Strategy of Research on Supported Metal Catalysts. Problems of Structure-Sensitive Reactions in the Gas Phase

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What Are Supported Metal Catalysts?

Supported metal catalysts comprise 0.1–20 weight percent of a metal of group 8 or 9 dispersed over the surface of a *support*, which is typically a high-surface-area oxide. They are widely used on an industrial scale and in research laboratories. Principal large-scale uses include hydrogenation of animal and vegetable oils (fat hardening), petroleum reforming to make high-octane gasoline, and treatment of vehicle exhaust to minimize environmental pollution. These materials are effective as catalysts because the active metallic phase is present as extremely small particles, having a *degree of dispersion* (that is, the fraction of atoms exposed at the surface) of 10–100%. They are firmly anchored to the support and are widely separated from each other, and hence do not readily coalesce, or sinter.

A Critique of Previous Research

Like all attempts at generalizations, the above statements, while reasonably accurate, reveal only a very small fraction of the wealth of information available in the open and patent literatures on these materials. Their very great practical importance has generated an enormous number of publications, the flow of which shows no sign of diminishing. However, despite the prodigious effect already deployed, many fundamental questions remain unanswered. In a recent review,[1] I expressed the opinion that "Reflection on the research carried out in the field of heterogeneous catalysis over the last four decades will show not so much a catalogue of problems solved as of problems shelved."

This sentiment is particularly true when applied to supported metal catalysts. One might have thought, or at least have hoped, that by now some of the outstanding questions might have received definitive answers. A number of facts are indeed firmly established, but disagreement enters as soon as one starts to consider their interpretation. It therefore behooves us to consider what are the objectives of research on supported metal catalysts and what are the reasons for the lack of faster progress in constructing acceptable theoretical models to account for the observations. My credentials for discussing these questions are that I have been continuously concerned with research and

development in this field for 44 years. How much wiser am I now than when I started? If I have not been getting satisfactory answers, is it because I have been addressing the wrong questions? What exactly are we trying to find out anyway? I would like to consider these matters in the context of examples taken from the recent literature and from my own experience. Emphasis is placed on so-called "structure-sensitive" reactions, particularly of hydrocