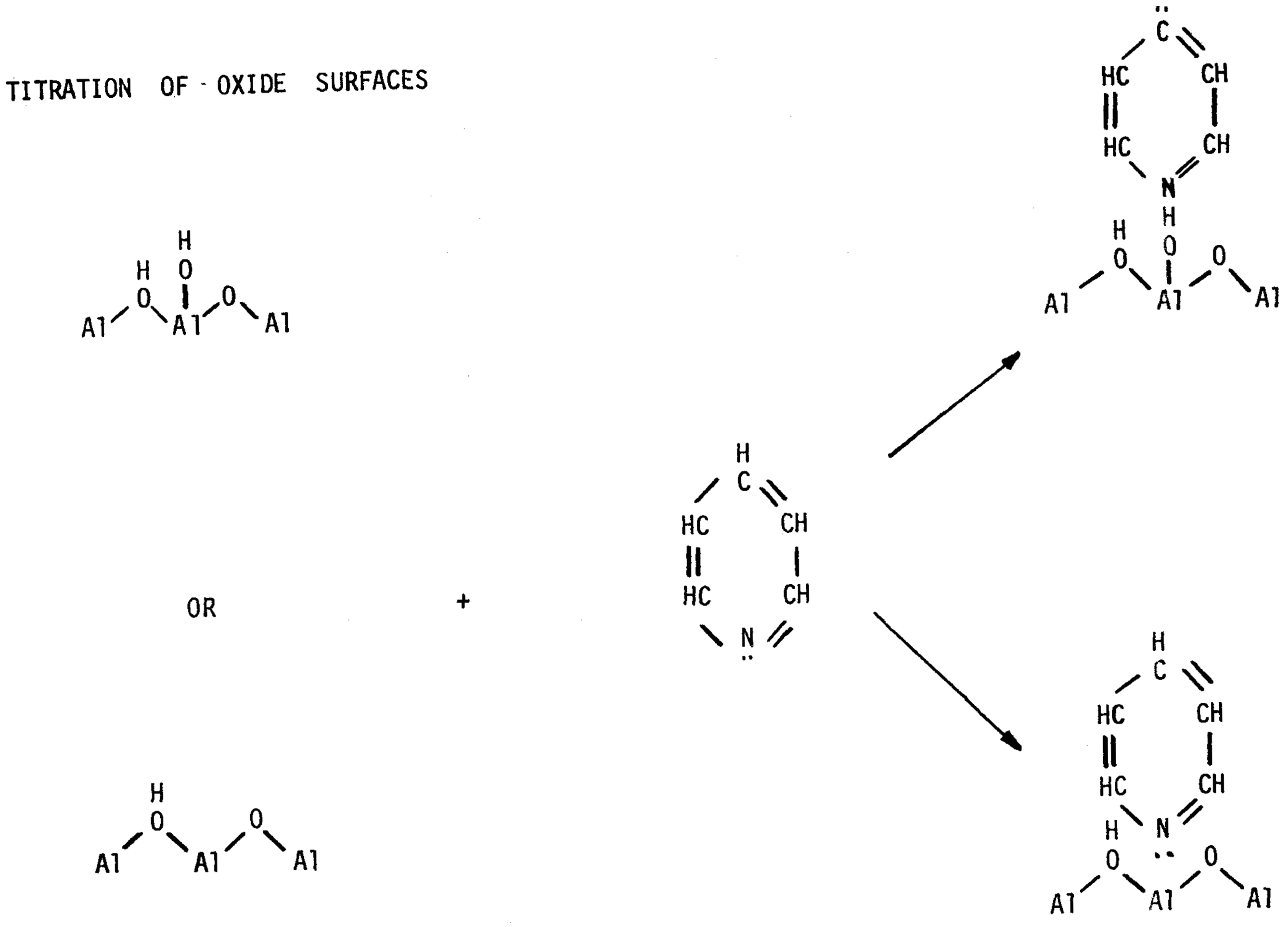

Fig. 1. Titration of oxide surfaces.

An example of the application of such a correlation to catalytic systems of practical importance is shown in Figure 2*c*. The cracking activity determined by a standard procedure of a series of catalysts for Light East Texas gas oil is seen to be in excellent agreement with expectations based on the cumene cracking results. In fact, given the uncertainties we are accustomed to in catalysis, such a result is indeed remarkable.

The success of this titration method, or numerous variants thereof, over the years in correlation of catalytic activity for reactions which are acid catalyzed is well established and has been reviewed in detail elsewhere (Goldstein, 1968). Yet, there are some complicating factors which make the task of interpretation of such correlations less obvious than might appear on first sight. Experimentally, these manifest themselves in two principal ways:

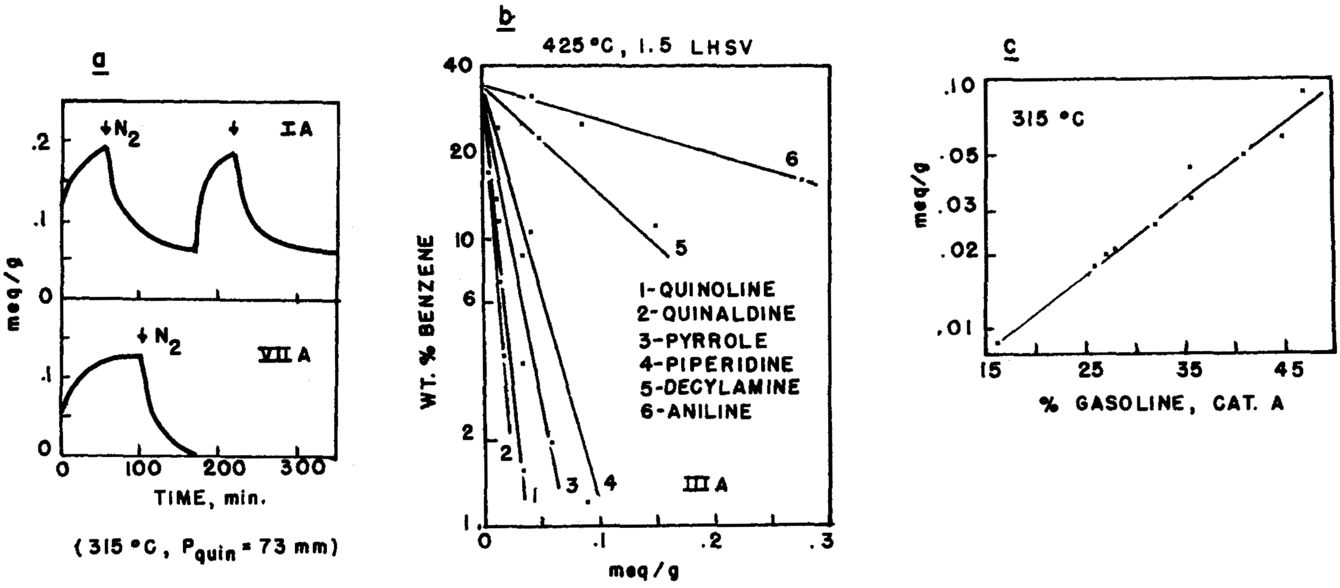

Fig. 2. Nitrogen compounds and silica-alumina. Catalysts are I A, III A: 12.5% Al_2O_3, 273 m^2/g; VII A, SiO_2 (calcined), 330 m^2/g. *(a)* Quinoline sorption at 315°C; *(b)* poisoning of cumene cracking activity; *(c)* correlation of activity with quinoline uptake for a variety of SiO_2-Al_2O_3, SiO_2-MgO, and SiO_2-ZnO_2 catalysts. (After Mills et al., 1950.)

1. Chemisorption capacities for a given catalyst vary for different adsorbates; hence the number of acid sites depends on the chemical system. Goldstein (1968) cites typical chemisorption capacities for commercial silica-alumina cracking catalysts to be 6×10^{12} and 3×10^{12} molecules/cm^2 for quinoline at 300° and 400°C, respectively, which are in turn about one-tenth the values obtained from ammonia chemisorption.

2. The surface acidity and number of adsorption sites determined by titration with a particular adsorbate may not correspond to the sites involved in a given reaction, even though it is acid catalyzed.

These factors are obviously interrelated and reflect the existence of a distribution of strengths of the acid sites on the surface of typical catalysts. A representative result is given by the work of Parera (1968) on the poisoning of oxide catalysts by organic bases, in which the particular interest was to compare the nature of the variation in activity vs. the amount of poison characteristic for various oxides and poisons. Some results for methanol dehydration on silica-alumina are shown in Figure 3. Two characteristic regions of relative activity may be identified: a linear region at smaller loadings of poison and an exponential decay in activity at higher loadings. It was shown that the linear region in these experiments was due to the deactivation of homogeneous sites, that is, of equal acid strength. The exponential portion of the curve is not so uniquely interpreted; it could indicate heterogeneity of the weaker acidic sites which, incidentally, do not contribute substantially to total dehydration activity, or it could be the result of interaction between poison molecules on adsorption at high surface coverage. As in the case of Mills et al. (1950), the amount of base required to effect a given loss of activity differs from case to case.

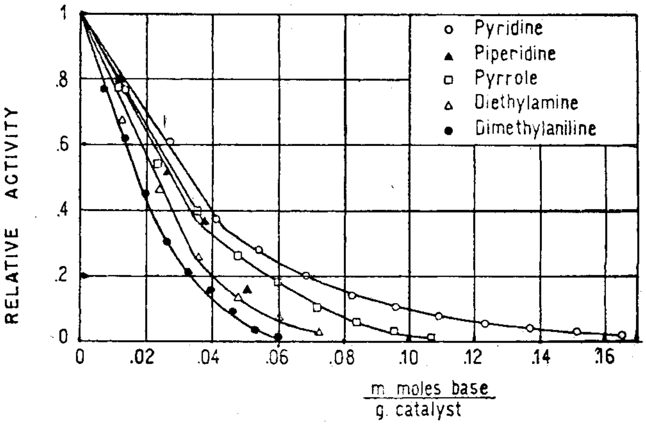

Fig. 3. Titration of activity of SiO_2-Al_2O_3 for methanol dehydration with various organic bases, $T = 228°C$. Catalyst is 13% Al_2O_3, 460 m^2/g. (After Parera, 1968.)

A classical work on the relationship between intrinsic acidity and catalytic activity is that of Pines and Haag (1960) for alumina. Model reactions, requiring different

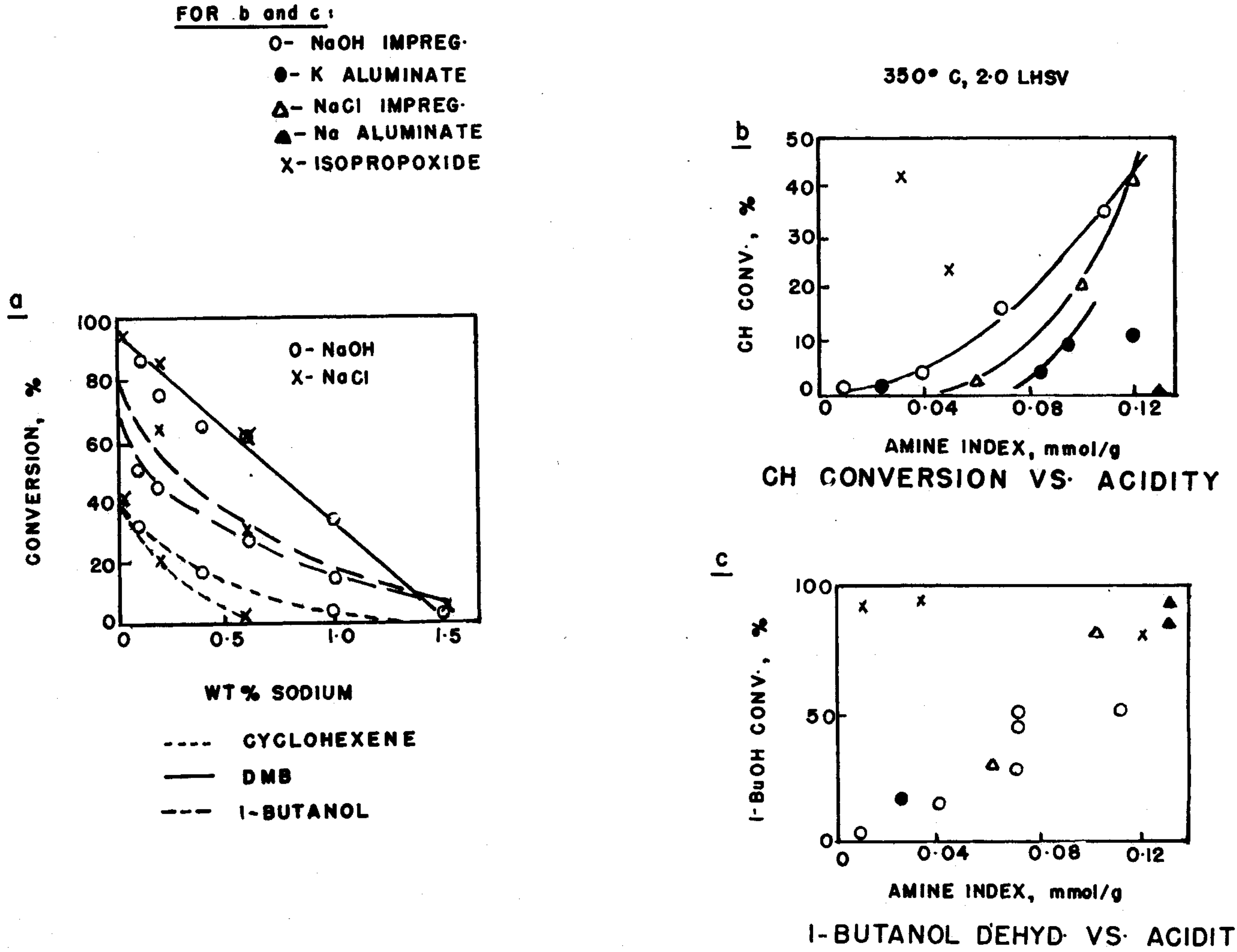

Fig. 4. Acidity of alumina and its effect on various reactions. *(a)* Conversion for isomerization and dehydration reactions on alkali impregnated alumina. *(b)* Correlation of activity with amine index for cyclohexane isomerization on a series of aluminas. *(c)* Correlation of activity with amine index for butanol dehydration on a series of aluminas. (After Pines and Haag, 1960.)

degrees of acidity for their catalysis, were carried out on a series of aluminas of differing intrinsic acidities. The major types of alumina studied were: pure—prepared from aluminum isopropoxide or from aluminum hydroxide and aluminum nitrate, impregnated—pure catalyst impregnated with sodium chloride or sodium hydroxide, and aluminate—alkali containing alumina precipitated from potassium hydroxide solution. The incorporation of alkali in the impregnated or aluminate catalysts decreases the acidity relative to the isopropoxide preparations, providing catalysts with a range of intrinsic acidities. The model reactions are the isomerization of cyclohexene (CH), the isomerization of 3,3-dimethyl-1-butene (3,3-DMB), and the dehydration of 1-butanol (BuOH). Carbonium ion mechanisms are involved in all these reactions, and the relative stability of these ions ($3° > 2° > 1°$) can be used as a measure of the acid strength required for catalysis. Hence the CH isomerization ($2° \rightarrow 1°$) should be more difficult to carry out than the 3,3-DMB isomerization, where the $2° \rightarrow 3°$ rearrangement is involved. Selectivity in this second isomerization is also a function of acid strength, however, since the transformation of the 2,3-dimethyl butene product obtained in the first step to produce 2-methylpentene involves a $3° \rightarrow 1°$ transformation and would proceed more slowly than the first step. Thus, the total reaction of 3,3-DMB can be used to indicate total acidity, and the selectivity between individual steps can be used to give some indication of the distribution of acid strength. Finally, the BuOH dehydration should also occur on both strong and weak acid sites.

The results of activity studies were in good agreement with expectations based on catalyst acidity. Pure isopropoxide catalysts demonstrated high activity for CH isomerization and alkali doped catalysts very little activity. The overall degree of 3,3-DMB isomerization was higher for all catalysts than CH isomerization, indicating that some acidity was effective in this reaction which did not participate in the CH isomerization, and the product distribution varied widely for materials of different acidity. Butanol dehydration also occurred on all types at conversion levels above the CH isomerization.

At the left of Figure 4 are given some results on the effect of acidity on these various reactions, where catalytic acidity has been changed by incorporation of alkali into the impregnated or aluminate samples. In all cases, activity is diminished by the presence of alkali, and the similarity in poisoning behavior for the various reactions suggests that similar types of sites are responsible for activity in all three cases. The elimination of CH activity before BuOH or 3,3-DMB activity indicates preferential poisoning of strong sites; the distribution of sites can be estimated from the difference in extinction points on curves 1 and 2-3, or by the difference in total activity with zero sodium content. Such methods give values of about 10^{13} strong acid sites per square centimeter and about 7.5×10^{13} total sites involved in BuOH dehydration. Thus pure alumina has about 10^{14} acidic sites per square centimeter, of which about 10% are effective in isomerization.

A further interesting result is the relationship between amine index, another measure of acidity, and catalytic activity. Apparently this index measures total acidity, and one can thus determine relative activities for a family of related aluminas, as shown in Figure 4*b*. However, if one attempts to compare activity for aluminas from different sources, no correlation is obtained, as shown by the differing curves in the figure for the various types of alumina in the CH isomerization. Total acidity seems to be correlated fairly well (Figure 4*c*), save for the isopropoxide catalysts, with amine index. The fact that amine index is generally a satisfactory measure of cracking catalyst activity may be at least indirect evidence of a relatively homogeneous activity of sites on silica-alumina. Since two types of chemisorption on silica-alumina were indicated on Figure 2, it might be concluded that only one is effective in cracking activity.

Active Sites on Some Other Oxides

In addition to the acidic oxides important in C—H and C—C bond transformation in hydrocarbons, a number of different oxides are important in oxidation reactions. Typical of these are oxides or mixed oxides of group Vb, VIb, and VIIb metals. In general, these are not amenable to investigation of surface sites via specific titration techniques as for the acidic oxides. Many of them are semiconductors, and electronic correlations have been more useful in description of their properties, as will be seen later.

However in one important area, oxidation of unsaturated hydrocarbons, evidence has been accumulated concerning the nature of surface active sites on oxides such as those of bismuth and copper by a combination of chemical and spectroscopic investigations for a large number of reactions (Haber, 1974). These are summarized in Table 4*a*. It is apparent here that there are a number of different types of sites on these catalysts, each of which is associated with a different surface intermediate complex and is active in catalysis of a different reaction.

At a somewhat lower level of detail in description of active sites in oxidation, we may say that cation sites appear to be of primary importance. In Table 4*b* are listed

TABLE 4*a*. ACTIVE CENTERS ON THE SURFACE OF SOME OXIDE CATALYSTS FOR OXIDATION OF UNSATURATED HYDROCARBONS (HABER, 1974)

Active center	Active complex	Product
Cations, Bi^{3+}, Co^{2+}, Sn^{4+}	π allylic complex	Dienes
O^{2-} in polyhedra of Mo, W, Sb, Nb	σ bonded allylic species	Unsaturated aldehydes and ketones
OH^- of basic character	Carboxylate type of complex	Unsaturated acids
OH^- of acidic character	Carbonium ion	Saturated ketones
O_2, O_2^-, O^-	Epoxy or peroxy complex	Total oxidation

TABLE 4*b*. ACTIVITY SEQUENCES FOR OXIDE CATALYSTS OF THE ELEMENTS OF THE 4TH PERIOD (GERMAIN, 1972)

Reactant	Sequence
H_2	Co > Cu > Mn > Ni > Fe > Zn > Cr > V > Ti
NH_3	Co > Cr > Cu > Mn > Ni > Fe > V > Zn
CH_4	Co > Ni > Mn > Cu > Cr > Fe > Ti > V > Zn
C_2H_4	Co > Cr > Mn > Cu > Ni > V > Fe > Ti > Zn
C_3H_6	Co > Cu > Mn > Cr > V > Fe > Ni
C_3H_6	Mn > Cu > Cr > Co > Fe > V > Ni
CO	Co > Cu > Ni > Mn > Fe > Zn > Ti > Cr > V
CO	Mn > Co > Ni > Cu > Zn > Ti > Fe > V > Cr
$C_6H_5 \cdot CH_3$	Co > Cu > Mn > Cr > Ni > V > Ti > Fe* > Zn
C_6H_6	Cr > Co > Mn > Ni > Fe > Cu > Ti > V > Zn

observed activity sequences for metallic oxides of elements of the fourth period for a number of oxidation reactions (Germain, 1972). It is apparent that the classifications according to decreasing activities are not the same; in part, these differences arise from the varying subjective measures used to establish a level of catalytic activity, and in part to differences in deactivation and stabilization of the various oxides. As an example, the location of iron in the sequence for toluene oxidation refers to a stabilized activity level; fresh ferric oxide would be located between manganese and chromium.

In spite of the individual variations indicated by the data of Table 4*b*, a general pattern for the activity of these oxides is suggested. That is, if it is assumed that activity is inversely related to the energy required for removal of the first oxygen, the following sequence is obtained:

$$\mathrm{Mn} > \mathrm{V} > \mathrm{Cu} > \mathrm{Co} > \mathrm{Fe} > \mathrm{Ni} > \mathrm{Ti} > \mathrm{Sn} > \mathrm{Zn} \qquad (A)$$

It is seen that this ranking is in general accord with the sequences of Table 4*b*. Thus, activity is approximately correlated to the oxygen-catalyst bond strength, in which the active oxygen is part of the oxygen lattice. This, in turn, suggests the following simple redox mechanism for catalytic oxidation:

$$A + \underset{*}{O} \rightarrow AO + * \qquad (I)$$

$$\tfrac{1}{2}O_2 + * \rightarrow \underset{*}{O} \qquad (II)$$

Depending on the relative values of the bonding energies associated with surface reduction (I) and oxidation (II), either of the steps can be rate determining. One of the more widely known applications of this approach in chemical reaction engineering is that of Mars and van Krevelen (1954) for naphthalene oxidation on vanadium pentoxide. Also, for the important case of carbon monoxide oxidation, (I) can be represented by (Garner and Veal, 1935)

$$\begin{array}{ccccccc} M^{2+} & O^{2-} & M^{2+} & & M^{2+} & CO_3^{2-} & M^{2+} \\ & & & + CO \rightarrow & & & \\ O^{2-} & M^{2+} & O^{2-} & & O^{2-} & M^{2+} & 2e \end{array}$$

and (II)

$$\begin{array}{ccccccc} M^{2+} & CO_3^{2-} & M^{2+} & & M^{2+} & CO_3^{2-} & M^{2+} \\ & & & + \tfrac{1}{2}O_2 \rightarrow & & & \\ O^{2-} & M^{2+} & 2e & & O^{2-} & M^{2+} & O^{2-} \end{array}$$

Identification of the oxidation and reduction steps directly with an active site taken to be the metal is an oversimplification if the metal can exist in several oxidation states. This will be seen in some of our subsequent discussion of thermochemical correlations and is considered in detail in an excellent review by Germain (1972).

Chemisorption/Titration Methods for Metal Surfaces

While the nature of active sites on oxide/oxidation catalysts is complex and still subject to considerable controversy, the situation for metals, at least on first glance, seems more simple. In this case we may associate active sites with surface metal atoms, either singly or in some combination. In what follows here we shall be principally concerned with the specific case of group VIII metals supported on oxide surfaces and more specifically with supported platinum, for which the most detailed information is available.

Chemisorption methods for characterization of group VIII metals are based on the well-known fact that hydrogen chemisorption on most of them is dissociative with hydrogen atom bonding to individual surface metal atoms; similarly, carbon monoxide chemisorption is nondissociative with bonding to surface atoms. These systems generally exhibit typical Langmuir adsorption isotherms, so that determination of monolayer adsorption gives directly the number of surface metal atoms via the chemisorption stoichiometry, H/M or CO/M, respectively. Further, for supported metals such data can supply at least qualitative information concerning the dimensions of individual metal particles or crystallites on the surface.

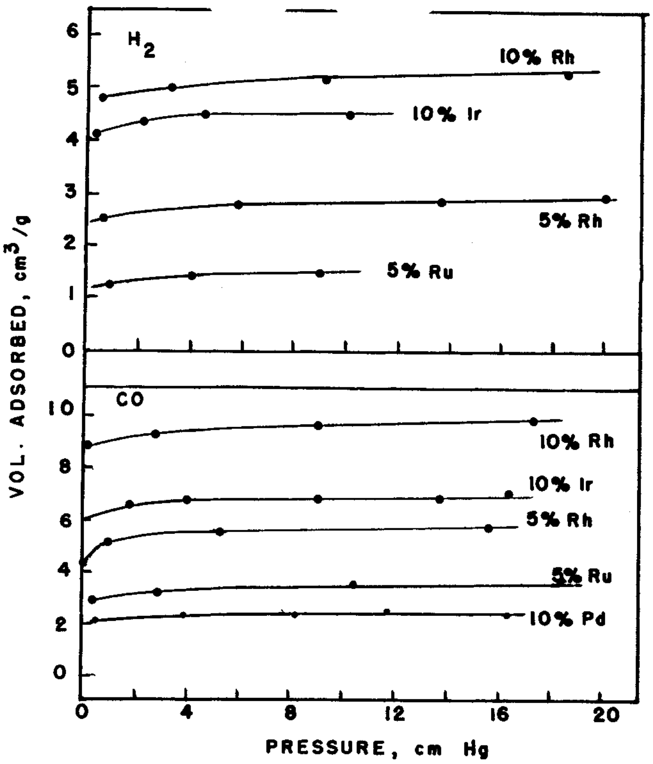

Fig. 5. Chemisorption of hydrogen and carbon monoxide on silica supported group VIII metals. (After Sinfelt and Yates, 1967.)

In Figure 5 are given some representative data on the chemisorption of hydrogen and carbon monoxide on several group VIII metals supported on silica as described in Table 5 (Sinfelt and Yates, 1967). Adsorption on the support was negligible in all cases illustrated here; this is not always so, and in general a correction for adsorption on the blank support is required (Sermon and Bond, 1973). The region of monolayer coverage is clearly indicated for these isotherms; again, this is not always so, and a more arbitrary interpretation may be required. Also given in Table 5 are a number of quantities derived from the ad-

Table 5. Surface Areas and Crystallite Sizes of Silica-Supported Metals (Sinfelt and Yates, 1967)

Catalyst*	H/M†	CO/M**	Surface area†† (m^2/g metal)	Crystallite size (Å)
10% Pd	—	0.11	47	106
10% Rh	0.48	0.44	214	23
5% Rh	0.53	0.52	237	20
5% Ru	0.27	0.31	121	42
10% Ir	0.78	0.58	186	14

* All metals supported on Cabosil (finely divided fumed silica).

† Atoms of hydrogen adsorbed (at 10 cm H_2 pressure) per metal atom.

** Molecules of carbon monoxide adsorbed (at 10 cm pressure) per metal atom.

†† Calculated from the hydrogen adsorption data.

sorption isotherms. The quantities H/M and CO/M give a measure of the dispersion or fraction of the metal exposed on the surface*; that is, the ratio of surface metal atoms to total metal atoms can be determined from H/M or CO/M if the stoichiometry of adsorption is known. More formally

$$\Phi = (G/M_T)/(G/M_s) \qquad (1)$$

where Φ is fraction exposed, (G/M_T) is the total uptake of gas on the metal, and (G/M_s) is the stoichiometry of the chemisorption. For the systems shown in Figure 5, it was shown by independent means that (G/M_s) was unity.

The metal surface areas shown are determined from the value of fraction exposed by

$$S_M = M_T \, A_M \, \Phi \qquad (2)$$

where S_M is the metal surface area, M_T is the total number of metal atoms in the sample, and A_M is the area occupied by a metal atom in the surface. The value for A_M may be estimated from the reported value of $6.5A^2$ determined for nickel (Klemperer and Stone, 1958) by adjusting for the difference in atomic radius between nickel and the metal under consideration by

$$A_M = A_{\rm Ni}\left(\frac{r_M}{r_{\rm Ni}}\right)^2 = 6.5\left(\frac{r_M}{r_{\rm Ni}}\right)^2 \qquad (3)$$

An average particle dimension may also be evaluated from metal surface areas by assuming the particles are cubes of dimension l with one side bound to the support according to

$$l = \frac{5}{S_M \rho} \qquad (4)$$

where ρ is the density of the metal, and S_M is the metal surface area per gram of metal.

An alternative method for surface characterization of supported platinum catalysts has been developed which involves titration of the oxidized surface rather than chemisorption on the reduced surface (Benson and Boudart, 1965). Oxygen is contacted with the reduced surface to form PtO_x, and the titration proceeds according to:

$$\mathrm{PtO}_x + \left(x + \frac{y}{2}\right)\mathrm{H_2} \rightarrow \mathrm{Pt} + x\,\mathrm{H_2O} \qquad \text{(III)}$$

If $x = y = 1$, then three hydrogen atoms are consumed for each platinum atom, so there is a considerable increase in sensitivity compared with static hydrogen chemisorption. The method, of course, yields the same basic information as chemisorption techniques.

Now, what use may be made of such data concerning specific areas, fraction exposed, and particle dimension for these supported metals? As in the case of the acidic oxides, reaction rate data may be reported on the basis of surface active sites rather than per unit weight or volume. The implications of this with regard to unambiguous comparison of results between various catalysts, reactions, and even laboratories are enormous. A convenient comparison of activities for catalysts of differing fraction exposed or particle size is given on the basis of the number of molecules reacted per second per surface metal atom or metal surface area. This specific rate or turnover number N was apparently first defined in the modern catalytic literature by Meyer and Burwell (1963). The turnover number corresponds to set conditions of temperature and reaction mixture composition; its systematic application in the interpretation of kinetic data for reactions on supported metals over the past few years has revealed some remarkable properties of these catalysts (Boudart et al., 1966).

TABLE 6. EFFECT OF CRYSTALLITE SIZE ON SPECIFIC ACTIVITY —A SUMMARY FOR PLATINUM ON ALUMINA OR SILICA

Structure insensitive reactions	Structure sensitive reactions
1. Cyclopropane hydrogenolysis (Boudart et al., 1966) $\mathrm{Pt/Al_2O_3}$, $\mathrm{Pt/SiO_2}$	1. p-Xylene exchange with deuterium (Hightower and Kemball, 1965) $\mathrm{Pt/Al_2O_3}$, $\mathrm{Pt/SiO_2}$
2. Nitric oxide reduction by ammonia—no oxygen (Pusateri, Katzer, and Manogue; 1974) $\mathrm{Pt/Al_2O_3}$	2. Nitric oxide reduction by ammonia—oxygen present (Pusateri, Katzer, and Manogue, 1974) $\mathrm{Pt/Al_2O_3}$
3. Ethylene hydrogenation (Dorling, Eastlake, and Moss, 1969) $\mathrm{Pt/SiO_2}$	3. Neopentane hydrogenolysis and isomerization (Boudart et al., 1968) $\mathrm{Pt/Al_2O_3}$, $\mathrm{Pt/SiO_2}$
4. Benzene hydrogenation (Dorling and Moss, 1966) $\mathrm{Pt/SiO_2}$; (Basset et al., 1974), $\mathrm{Pt/Al_2O_3}$	4. Hydrogenolysis of methylcyclopentane (Corroleur et al., 1972) $\mathrm{Pt/Al_2O_3}$, $\mathrm{Pt/SiO_2}$

Most importantly, it has been found that in some reactions the turnover numbers depend strongly on fraction exposed or metal particle size; for other reactions the turnover numbers are independent of this. In the former case, the reaction is termed structure sensitive or demanding, in the latter structure insensitive or facile. These systems have been treated in detail by Boudart (1972), so here our attention will be confined to some specific results for supported platinum catalysts as shown in Table 6.

There is no difficulty in recognizing a structure sensitive reaction despite scatter in data. Hightower and Kemball (1965) report that in the reaction of p-xylene with deuterium on platinum/silica and platinum/aluminum oxide the ratio of the rates of exchange to the rates of deuteration vary from 10 to 300 as the fraction exposed varies from 0.33 to 0.43. Pusateri et al. (1974) suggest that the reduction of nitric oxide by ammonia in an oxygen atmosphere is a structure sensitive reaction, since the rate of reaction increases by a factor of 6 as the fraction exposed decreases by a factor of 6. Boudart et al. (1968) have called the hydrogenolysis and isomerization of neopentane a structure sensitive reaction. Although there is variation in the specific activity of this reaction, the general trend is for the selectivity of isomerization to decrease on catalysts containing small average particle sizes. Corroleur et al. (1972) also conclude that the hydrogenolysis of methyl cyclopentane is structure sensitive because as the metal particle size of the catalyst decreases by a factor of 10, the ratio of the rates of 3-methyl pentane to n-heptane decreases by the same amount.

In the last three studies, there is a trend of increasing reaction rate on catalysts with supported metal particles of large dimensions. This indicates that the above reactions occur on special surface sites found more frequently on large dimension metal particles. Boudart et al. (1968) conclude that the neopentane isomerization and hydrogenolysis reactions occur through an intermediate which must be adsorbed on three adjacent sites on the metal particle. The sites for this adsorption occur more frequently on a catalyst with a large mean crystallite size.

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* The term *dispersion* has commonly been used in the literature for this measure; however, it can be misleading in certain circumstances. The IUPAC Commission on Colloid and Surface Chemistry has recommended the use of *fraction exposed* as a suitable alternate.

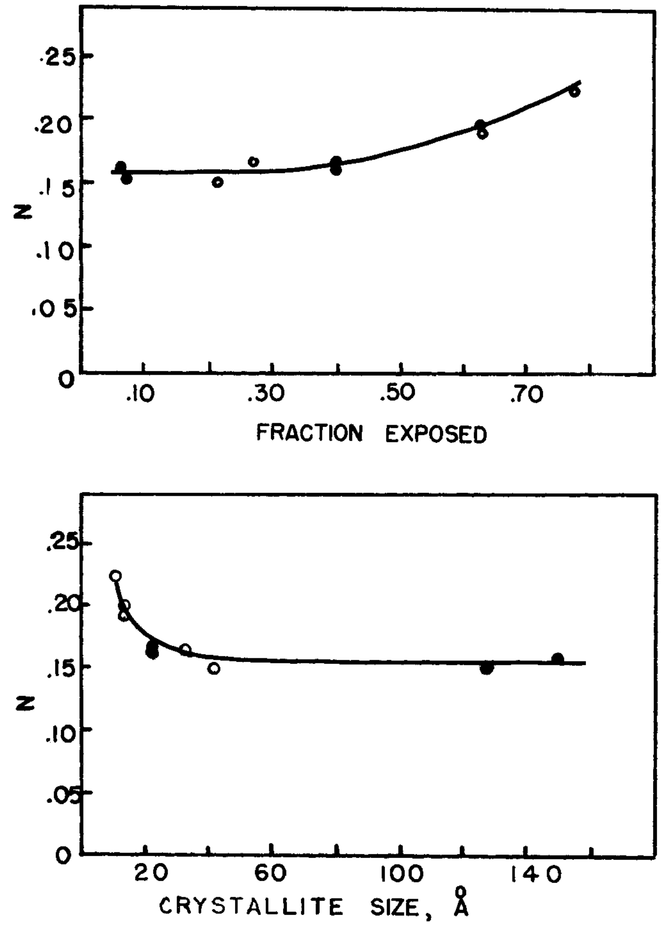


Fig. 6. Turnover number (molecules reacted/surface atom-second) vs. (*a*) dispersion and (*b*) crystallite size for cyclopropane hydrogenolysis on Pt/SiO$_2$. ●—catalyst prepared by impregnation; ○—catalyst prepared by ion exchange. $T = 0°C$. $P_{H_2} = 0.941$ atm, $P_{C_3H_6} = 0.059$ atm. (After Schipper, 1975.)

The identification of a structure insensitive (facile) reaction is more difficult. Pusateri et al. (1974) suggest that the reduction of nitric oxide by ammonia without oxygen present is a structure insensitive reaction. Their data indicate that the turnover number is constant within ±5%. However, only two catalysts were analyzed in detail, so that the turnover number was not determined over a range of particle sizes.

Dorling and Moss (1966) have reported that the reaction of benzene hydrogenation is structure insensitive. However, there is a general trend in their data which suggests that the turnover number decreases with the fraction exposed. In fact, the turnover number decreases consistently from 4.5×10^{13} to 2.7×10^{13} molecules/cm^{2}s as the fraction exposed decreases from 0.65 to 0.01. Therefore, there is an apparent effect of particle size on the catalytic behavior for this reaction, even though the authors call it structure insensitive. In a later study, Dorling et al. (1971) also conclude that the hydrogenation of ethylene over platinum on silica catalysts is structure insensitive. However, the data again indicate that the specific activity decreases when the average crystallite size increases. At −80°C, the specific activity is 19.6×10^{12} molecules/cm^{2}s on a catalyst with a crystallite size of 55Å, while on a catalyst with crystallites of 70Å the specific activity is 1.7×10^{12} molecules/cm^{2}s.

These results suggest that considerable advances have been made in understanding and correlating the trends of activity of supported metal catalysts via exploiting what is known concerning the chemical nature of their surface sites. Yet the last two examples indicate some uncertainty in the identification of truly structure insensitive reactions. Perhaps the most precise investigation of this sort to date is that of Schipper (1975) on the hydrogenolysis of cyclopropane over a series of platinum/silica catalysts. The major results of one series of experiments are shown in Figure 6, where the turnover number is plotted vs. fraction exposed (dispersion) and crystallite size. It is seen that this reaction (which has been considered more or less to be a model structure insensitive reaction) is, indeed, structure insensitive for fractions exposed up to about 0.40 but becomes structure sensitive for higher values. This result can be interpreted via a geometric correlation, as discussed later.

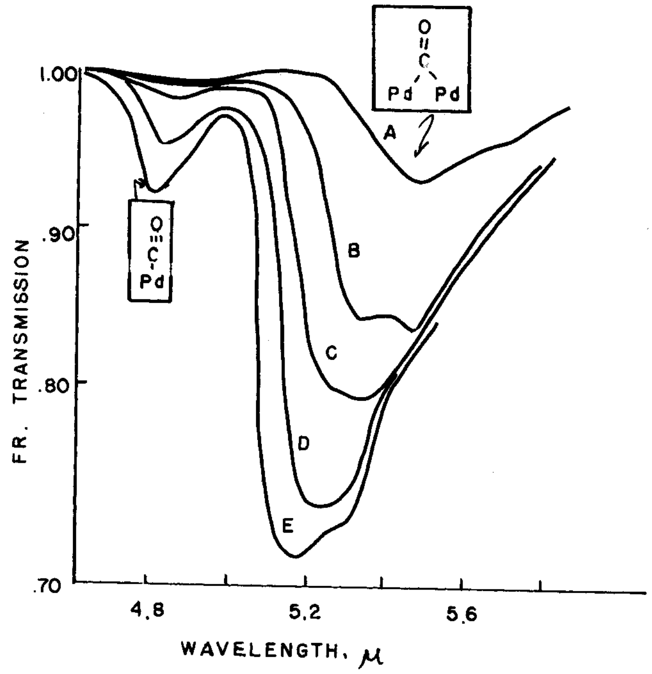
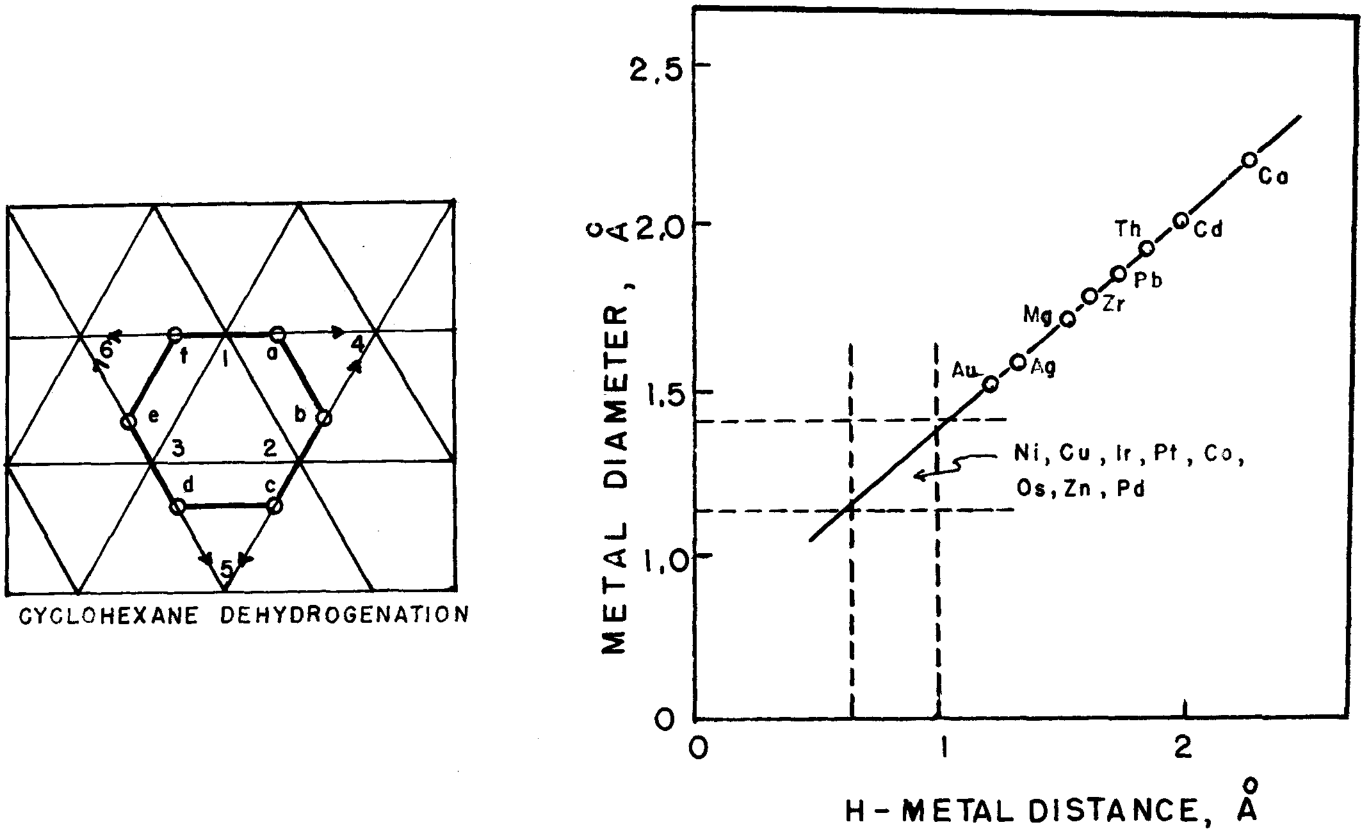


Fig. 7. Infrared spectra of linear and bridge bonded CO on supported Pd. Surface coverage of CO: $A = 0.20$, $B = 0.45$, $C = 0.65$, $D = 0.85$, $E = 1.0$. (After Eischens and Pliskin, 1958.)

As in the case of the titration of acidic oxide surfaces, several complicating factors exist which can becloud the interpretation of chemisorption or titration data. As seen from Equation (1), or reaction III, knowledge of the stoichiometry of the chemisorption or titration is essential to the method. There are a number of factors which can introduce uncertainty into the stoichiometry.

In the case of the hydrogen-oxygen titration procedure, the stoichiometry of III is apparently a function of platinum particle size. As one decreases particle size, the values of x and y approach 1 and 2 (or ½ and 1), respectively (Sermon and Bond, 1973). This variation may be due either to changes in the stoichiometry of the H-O reaction or to a variation of the composition of PtO$_x$ with particle size. The nature of the catalyst support may also play a role in such variation.

For hydrogen chemisorption, the stoichiometry on group VIII metals (with the exception of palladium) is well established as one hydrogen atom per surface metal atom; however, the possibility exists that there may be some migration of hydrogen from the metal surface to the support after initial chemisorption (spillover). This would result in erroneously large measured values for the fraction of metal exposed. Such effects have been reviewed in detail by Sermon and Bond (1973). The solubility of hydrogen in palladium makes chemisorption measurements on this metal somewhat risky, although in principle solubility effects can be accounted for if one is willing to correct with data on bulk metal properties.



CYCLOHEXANE DEHYDROGENATION

Fig. 8. Multiplet theory correlation of reactions of six membered rings (After Trapnell, 1951.)

Use of carbon monoxide in chemisorption measurements is complicated in some cases by the existence of two different forms of the adsorbed molecule: linear, in which a single molecule is associated with single metal atom, and bridged, in which a single molecule is associated with two surface metal atoms. These structures are easily identified by the infrared spectra of the surface species after chemisorption, as shown in Figure 7 (Eischens and Pliskin, 1958). In fact, this method was used to verify the unit stoichiometry used in interpretation of the isotherms given in Figure 5.

A final problem in correlations based on chemisorption or titration data on metals is also similar to that for oxides. The chemisorption stoichiometry is specific to the adsorbed molecule; the number of sites counted may or may not correspond to those effective in some reaction carried out on the surface. Hence, turnover numbers reported per surface metal atom may not be in general absolute rates of reaction. However, since these measures find most useful application in comparisons, they are often used on a relative basis, and such distinction may not be important.

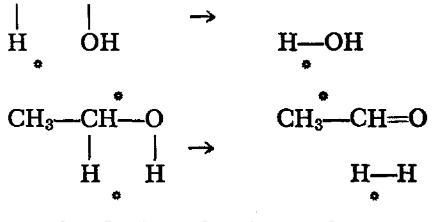
Supported metals may also be characterized as to the particle dimension by a number of other methods, including x-ray diffraction line broadening, transmission electron microscopy, small angle x-ray scattering, and relative magnetization. A survey of comparisons among these methods is impossible here; the current state-of-the art is well represented by the recent results of Renouprez et al. (1974) for a series of platinum/aluminum oxide catalysts. The techniques evaluated were hydrogen chemisorption with a pulse technique used, carbon monoxide chemisorption, small angle x-ray scattering, and electron microscopy. These techniques yielded specific surface areas of exposed platinum atoms which agreed within ± 15% and are the best results found in the literature. However, even better agreement (±8 to 10%) is required to permit unambiguous observations of the effects of crystallite size on the catalytic behavior of these supported metal catalysts, and further work is still needed to refine and develop such techniques of catalyst characterization.

RELATIONSHIP OF ACTIVE SITES TO SURFACE STRUCTURE

The idea of associating active sites with the geometric properties of a surface has held attraction over the years for many workers in catalysis and is currently enjoying a resurgence of interest due to the detail on surface structure provided by experimental techniques such as scanning electron microscopy (SEM) and low energy electron diffraction (LEED).

Early Geometric Concepts—The Multiplet Theory

The first formal attempt at developing a geometrically based theory of catalysis was that of Balandin (1929), in which catalytic reactions were postulated to be effected solely by the attraction of different parts of the reactant molecule for different atoms on the catalyst surface. This group, or multiplet, of surface atoms effects reaction entirely via short range forces on different parts of the molecule. For example, the dehydration/dehydrogenation of ethanol is pictured to proceed via a duplet mechanism as follows:



$$\begin{array}{ccc} \overset{*}{CH_2}\text{—}CH_2 & & CH_2\overset{*}{=}CH_2 \\ | \quad\;\; | & \rightarrow & \\ \underset{*}{H} \quad OH & & H\underset{*}{\text{—}}OH \end{array}$$

$$\begin{array}{ccc} CH_3\text{—}\overset{*}{CH}\text{—}O & & CH_3\text{—}\overset{*}{CH}=O \\ | \quad\;\; | & \rightarrow & \\ H \quad \underset{*}{H} & & H\underset{*}{\text{—}}H \end{array}$$

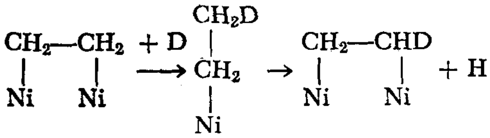
where *—* is the duplet. The theory does not envisage chemical bonding (that is, chemisorption) with the surface nor elucidate the nature of the multiplet and thus is immediately at odds with modern concepts of surface reaction. In fact, according to Trapnell (1951) "... It is true to say that for the vast majority of catalytic reactions, the multiplet theory does not enable prediction to be made of a good catalyst, of the reaction path which will predominate when more than one path is possible, and so on. . . ."

Why then spend time discussing a theory with such deficiencies? The answer is that for a single class of reactions, the interactions of six membered rings on surfaces, the geometric concepts involved in the multiplet theory provide a remarkable correlation of catalytic activity. The success attained in this area undoubtedly led to subsequent more refined, geometric correlations. The principles of the multiplet theory for six member rings and the correlation obtained are shown in Figure 8. It is taken that a reaction such as cyclohexane dehydrogenation occurs on an octahedral face of the catalyst, as shown on the left of Figure 8. Hydrogen atoms on the ring at carbons a and b are attracted to metal atom 4, forming a hydrogen molecule as are the combinations c—5—d and e—6—f Carbon-carbon bond formation occurs via the combinations a—1—f, b—2—c, and d—3—e. The short-range forces of importance according to this picture must then be related to the metal atom diameter and the hydrogen-metal atom distance involved in the multiplet, which in this case is a sextet. The activity of various surfaces should then be correlated with these two characteristic distances on the octahedral face [that is, (111) surface for face centered cubic metals], which is indeed the case as shown on the right of Figure 8 where the active catalysts all fall within the small area indicated for nickel, etc. Applications of the multiplet theory to a number of different reactions have been reviewed by Trapnell (1951) and Balandin (1969). For our present purposes, we may conclude that in spite of its deficiencies, the multiplet concept does provide some evidence of a relationship between surface activity and surface structure.

Lattice Spacing and Surface Activity

Subsequent to Balandin, many of the concepts relating lattice spacing and surface activity were developed on the basis of results obtained for the hydrogenation (or deuteration) of low molecular weight olefins on nickel (Griffith, 1948). For ethylene, two classical mechanisms of the deuteration reaction have been proposed, the associative mechanism mechanism (Horiuti and Polanyi, 1934)

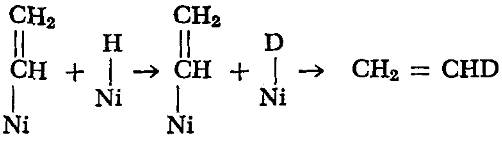
$CH_2 = CH_2 \rightarrow$



$$\underset{\substack{\mid\\ \text{Ni}}}{CH_2}-\underset{\substack{\mid\\ \text{Ni}}}{CH_2} + D \longrightarrow \underset{\substack{\mid\\ \text{Ni}}}{\overset{\substack{CH_2D\\ \mid}}{CH_2}} \rightarrow \underset{\substack{\mid\\ \text{Ni}}}{CH_2}-\underset{\substack{\mid\\ \text{Ni}}}{CHD} + H \qquad (IV)$$

or the dissociative mechanism (Farkas and Farkas, 1938)

$CH_2 = CH_2 \rightarrow$



$$\underset{\substack{\mid\\ \text{Ni}}}{\overset{\substack{CH_2\\ \|}}{CH}} + \underset{\substack{\mid\\ \text{Ni}}}{H} \rightarrow \underset{\substack{\mid\\ \text{Ni}}}{\overset{\substack{CH_2\\ \|}}{CH}} + \underset{\substack{\mid\\ \text{Ni}}}{D} \rightarrow CH_2 = CHD \qquad (V)$$

Subsequent experimentation demonstrated that the formation of free H or D from the olefin did not occur, thus supporting the Horiuti-Polanyi mechanism. Such a mechanistic picture immediately suggests that the nickel atom spacing in the lattice will have some influence on the activity of a given surface.* The point was investigated in detail by Twigg and Rideal (1940), who considered the three low index planes of nickel shown on Figure 9*a*. If the C—C bond length in the chemisorbed olefin is taken as that in paraffins, 1.54 Å, and the C—Ni bond length as that in $Ni(CO)_4$, 1.82 Å, the following bond angles can be calculated for chemisorption on the nickel-nickel pairs indicated:

2.48 Å—105° Ni—C—C bond angle

3.51 Å—123° Ni—C—C bond angle

Since the strain free angle is about 109 deg., it can be inferred that the 2.45 Å spacing would more strongly bond the olefin and consequently be less active in catalysis. This was confirmed experimentally by Beeck (1950) in his elegant study of the catalytic properties of orientated metallic films. In Figure 9*b* are shown the activities of a series of metals for ethylene hydrogenation correlated with a characteristic lattice spacing for each metal. For bcc the spacing is taken across the (110) plane of the unit cell and for fcc the a_0 distance of the unit cell. Of particular interest is the comparison between nickel (110), containing a high proportion of the 3.51 Å nickel-nickel pairs, and polycrystalline nickel, which probably consists of about equal amounts of (110), (100), and (111) planes. Indeed, the (110) face is about five times more active for this reaction. The correlation of Figure 9*b* should also be useful for estimation of the relative activities for hydrogenation of other low molecular weight, linear olefins, since their chemisorption will be similar, and the geometric factors discussed above are substantially unchanged. Hence, we have a type of a priori correlation based on reasonable extrapolation of experimental results for similar reactions on the same series of catalysts.

Some Recent Geometric Approaches

More recent work in catalysis employing geometric concepts has tended to move away from using lattice spacing as the sole factor of importance. In the case of metals, considerable attention has been given to the role of edge and corner atoms on small crystallites (van Hardeveld and Hartog, 1972) or stepped planar surfaces (Somorjai et al., 1972). For oxides, computer simulation methods based on models of partially dehydroxylated surfaces have shown some promise (Peri and Hannan, 1965; Dabrowski et al., 1970). Finally, and most recently, there have emerged a number of methods for carrying out detailed quantum-mechanical calculations on the electronic structure of metal clusters of importance in catalysis (Slater and Johnson, 1974). While this latter approach is obviously not a geometric correlation, it is geometry dependent and does provide some insight into the interrelationship between geometric and electronic correlations discussed later.

Van Hardeveld and Hartog consider the geometry of supported fcc metal catalysts to be composed of arrangements of face centered cubic cells which, for a given number of molecules in a crystallite, will have only one configuration of lowest free energy. Typical arrangements are octahedral, tetrahedral, and cubo-octahedral structures. For example, three types of surface atom configurations are shown in Figure 10*a* for a fcc octahedron, along with the ratio of their number $N(C_j)$ to the total number of surface atoms N_s as a function of the equivalent spherical

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* This is not the entire story, however; the fact that exchange can occur between normal and deuterated olefins provides support for the dissociative mechanism. More modern approaches reject both of these classical mechanisms in favor of π bonding with available metal *d* orbitals. This has little effect on the geometric arguments advanced here, since the π complex mechanism postulates analogues of both associative and dissociative bonding.

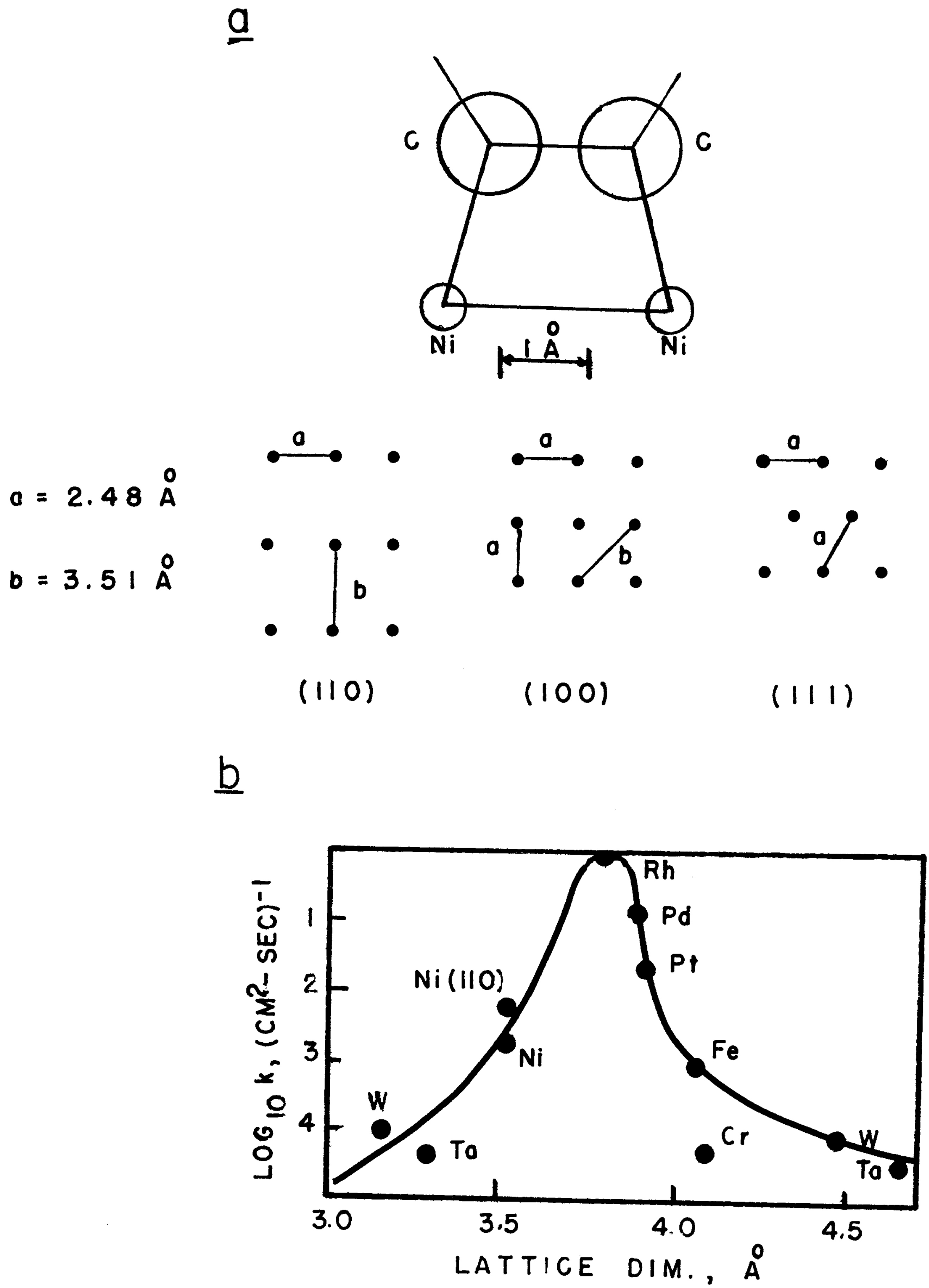

Fig. 9. Lattice spacing correlation for ethylene hydrogenation. *(a)* Associative adsorption of ethylene on Ni and lattice spacing of the three low index planes of Ni (after Griffith, 1948, and Thomas and Thomas, 1967). *(b)* Beek's correlation of activity of various metal films for ethylene hydrogenation (after Beeck, 1950).

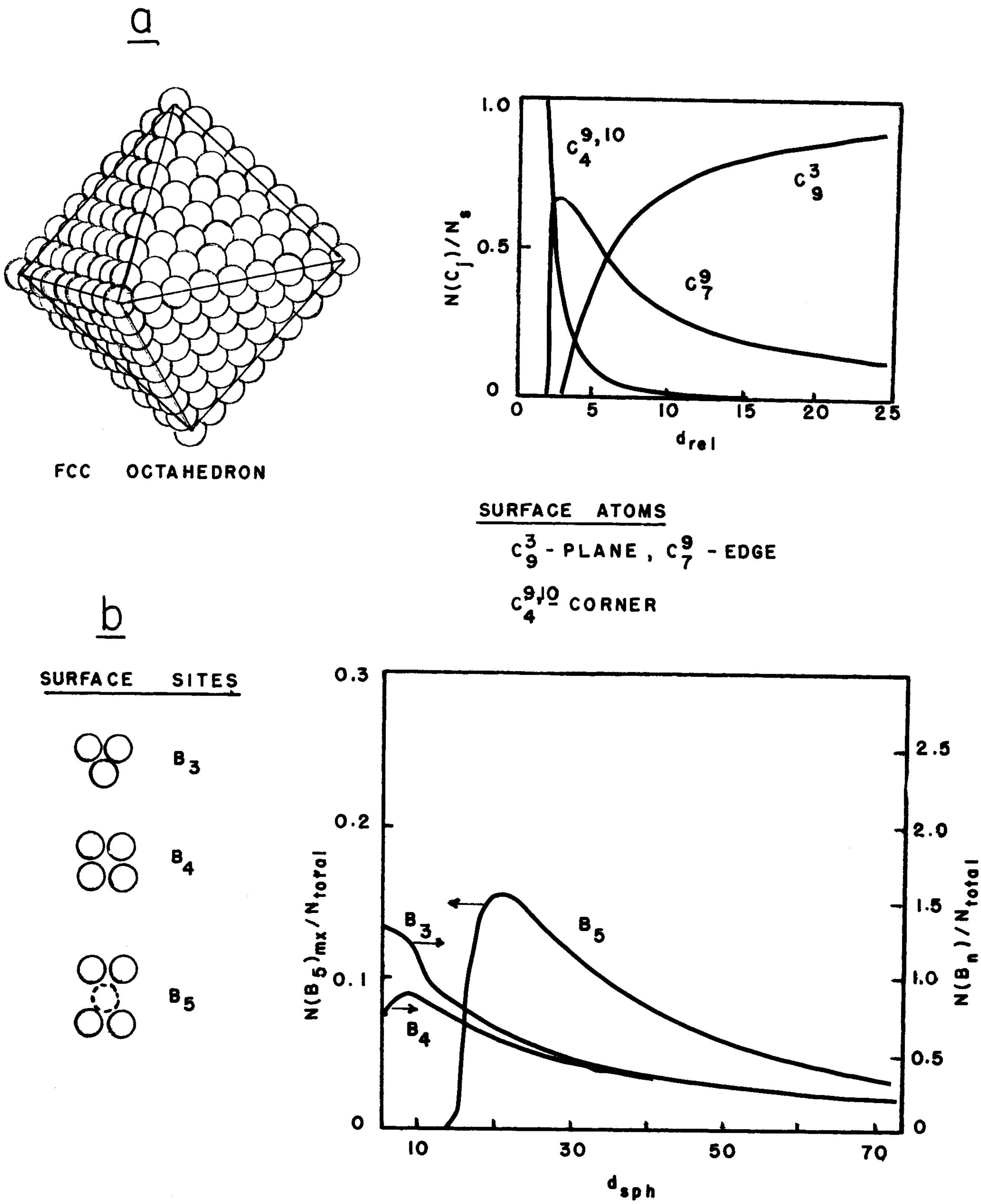

Fig. 10. Geometry of supported crystallites. *(a)* **Surface atom statistics for a fcc octahedron.** *(b)* **Surface site statistics for a cubooctahedron. (After van Hardeveld and Hartog, 1969, and van Hardeveld and van Montfoort, 1966.)**

diameter d_{rel}. This diameter for fcc crystals is equal to $1.105(N_T)^{1/3}$, where N_T is the total number of atoms in the crystal. There is a sharp decrease in the corner atoms between $5 < d_{rel} < 10$ Å, a more gradual decrease of edge atoms over the range $5 <$ rel < 25 Å, and a continuous increase in the population of surface atoms.* In addition to considering the statistics of individual atoms, groupings of atoms forming characteristic surface sites can also be identified. Figure 10*b* shows three arrangements, B_n, where n is the number of atoms surrounding the site, with the corresponding statistics for a cubo-octahedron. Working with a series of nickel/silica catalysts of different crystallite dimension, van Hardeveld and van Montfoort (1966) found that nitrogen was adsorbed at room temperature only on those with crystallite dimension in the range of

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* The notation employed for these atoms, which is not necessary for the present discussion, is described in detail by van Hardeveld and Hartog (1969).

15 to 70 A. This is clearly the region in which B_5 sites predominate, and it was concluded that nitrogen adsorbs on B_5 sites over the subsurface atom (central in the figure) with the formation of an induced dipole in the adsorbed molecule.

This type of detailed geometric interpretation of active sites in correlation of experimental data has also been used by these workers to explain experimental results on the simultaneous exchange and deuteration of benzene on supported nickel and iridium catalysts. As a final example of such interpretation, we refer again to the data on cyclopropane hydrogenolysis of Figure 6*b*. The turnover number drops by a factor of about two in the range from 10 to 40 Å and then remains constant. A comparison of these data with surface statistics based on the simple crystallite model of isodimensional fcc cubes with five (100) planes exposed (Schipper, 1975) is given in Figure 11. The similarity in shape and location of the region of changing turnover number to the corresponding calculated edge and corner atom densities suggests strongly that structure sensitivity in this reaction is induced by edge or corner sites.

Another rather detailed geometric approach to the correlation of catalytic activity is a Monte Carlo simulation method suggested by Callahan and Grasselli (1963) and developed by Peri (1965) for particular application in interpreting the effects of dehydroxylation on alumina surfaces. By removal of OH from an initially completely hydroxylated surface in a random (Monte Carlo) manner, he was able to identify the appearance of several characteristic types of surface sites. These in turn could be associated with the infrared spectra of various alumina surfaces at different degrees of hydration. This approach was modified and extended by Dabrowski et al. (1970) to computer simulation of the dehydration of ethanol on the (100) surface of γ-alumina. The method is based on recognizing that most surface reaction mechanism postulates imply specific geometric configurations, just as in the case of the Horiuchi-Polanyi mechanism discussed in the previous section. For the ethanol dehydration, one possible mechanism is as follows:

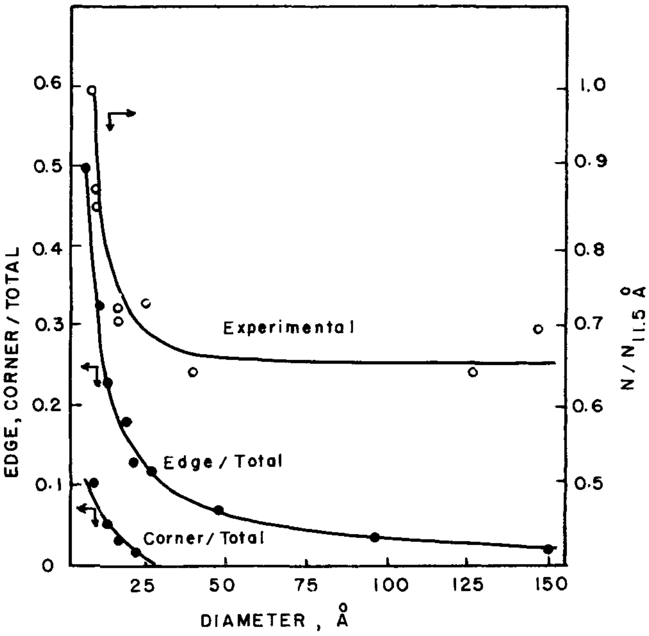
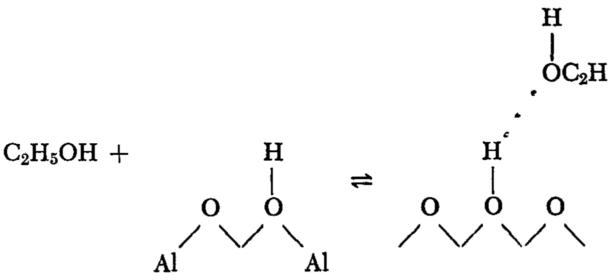
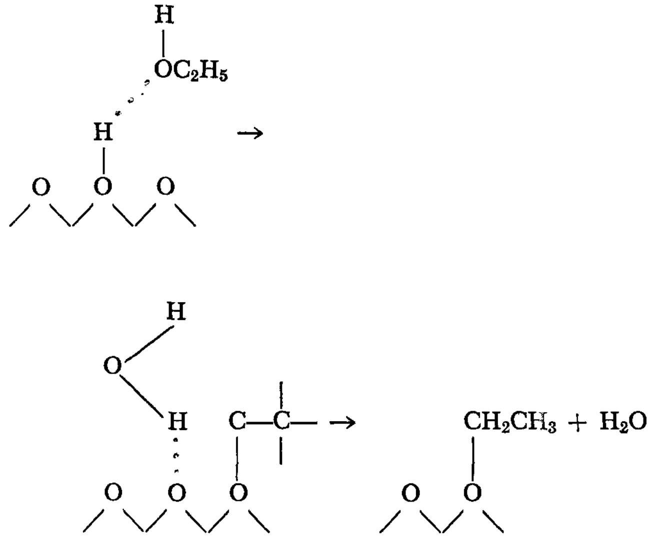


Fig. 11. Comparison of structure sensitivity of cyclopropane hydrogenolysis with edge/corner site densities on Pt/SiO₂.

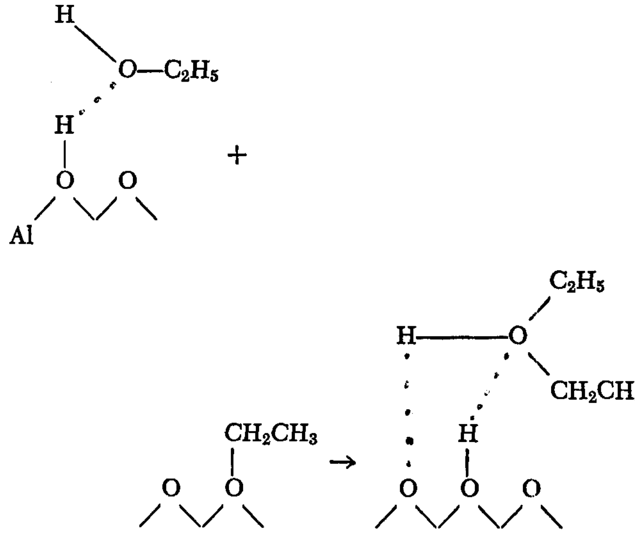
1. Weak adsorption of ethanol:



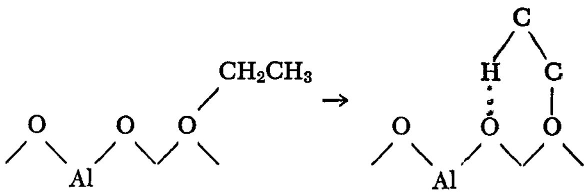
2. Chemisorption of the weakly adsorbed ethanol:



3. (*a*) Ether formation:



(*b*) Ethylene formation:



(product of reaction 2)

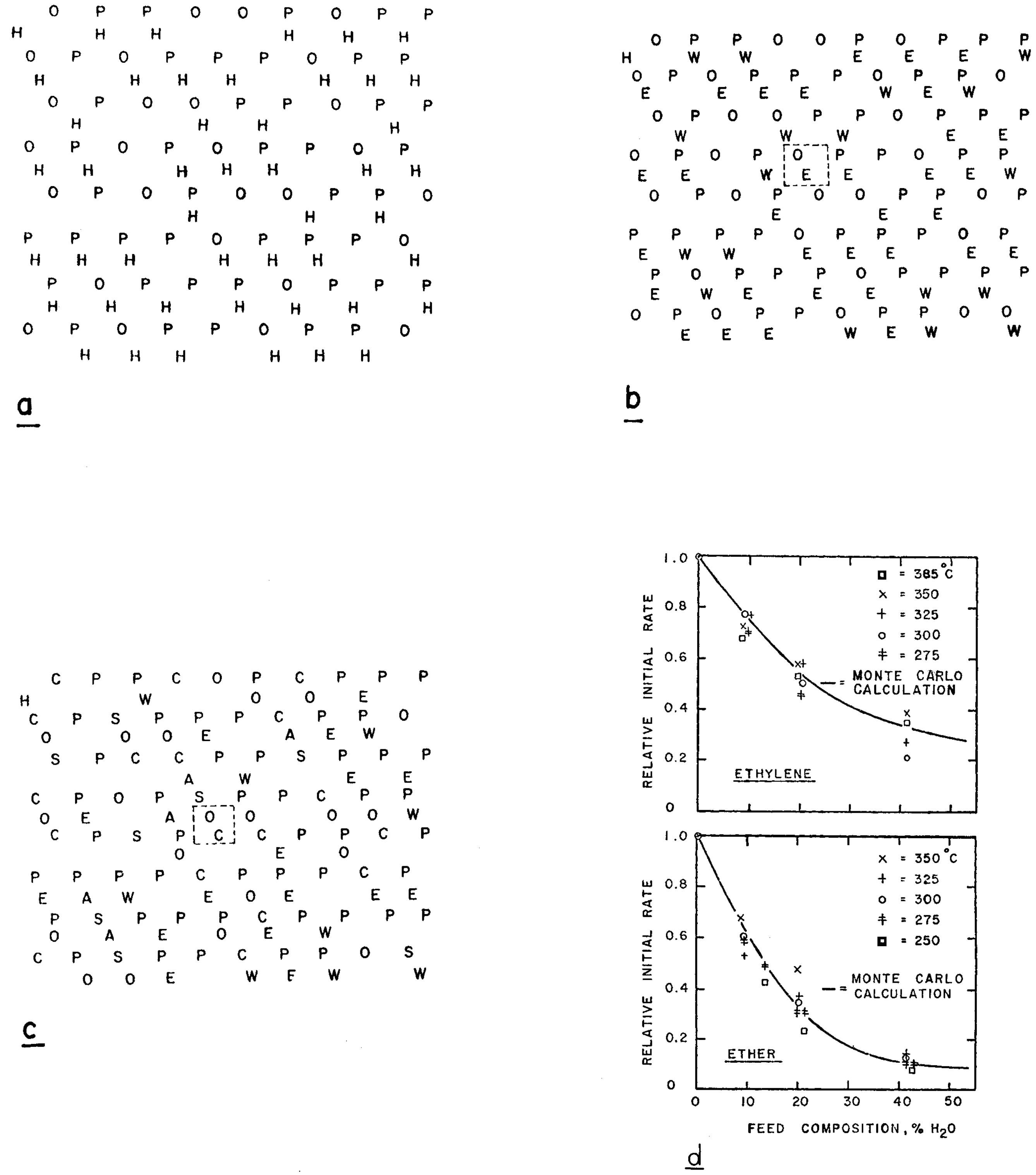
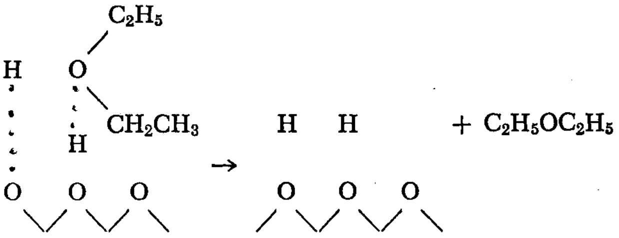
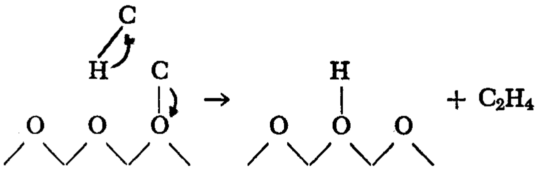


Fig. 12. Surface arrays and computed results for the Monte Carlo simulation of ethanol dehydration on (100) γ alumina. *(a)* Hydroxylated surface, *(b)* ethanol (60%) water (40%) adsorption on surface, *(c)* formation of ethoxy complex, *(d)* comparison of calculation with experiment. *O*—oxygen, *H*—hydrated site, *E*—adsorbed ethanol, *W*—adsorbed water, *C*—ethoxy complex, *S*—site hydrated by adsorbed water. (After Dabrowski et al., 1970.)

4. (*a*) Desorption of ether:



(*b*) Desorption of ethylene:



The reaction step 3(*a*) postulates, for example, that an alkoxide complex must be adjacent to a weakly adsorbed

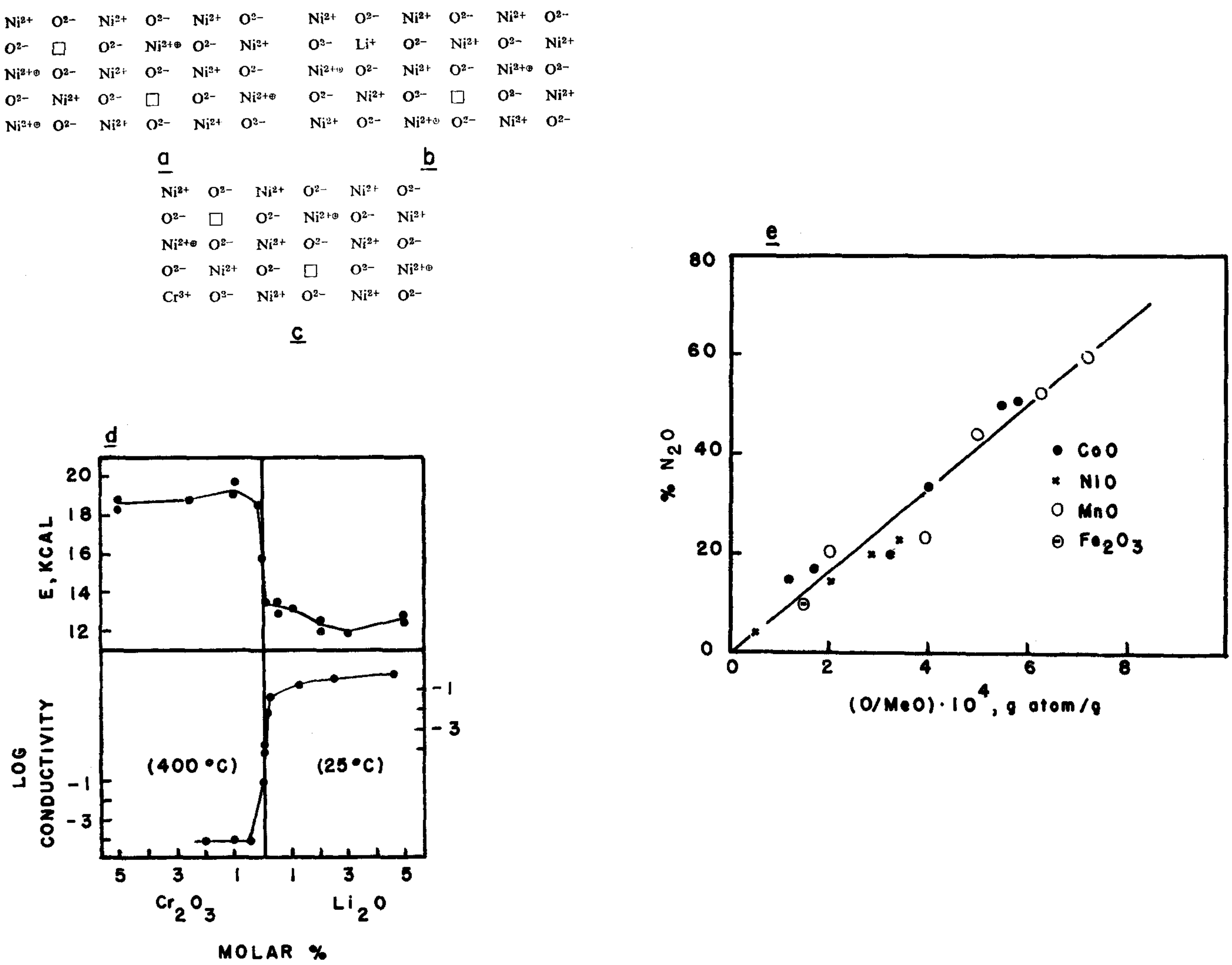


Fig. 13. Examples of activity correlations for semiconductors. *(a-c) p* type nickel oxide with cation vacancies and positive holes doped with Li^+ and Cr^{+3} (After Thomas and Thomas, 1967). *(d) Correlation of activation energy and electrical conductivity for doped NiO in catalysis of CO oxidation (after Schwab, 1957). (e)* Activity of some semiconductor oxides for ammonia oxidation in terms of lattice oxygen excess (after Krauss, 1948).

ethanol for ether formation to occur. Similarly, ethylene formation requires the presence of an oxide adjacent to the ethoxide for hydrogen abstraction. The simulation computation is carried out in several stages as illustrated in Figure 12. The surface is described as a planar oxide matrix to which aluminum ions and water (as H and OH) have been added. The resulting hydroxylated surface is depicted in Figure 12*a*. Chemisorption of reaction mixture on the surface is carried out by specifying the surface composition according to the degree of surface hydration and competitive adsorption coefficients (values experimentally determined). This transforms Figure 12*a* to 12*b*. Now, a logical search is performed on the array of Figure 12*b* to find the geometric configuration required for formation of an ethoxy complex (that is, lattice oxide adjacent to adsorbed ethanol). Identification of such configurations then maps Figure 12*b* into 12*c*, in which operation water is desorbed from the surface as per reaction 2. The formation of products is determined by search of array from Figure 12*c*, locating a surface complex and testing the elements surrounding for weakly chemisorbed ethanol (ether formation) or oxide (ethylene formation). For incompletely hydroxylated surfaces, the Monte Carlo aspect of the simulation is introduced by random selection of the sites on which step 1 occurs.

While the simulation cannot be used to calculate absolute quantities, relative numbers of these reaction configurations with respect to systematic changes in the surface, such as initial degree of dehydration or index plane, are sufficient to predict trends in activity and product distribution. Figure 12*d* gives the results obtained by Dabrowski et al. for the product distribution as a function of feed composition in comparison with experimental data. It is seen that the essential trends revealed experimentally are well predicted by the simulation. Further discussion of the method for this reaction is given by Butt and Starzec (1974); simulation of thiophene hydrogenolysis on molybdenum trioxide is reported by Welsch and Butt (1973). It would appear that the results obtained by such simulation, based on reasonable models, are useful in defining critical or sensitive parameters, important operating variables, and perhaps conditions under which experimental studies can be most beneficial.

ELECTRONIC CORRELATIONS

Classical correlations of catalytic properties with electronic properties have relied on the dubious premise that bulk properties could be used for interpretation of surface phenomena. This view is bound to be somewhat self-limiting when we recall, for example, that different crystal faces of the same metal, which must be characterized by the same bulk electronic factors, can have widely different activities for a given reaction. In the following we will only briefly review some of these classical approaches; it would appear that the real progress is now being made through the application of quantum chemical calculations of electronic structures for systems important in catalysis.

For Semiconductors

Electronic correlations have been popular on semiconductor materials because of the close association of their electronic properties with lattice defect structure and the fact that the rate limiting step for a number of reactions which have been studied on these materials apparently involves some type of electron transfer. A typical correlation of this nature is illustrated in Figure 13 for the oxidation of carbon monoxide on nickel oxide. This oxide is normally metal deficient, so that we might represent its lattice structure schematically as in Figure 13*a*, with cationic vacancies and electrical conductivity determined by the resulting positive holes (p type). If monovalent cations such as lithium are incorporated into the lattice (Figure 13*b*), there results an increase in the number of positive holes and hence an increase in conductivity. Conversely, if trivalent ions such as chromium are added, the number of holes decreases and conductivity goes down (Figure 13*c*). The influence of conductivity on the catalytic activity of nickel for oxide oxidation (Figure 13*d*) is pronounced (Schwab, 1957), with a substantial decrease in activation energy for high conductivity material. Two points are suggested by this result. First, very large changes in catalytic properties are caused by very small concentrations of the added cation, suggesting that such properties may, in practical cases, essentially be determined by impurities which are nearly undetectable. Second, in the absence of impurities, the activity of a series of nonstoichiometric p types of semiconductors should be related to the stoichiometric excess of oxygen in the lattice. A very nice correlation of this type is provided by Krauss (1948) for the oxidation of ammonia over a series of p types of semiconductors, shown in Figure 13*e*. It is seen that activity, in terms of conversion to nitrous oxide, is linearly correlated with the stoichiometric excess of oxygen in the lattice.

The correlations illustrated here have been for examples involving p types of semiconductors; results of a similar nature have been reported for a number of n type materials as well (particularly for reactions on zinc oxide). A detailed theory for the catalytic activity of semiconductors has been proposed by Wolkenstein (1960); however, for purposes of quantitative correlation, so many parameters are involved that it seems to offer no particular advantage over the more simple ideas offered here. Recent summaries of semiconductor catalysis are given in the texts of Thomas and Thomas (1967) and of Clark (1970).

For Metals

Electronic correlations for metallic catalysts have generally been based on the Pauling (1949) theory of metals, which proposes that bonding between atoms in metallic crystals is covalent, involving dsp hybrid orbitals. In addition, electrons are found in metallic d orbitals and nonbonding atomic d orbitals which determine the magnetic and conductivity properties of the metal. The percentage d character of a metal refers to the extent to which d electrons act in the dsp orbitals. It is, thus, a measure of the strength of the metal-metal bond; also, for metals within a given period, as the percentage d character increases (stronger bonding) the effective metallic radius will decrease. Just why catalytic activity should be correlated with percentage d character is not entirely clear, since it implies the assumption that bonding in chemisorption and surface reaction is similar to that in the intermetallic bonds. Nonetheless, such a correlation has proven useful in a number of instances, and an approximate method for computing heats of chemisorption has been developed on the basis of the Pauling theory by Eley (1950). Table 7, taken from Hayward and Trapnell (1964), gives some idea of the precision of such calculations. For hydrogen, the computed results are of the correct order of magnitude, and the general trends are observed. For oxygen, carbon monoxide, and nitrogen, the divergence with experiment is clearly greater. Interestingly, in accord with these results successful activity correlations with percent d character seem to be for reactions in reducing atmospheres. In Figure 14 are given two examples of this; the data of Beeck (1950), cited previously in geometric correlation, is also well represented by the electronic correlation, as are the data reported by Sinfelt (1969) for ethane hydrogenolysis on supported metals. We see in the latter correlation (Figure 14*c*) that the metals in the first long period behave in a different manner than those in the next two long periods. Sinfelt suggests this as evidence of a second factor of importance in setting activity, either a secondary geometric factor or differences in the relationship between bond strength in the metal crystal and in the surface layer for metals in the different periods.

TABLE 7. CALCULATED AND EXPERIMENTAL HEATS OF CHEMISORPTION

Gas	Metal	q(exp)	q(calc), J/kg mole $\times 10^{-6}$
H_2*	W	188	154
	Mo	167	119
	Mn	71	58
	Ni	126	78
	Fe	134	80
	Rh	117	103
	Pd	109	72
O_2†	W	812	1 000
	Mo	720	984
	Rh	494	883
	Pd	280	770
	Pt	293	674
CO†	Ti	640	306
	W	343	293
	Ni	176	222
	Fe	193	251
N_2†	W	398	800
	Ta	586	812
	Fe	293	624

* q(exp) is differential heat at low surface coverage.
† q(exp) is integral heat.

Electronic correlations of catalytic activity, based on the free-electron theory of metals, have also been attempted. Dowden (1950) has given rules for bond formation in which the major factors influencing the nature of chemisorption are the metal's work function and the gradient of the density of electron energy states at the Fermi surface. A considerable amount of experimentation with alloys has been reported in attempts to correlate changes in activity with composition by using this theory. The results have been similar to correlations based on the Pauling theory; there does seem to be some relationship between the factors identified by Dowden, but there are many exceptions, and successful correlation is generally qualitative. Part of the difficulty may reside in experiment rather than theory; significant differences between bulk and surface compositions exist in many alloy systems (Burton et al., 1975), as will be discussed later.

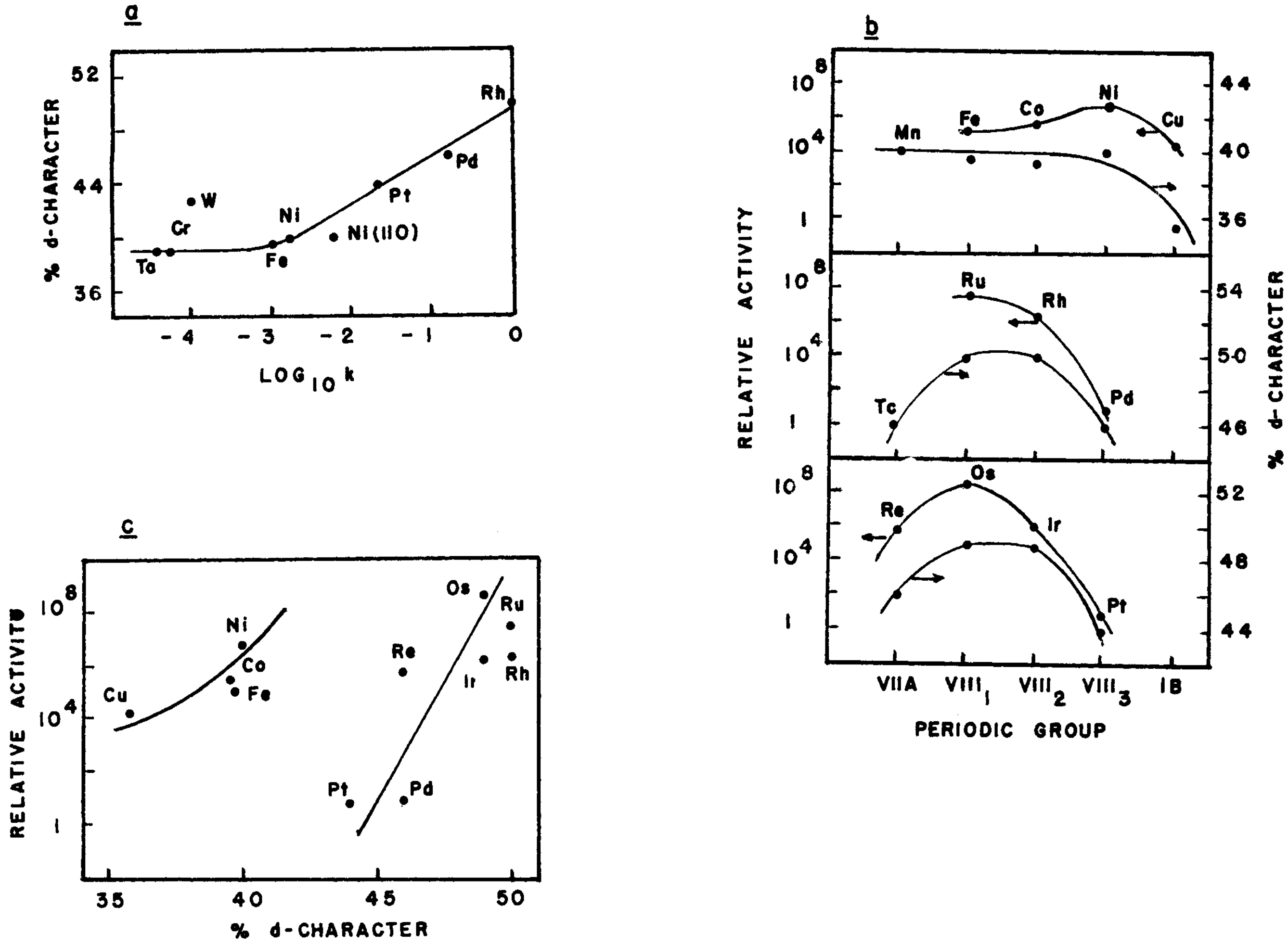


Fig. 14. Electronic correlations for hydrogenation and hydrogenolysis reactions on metal films and supported metals. (a) Ethylene hydrogenation (after Beeck, 1950). (b) and (c) Ethane hydrogenolysis, $T = 205°C$, $P_{C_2H_6} = 0.03$, $P_{H_2} = 0.20$ atm. (After Sinfelt, 1969.)

Microscopic Electronic Structure Calculations

Significant advances have been made in the past 5 yr. in the development of theoretical methods for computation of the electronic structures of systems important in catalysis, such as metallic clusters and electron transfer and bonding on chemisorption of simple molecules on ideal surfaces. A number of such methods are currently under development; we mention here the self-consistent field X-alpha scattered wave approach of Slater (1965) and Johnson (1966) and the discrete variational method of Ellis and Painter (1970). It is, of course, impossible to go into detail on these here, but a single example of some recent results should be sufficient to demonstrate their power and potential future importance to the development of quantitative theories of catalysis.

Figure 15 shows what happens to a carbon monoxide molecule as it approaches a cluster of nine nickel atoms (Waber et al., 1974). At the top of the figure are shown the changes in valence levels as the molecule approaches the surface. The pronounced changes in these levels arise solely from the strong potential field exerted by the metal on the carbon monoxide molecule. When the $2\pi^*$ orbital, which is unoccupied, falls below the Fermi Level of bulk nickel (E_F, shown on the right of the figure), then significant electron transfer from the metal could occur. This occurs at a carbon-nickel plane distance of approximately 3 bohr units.

The results of a more refined calculation, in which metal orbitals from the Ni_4CO nearest neighbor cluster are also included in the calculation, are shown on the bottom of Figure 15. Here changes in charge within the molecule are given as a function of distance from the surface. For free carbon monoxide ($h = \infty$), the oxygen atom is essentially neutral, the carbon atom has a deficit of one electron, and the remaining electron is associated with the carbon-oxygen bond. As a distance of 3 bohr units is approached, the electron deficit on carbon (which is nearest the nickel surface) rapidly disappears, electrons are shifted from the carbon monoxide bond, and there is some transfer to the oxygen. The net charge transfer shown is the movement of electrons from the metal into the carbon monoxide molecule.

Accumulated evidence from chemical studies, mainly on hydrocarbons, suggests that semiempirical molecular orbital methods can be used to estimate binding energies at different surface sites (Pople and Beveridge, 1970). To the extent that these are reliable in estimation of relative binding energies, such calculations can be most helpful in interpreting experimental results such as heats of chemisorption or temperature programmed desorption spectra. The immediate objective of such work would be to distinguish among several models of an active surface, which together with the approaching molecule forms the surface intermediate species, in order to identify the nature of catalytically important species.

As stated previously, such calculational methods are still under development, and workers in the field are careful to

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† In this calculation the complete metal-molecule potential is included, but only orbitals of the molecule are considered.

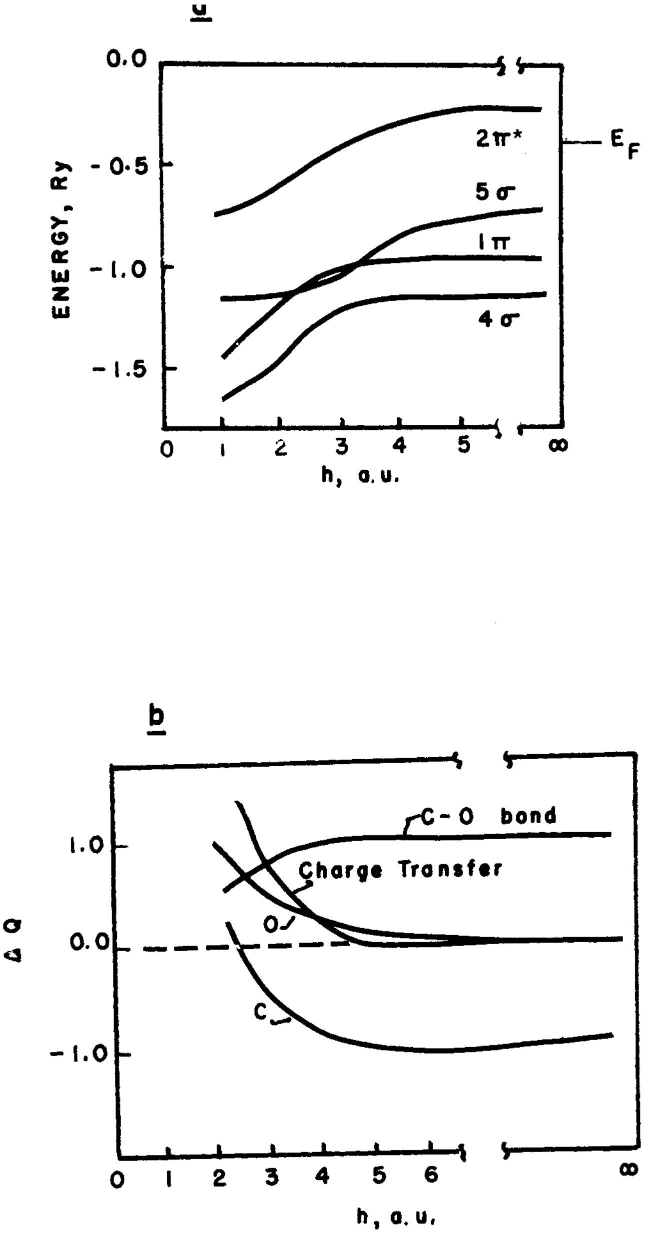

Fig. 15. Interaction of CO with a Ni cluster. (*a*) Changes in energy level C and O orbitals only, $Ni_9(100)$ cluster. (*b*) Changes in electronic structure of the CO molecule. (After Waber et al., 1974.)

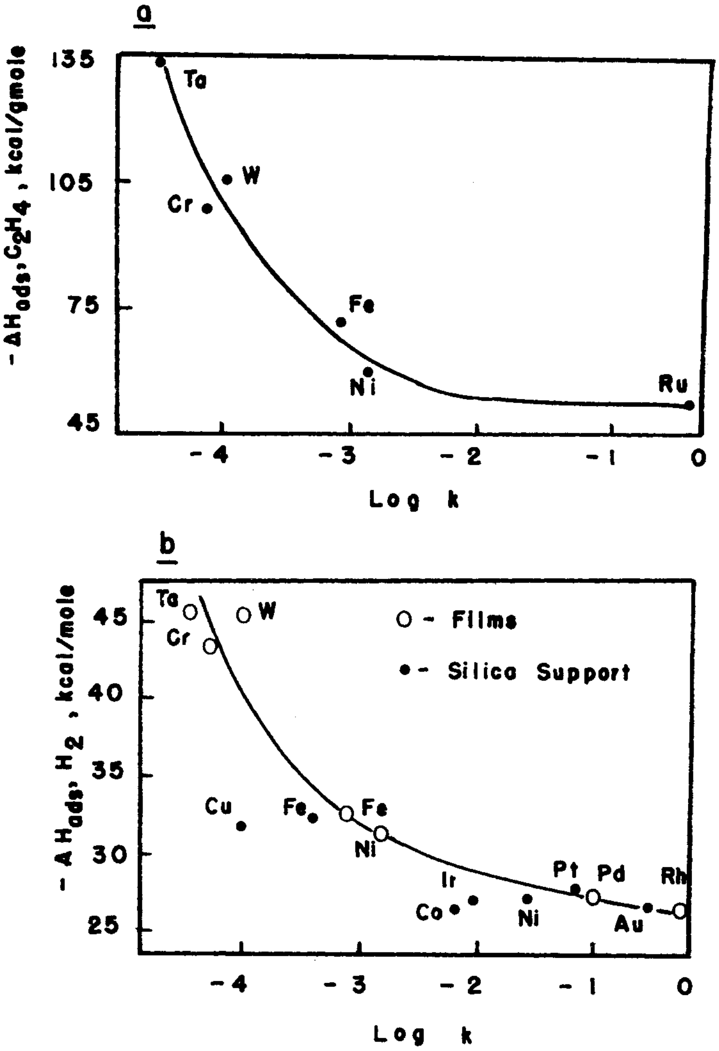

Fig. 16. Correlation of catalyst activity via heat of chemisorption of reactants for ethylene hydrogenation. (*a*) Via ethylene. (*b*) Via hydrogen. (After Beeck, 1950, and Schuit and Van Reijen, 1958.)

state the limitations of such results. However, even if absolute results are not possible at present, trends that can be identified in systematic calculations may still be of considerable value in the clarification of so-called electronic correlations. Further, the results obtained are subject to rather detailed experimental tests based on the electronic spectra of chemisorbed molecules.

SURFACE SPECIES AND REACTION INTERMEDIATES

Although the correlations discussed to this point differ in some extent to the particular property they are concerned with, there is a degree of interrelation among them, as was pointed out at the beginning of this review. The concept of formation of some type of surface intermediate upon chemisorption of a reactant molecule on the catalytic surface is accommodated by all these approaches, so it seems reasonable that some type of correlation could profitably be developed on this basis alone. True enough; the original postulate of Sabatier (1913) was to associate intermediates, at least qualitatively, with known bulk compounds; the problem is how to identify what is the surface species important as a reaction intermediate. Great strides in the identification of surface intermediates have been made in recent years by using various spectral techniques which, unfortunately, it is impossible to summarize here. However, on an a priori basis it would seem reasonable to attempt correlation of the catalytic activity simply with the first step involved in the process, that is, chemisorption. Certainly the strength of reactant chemisorption is important in the surface reaction; a very strong bond would yield a surface species essentially immobile with a high activation energy requirement for further chemical transformation; a very weak bond would lead to desorption from the surface before chemical transformation. The relevant quantity here is clearly the heat of adsorption, and one would expect correlation of maximum activity with chemisorption bonds which are intermediate in strength. Again, we turn to the work of Beeck (1950) on ethylene hydrogenation over metal films. Figure 16 shows the correlation of activity with the heats of chemisorption of both ethylene and hydrogen; in addition, data are included for ethylene chemisorption on some silica supported metals (Schuit and Van Reijen, 1958). In this case the maximum rate corresponds to rhodium, and we obtain a correlation between decreasing activity and increasing heat of chemisorption in both cases and for both films and supported metals in the case of ethylene.

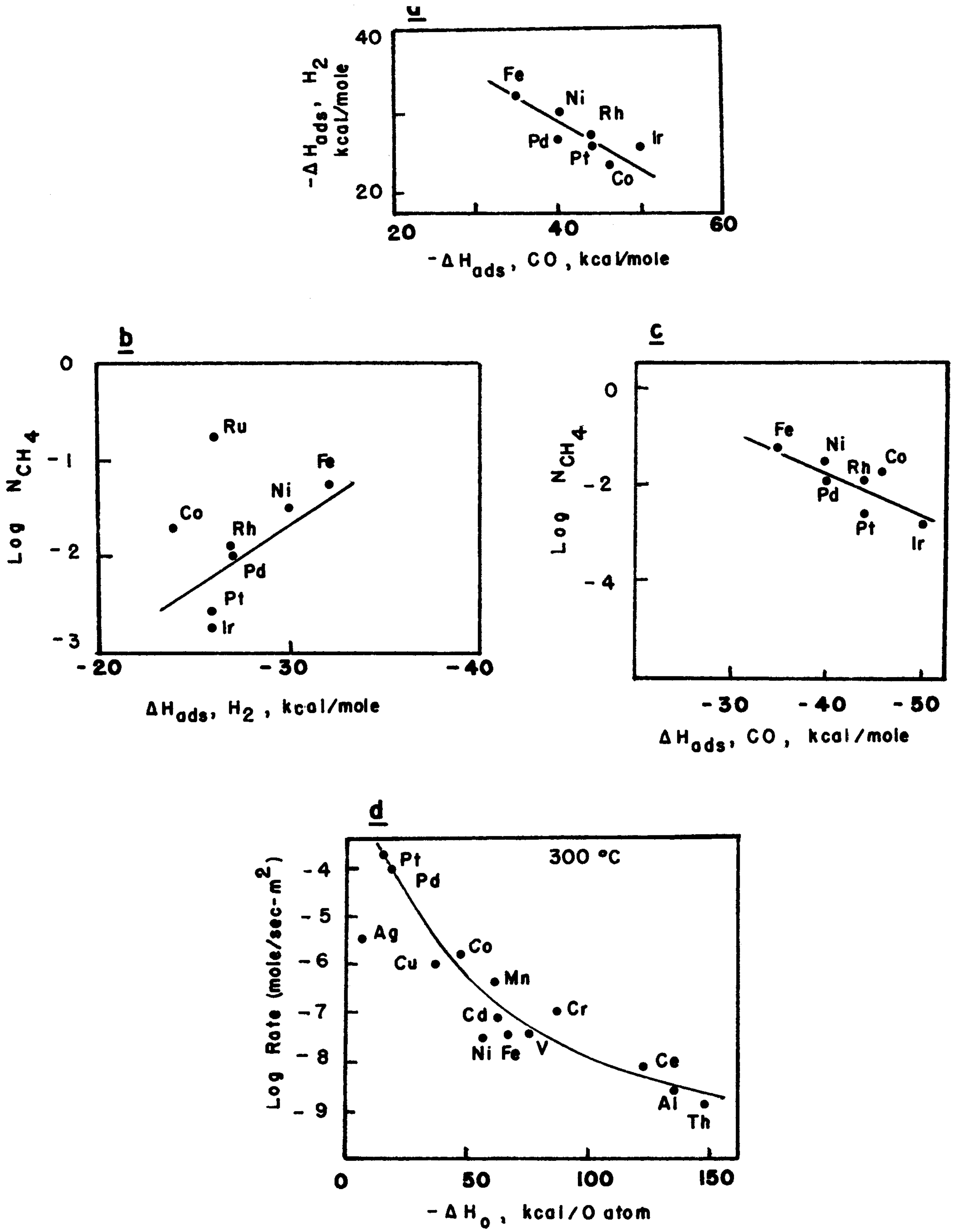

Fig. 17. Further thermochemical correlations. *(a)* Heats of adsorption of H_2 and CO on supported group VIII metals. (*b*) and (c) Turnover number for methane formation (molecules/site-second) vs. heats of adsorption of H_2 and CO (after Vannice, 1975). *(d)* Hydrocarbon oxidation on metal oxides in terms of the heat of formation of the oxide. (After Morooka and Ozaki, 1966.)

More recent data of this sort have been reported by Vannice (1975) for the activity of supported group VIII metals for the carbon monoxide-hydrogen synthesis methanation) reaction. Figure 17*a* gives data for the heats of adsorption of carbon monoxide and hydrogen on the series of metals, showing a consistent decrease in the value for hydrogen with increasing values for carbon monoxide. In other words, the metals on which carbon monoxide is most strongly adsorbed are those on which hydrogen is most weakly adsorbed. Thus, one would expect differing trends in the correlation of activity of the series for methanation. This is observed in Figures 17*b* and *c*. In terms of surface coverage, the closer the heats of adsorption of hydrogen and carbon monoxide, the more nearly equal will be their surface coverages. It is seen that this is most nearly satisfied by iron, for which the turnover number for methane formation is a maximum. This result is in nice agreement with expectations based on the analysis of Boudart (1968), who has shown that the rate of a bimolecular reaction on a uniform surface is maximum for equal coverages of the two reactant species.

For oxidation reactions, an interesting variant on this type of correlation has been successfully employed by Morooka et al. (1966, 1967). We recall the general activity sequence of (A). Now in the general redox mechanism of (I) and (II) the first step involves a reduction of the metal oxide; if this step is the slow one in the redox sequence, then activity should be related to the strength of the bonding of oxygen to the active center. Figure 17*d* gives the correlation of Morooka for propylene oxidation on a series of oxide catalysts in which the strength of the oxygen-active center bond has been taken to be related to the heat of formation of the appropriate oxide. The pronounced decrease in activity with increasing heat of formation is strong evidence that (I) is the rate determining step for this oxidation. Corresponding results are reported also for the oxidations of ethylene, propane, acetylene, and isobutene over this series of oxides. For metals which have several oxidation states, the reduction step (I) is probably from higher to lower oxidation states, and correlation would be expected with respect to the enthalpy of oxidation of the lower oxide per oxygen atom.

A final correlation, perhaps more strictly in accord with Sabatier's postulate, is that of Rootsaert and Sachtler (1960) for formic acid decomposition on metal catalysts. Here infrared evidence suggests that formate intermediates are created upon chemisorption of formic acid on the metals of groups Ib and VIIIb; hence a correlation of catalytic activity vs. heat of formation of the various metal formates was attempted, with the result shown in Figure 18. The temperature required for a given reaction rate is used as a measure of activity, and we see both sides of the volcano correlation expected intuitively for surfaces which range from very weak to very strong in their chemisorption ability for the reactant. This behavior was seen before in Beeck's geometric correlation for ethylene hydrogenation on metal films (Figure 9*b*) and is suggested by the results of Vannice on methanation (Figure 17*b* and *c*). It is surprising that the number of systems for which a complete correlation of this type exists is relatively few, although the enormous amount of effort and experience required to produce the simple diagram of Figure 18 may be one factor.

SOME USEFUL EMPIRICAL APPROACHES

The correlations discussed to this point have all attempted to derive results from some theoretical concept of the nature of catalytic reaction, even though we have seen that the end results are sometimes semiempirical in nature. There are two other types of correlations which are important, which are based wholly on fitting experimental observations, and which are essentially empirical. These are correlations based on the compensation effect between kinetic parameters describing rates of reaction and correlations describing the change in activity of catalysts due to deactivation by various mechanisms.

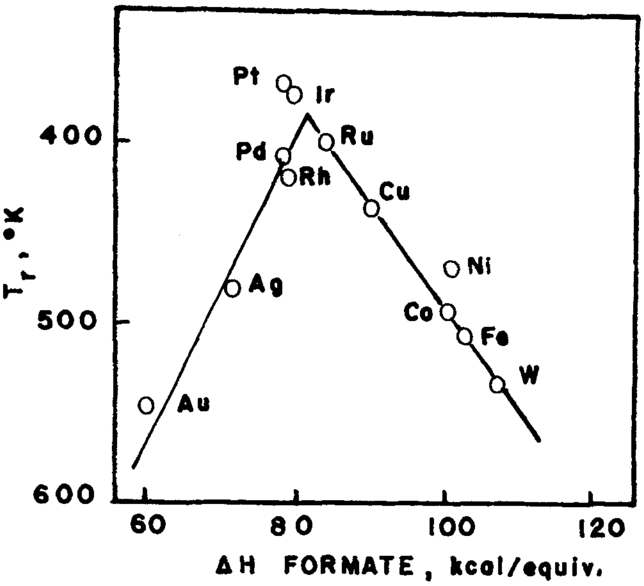

Fig. 18. Activity correlation (temperature for set conversion) for formic acid decomposition on metals of groups I-b and VIII-b. (After Rootsaert and Sachtler, 1960).

Compensation

Compensation effects in catalysis are observed in two general cases: for the same reaction carried out on a series of different catalysts, or for a series of related reactions carried out on the same catalysts. These have been termed activity and selectivity compensation, respectively, by Boudart (1968). Basically, by compensation we mean that when kinetic data can be represented in terms of a rate constant in the form

$$k = A \exp(-E/RT) \tag{5}$$

there exists a relationship between the preexponential factor A and the activation energy E of the form:

$$\ln A = a + b\,E \tag{6}$$

There are numerous examples of compensation, particularly activity compensation, available in the literature; three typical cases are illustrated in Figure 19. The correlations of Sinfelt (1969) and Vannice (1975) represent cases of activity compensation; the correlation of Franklin and Nicholson's (1956, 1957) data by Boudart (1957) is a case of selectivity compensation.

While compensation effect correlations in general are empirical, in some instances at least there seems a reasonable basis for their existence. For the methanation reaction over group VIII metals, Vannice has proposed the following sequence of elementary steps:

$$\begin{array}{lll}
CO \rightleftharpoons CO_{ads} & (K_{CO}) & \\
H_2 \rightleftharpoons H_{2\,ads} & (K_{H_2}) & \\
CO_{ads} + H_{2\,ads} \rightleftharpoons CHOH_{ads} & (K_1) & \text{(VI)} \\
CHOH_{ads} + (y/2)\,H_{2ads} \rightarrow CH_{y ads} + H_2O & (k_1, \text{slow}) & \\
CH_{y ads} + H_2 \rightarrow CH_4 & (\text{fast}) &
\end{array}$$

By following the assumption that $CHOH_{ads}$ is the most abundant surface intermediate, and that hydrogen is weakly adsorbed compared to carbon monoxide, the rate equation is

$$r_{CH_4} = k_2 (K_{H_2} K_{CO} K_1)^{n-y/2}\, K_{H_2}{}^{y/2}\, P_{CO}{}^{n-y/2}\, P_{H_2}{}^{n} \tag{7}$$

On comparison with the empirical power law correlation

$$r_{CH_4} = A\, e^{-Em/RT}\, P_{CO}{}^{Y}\, P_{H_2}{}^{X} \tag{8}$$

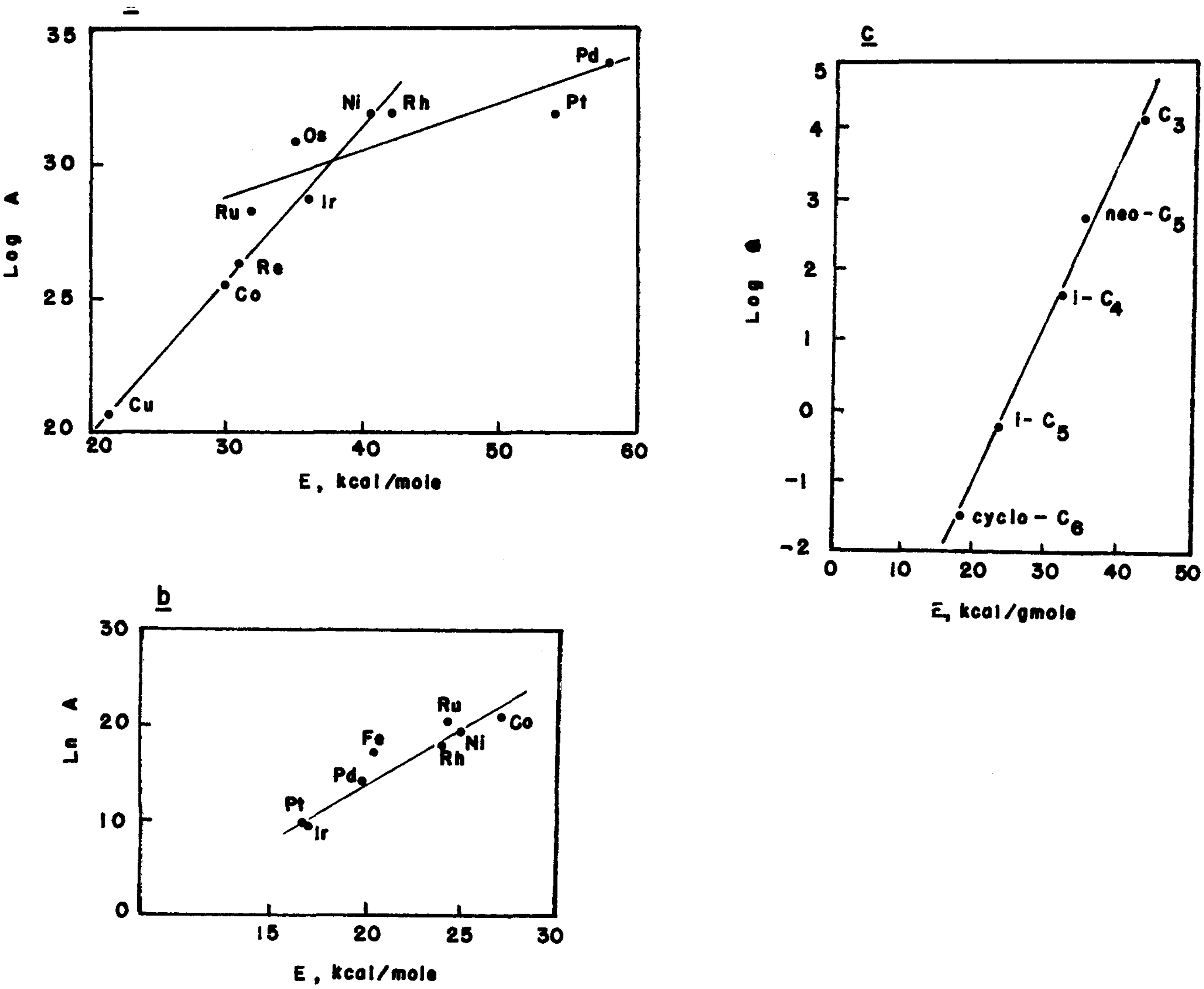

Fig. 19. The compensation effect for activity and selectivity in catalytic reactions. (*a*) Ethane hydrogenolysis over SiO_2-supported metals (after Sinfelt, 1969). (*b*) Methanation over supported group VIII metals (after Vannice, 1975.) (*c*) Hydrocarbon cracking on silica-alumina (after Boudart, 1968).

The following association may be made:

$$A\, e^{-Em/RT} = k_2 (K_{CO} K_1)^{n-y/2}\, K_{H_2}{}^{n} \tag{9}$$

Now the rate and equilibrium constants on the right-hand side of Equation (9) may be written in terms of entropy and enthalpy (or activation energy) factors as

$$k_2 = e^{S^\ddagger/R}\, e^{-E^\ddagger/RT}$$

$$K_i = e^{\Delta S^0_{a,i}/R}\, e^{-\Delta H^0_{a,i}/RT}; \quad i = H_2\, CO$$

where $S^\ddagger$ and $E^\ddagger$ are the entropy and energy of activation in the rate determining step, and $\Delta S^0_{a,i}$ and $\Delta H^0_{a,i}$ are the entropy and enthalpy of adsorption for either hydrogen or carbon monoxide. If we insert these forms into Equation (9), take the logarithm of both sides, and associate all entropic factors with A and all energy or enthalpy factors with Em, the following results are obtained:

$$\ln A = \frac{1}{R}\,[S^\ddagger + n\,\Delta S^0_{a,H_2} + (n - y/2)\,\Delta S^0_{a,CO} + C_1] \tag{10}$$

$$Em = E^\ddagger + n\,\Delta H^0_{a,H_2} + (n - y/2)\,\Delta S^0_{a,CO} - C_2 \tag{11}$$

Here C_1 and C_2 are constants. The compensation effect can be explained by noting that linear relationships between enthalpy and entropy of chemisorption; that is

$$-\Delta S^0_{a,i} = C_3\,\Delta H^0_{a,i} + C_4 \tag{12}$$

have been shown to exist for many catalytic reactions (Boudart et al., 1967). Substitution for $\Delta H^0_{a,i}$ from Equation (12) into Equation (11), and the result into Equation (10), gives a linear correlation of the form of Equation (6).

The reader should also be aware that there are various cases of false compensation in the literature which arise as a consequence of experimental error in kinetic measurements. This can particularly be a problem in experiments where activation energies are determined over a narrow range of temperature. If Equation (5) is used to represent specific rate constants at temperatures T_1 and T_2, respectively, then

$$\ln\left(\frac{k_2}{k_1}\right) \approx \frac{E}{RT^2}\,\Delta T \tag{5a}$$

where $T_1 \approx T_2$. This gives

$$\frac{dk_2}{k_2} - \frac{dk_1}{k_1} = \frac{\Delta T}{RT^2}\,dE$$

The maximum error in activation energy, with random error in k_1 and k_2 assumed, is then

$$\partial E = \frac{2RT^2}{\Delta T}\,\frac{\partial k}{k} \tag{5b}$$

Calculation of the corresponding preexponential factor from Equation (5) via

$$d\frac{(\ln A)}{dE} = \frac{1}{RT} \qquad (5c)$$

shows that any error in activation energy will be in the frequency factor as an apparent compensation. The appearance of ΔT in the denominator of Equation (5*b*) is responsible for the sensitivity of such apparent compensation to the temperature range involved in experimentation. A good example of this is provided by the data of Goodridge and Quazi (1967) and the analysis of Ruthven (1968) for kinetics of the water gas shift reaction on a series of commercial catalysts.

Deactivation

The discussion so far has ignored the omnipresent fact of catalyst mortality. Common causes of deactivation are poisoning by strong chemisorption of impurities on the active site, coking or fouling resulting from the formation of hydrogen deficient carbonaceous residues on the surface in hydrocarbon reactions, and sintering which is the loss of active surface by various processes of agglomeration. Poisoning and sintering are most often rather slow processes, coking rather rapid. As a result, much of the correlation for the former two has been done via the process of kinetic models in which the catalyst activity is viewed as quasi stationary and the effects of deactivation on reaction kinetics are separable (Szepe and Levenspiel, 1970), which allows the expression of an instantaneous rate of reaction as the product of individual factors which are independent of each other. For the main reaction we write the rate equation as the product of three terms, one containing the concentration dependence, one the temperature dependence, and one the activity dependence:

$$r_M = r_1(c)\, r_2(T)\, r_3(s) \qquad (13)$$

Here c is concentration, T temperature, and s the activity. The rate of deactivation is given separately by

$$r_s = \frac{ds}{dt} = r_4(c)\, r_5(T)\, r_6(s) \qquad (14)$$

The basic problem in correlation of poisoning or sintering deactivation is the form to use for Equation (14), or, if adsorption capacity is used as a measure of the extent of deactivation (Figure 3), what the relationship is between amount adsorbed and activity. In many instances, this has been taken to be linear:

$$k = k^0(1 - \theta/\theta_T)$$

Here k is the current rate constant, k^0 the initial rate constant, θ_T the total capacity, and θ the current level of adsorption of poison. In fact, this type of nonselective poisoning is probably fairly rare, as the data of Figures 3 and 4 would indicate and as we have had occasion to find out in this laboratory for sulfur poisoning of nickel catalysts (Weng et al., 1975). For sintering of supported metals, the rate of loss of active surface appears in most cases to be well correlated by

$$\frac{dA}{dt} = -k_s A^m \qquad (15)$$

where A is the current surface area, k_s a sintering rate constant (often with a very high activation energy), and m an empirical constant whose values have been reported to range from 2 to 13. One striking factor concerning the sintering of supported metals (the bulk of the data available are for supported platinum) is the high activation energies associated with the process. If k_s in Equation (15) is written in Arrhenius form, apparent activation energies ranging from 6.28×10^7 J/kg mole (in hydrogen atmosphere) to 3.77×10^8 J/kg mole (in nitrogen atmosphere) have been reported for platinum supported on alumina (Wanke and Flynn, 1975). In general, it appears that activation energies for sintering are higher in oxidizing atmospheres than in reducing atmospheres, and owing to the large activation energies often involved, sintering can indeed be a very slow process. There have been several theoretical treatments showing the physical basis for correlation of sintering rates via Equation (15); this topic is treated in detail in a current review by Wanke and Flynn (1975).

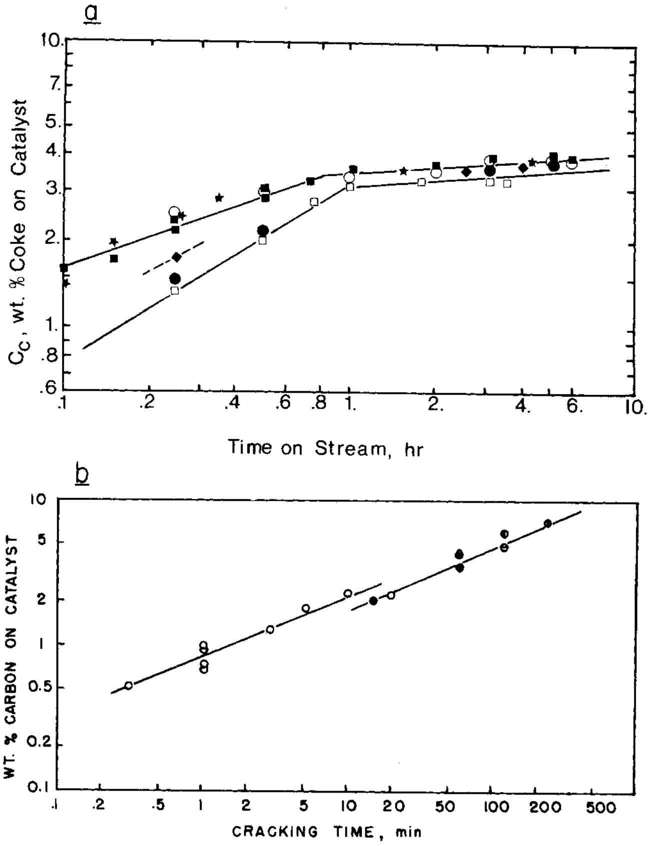

Fig. 20. Voorhies correlations of coke deposition on cracking catalysts. (*a*) Cumene cracking on H mordenite. Upper curve, 260°C, lower, 350°C (symbols represent various pretreatment conditions; after Butt et al., 1975). (*b*) Gas-oil cracking on silica-alumina. Lower curve *SV* = 1.2 vol./vol./hr., West Texas GO., natural catalyst; upper curve, *SV* from 0.3 to 1.2 vol./vol./hr., East Texas GO., synthetic catalyst (after Voorhies. 1945).

Catalyst deactivation by coking is, on the other hand, normally a rather rapid process whose chemical mechanism, even in the most thoroughly investigated systems, is ill defined. As a result, the coking correlations which are employed in practice tend to be strictly empirical. Weekman (1968) has shown that the decay of cracking catalysts can be correlated with time of utilization by either exponential or logarithmic expressions:

$$\begin{aligned} k &= k^0\, e^{-\alpha t_c} \\ k &= k^0/t_c{}^n \end{aligned} \qquad (16)$$

Here α and n are empirically determined constants. Wojciechowski (1974) has shown that a hyperbolic decay correlation, also based on time on stream, works well:

$$k = k^0/(1 + \beta t_c{}^n) \qquad (17)$$

Here again β and n are fitted constants. Probably the most successful general correlation for coking, and the oldest, is that of Voorhies (1945) which proposes

$$C_c = a\, t_c^{\,n} \tag{18}$$

with a and n constants and C_c the weight of coke on the catalyst. This has been shown to work on anything from A (alumina) to Z (zeolites); two examples are shown in Figure 20 (Voorhies, 1945; Butt et al., 1975). Note, however, that the correlation is for weight of coke on catalyst, not catalyst activity, so the question of the nature of the relationship between the two again arises. The break in the linear correlation observed for the deactivation of mordenite in Figure 20 is associated with a rapid initial deposition of coke on the very active surface, forming a well-defined outer shell. Subsequent to this period, diffusion through the shell appears to control the rate of coking and the decline in activity. Further details on coking correlations are given in a recent review (Butt, 1972).

ON ALLOYS

As mentioned briefly before, alloys have played a role from time to time in experimental studies of electronic correlations, since the electronic properties of many alloys (for example, copper-nickel, palladium-gold) are determined by composition. By and large, such attempts have met with indifferent success (Clark, 1970). A prime reason for this difficulty in working with alloys is the fact that surface composition and bulk composition may well differ. While most workers acknowledge this possibility, nonetheless most correlations are conducted in terms of bulk composition.

Understanding the relationship between bulk and surface composition in alloys would thus appear to be a crucial factor in understanding the properties of this increasingly important class of catalysts. Rather little progress has been made in this direction, at least for alloy crystallites of small dimension, until the recent analyses of Ollis (1971), Hoffman (1972), and Burton et al. (1975). In the latter case, a model based on regular solution theory gives the following result for the surface/bulk composition relationship for single phase (bulk) binary alloys:

$$\frac{X_A{}^s}{X_B{}^s} = \left(\frac{X_A{}^b}{X_B{}^b}\right) e^{\Delta F/RT} \tag{19}$$

Here $X_i{}^s$ and $X_i{}^b$ are surface and bulk atomic fractions, respectively, and ΔF the free energy change when an atom of A is transported from the bulk to the surface. The value of ΔF is obtained from

$$\Delta F = \Delta Z(H_B - H_A)/Z \tag{20}$$

where H_A and H_B are the heats of sublimation of A and B, Z is the number of nearest neighbors for a bulk atom, and ΔZ is the deficiency in nearest neighbors for a surface atom.

This analysis was applied (Burton et al., 1975) to the data of Sinfelt et al. (1972) on the kinetics of the hydrogenalysis of ethane over copper-nickel. The rate determining step in that reaction was reported to be C—C bond rupture on the surface; hence the overall rate of reaction can be written as:

$$\begin{aligned} r_0 = {} & (k_s = \text{rate of C—C bond rupture at the surface site}) \\ & \cdot\ (\theta_s = \text{fraction of surface sites covered})\ \cdot\ (X_s = \\ & \text{concentration of surface sites which are catalytically} \\ & \text{active}) \\ = {} & k_s\, \theta_s\, X_s \end{aligned} \tag{21}$$

The quantity X_s is related to surface composition as determined from Equation (19). For the copper-nickel system, calculation of the surface/bulk composition relationship gives some interesting results, shown in Figure 21*a*. Over almost the entire range of bulk composition, the surface is primarily composed of copper. However, it is known that pure nickel is a very active catalyst for ethane hydrogenolysis, while copper is almost inactive, so the surface active site must be associated with nickel atoms, and X_s in Equation (21) must refer to nickel surface concentration. Thus

$$X_s \propto (X_{Ni}{}^s)^n \tag{22}$$

where n refers to the number of nickel atoms constituting an active site. Rewriting Equation (21) in Arrhenius form, and substituting for X_s from Equation (22), we have

$$r_0 = k_s{}'\, e^{-E/RT}\, (X^s{}_{\rm Ni})^n \tag{23}$$

Substitution for $X^s{}_{\rm Ni}$in terms of bulk nickel concentration gives

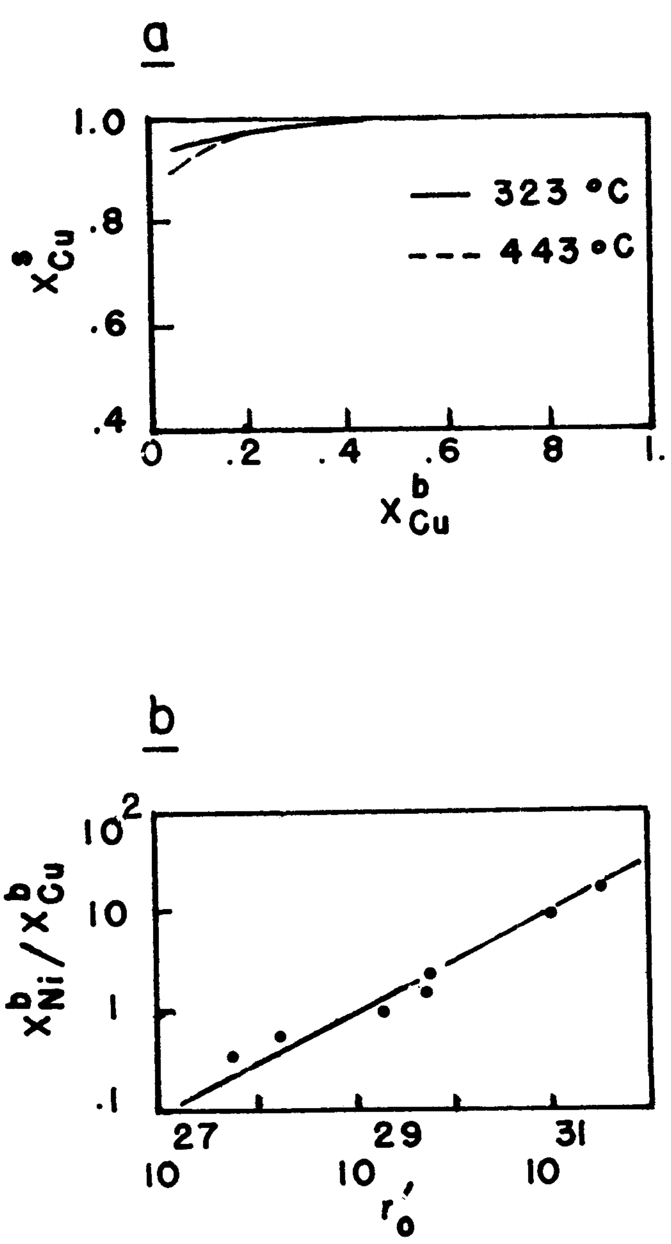

Fig. 21. (*a*) Relationship of bulk to surface copper composition in a Cu-Ni alloy (after Burton and Hyman, 1975). (*b*) Correlation of the kinetics of ethane hydrogenolysis on Cu-Ni catalysts according to a regular solution model for surface composition (after Burton and Hyman, 1975).

$$r_0 = \left(\frac{X^b{}_{\mathrm{Ni}}}{X^b{}_{\mathrm{Cu}}}\right)^n k_s' \, e^{-(E+n\Delta F)/RT} \qquad (24)$$

where the approximation $X^s{}_{\mathrm{Cu}} \approx 1$ has been made. Now, the original kinetics of Sinfelt et al. were well correlated by an Arrhenius form

$$r_0 = r_0' \, e^{-E_a/RT} \qquad (25)$$

so that comparison of Equations (24) and (25) indicates that if the analysis is correct, a log-log plot of r_0 vs. $(X^b{}_{\mathrm{Ni}}/X^b{}_{\mathrm{Cu}})$ should be linear with slope n. This result is shown in Figure 21*b*, with a good linear correlation obtained for $n = 2$, suggesting that the surface active sites are paired nickel atoms.

Burton et al. also report corresponding regular solution theories for alloys having bulk miscibility gaps. The major difference is that for alloys demonstrating no miscibility gaps, component segregation occurs only to sites having a deficiency of nearest neighbors, whereas when miscibility gaps are possible, segregation can extend into the interior of the crystal. For very highly dispersed alloys, the distinction is perhaps not so important; preferential segregation to sites of lower coordination number of the more volatile component (weaker metal-metal bonds in the pure material) in either case would imply its concentration enhancement at corners and edges. The striking success of this simple approach in this instance provides hope that some foundation has been established for interpretation of catalytic kinetics on alloy surfaces. To be sure, only one catalyst/reaction system is involved here; further test of the correlation will depend, as we have seen in so many of the examples discussed in this review, on many painstaking and systematic studies of reaction kinetics on alloy catalysts.

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THE AUTHOR

John B. Butt experienced his first encounter with catalysis at Yale around 1958 in his doctoral research under the wise guidance of Harding Bliss and Charles Walker. While intellectually stimulating, that experience was also humbling, since the catalyst never seemed to do what it was told. In subsequent years on the faculty at Yale he developed parallel and overlapping research interests in chemical reaction engineering and catalysis, yet to this day he does not seem to be able to get catalysts to obey orders. In 1969 Northwestern University became the business address, and since 1972 he has been associated with the Ipatieff Catalytic Laboratory as well as the Department of Chemical Engineering at Northwestern. Due to a certain preoccupation with catalyst poisoning problems however, Professor Carberry has suggested the name be changed to the Lucrezia Borgia Laboratory. This item is submitted without comment.

Outside interests consist of a mediocre level of ability in tennis, sailing and the French language, and some competence in the history of the great Commonwealth of Virginia.

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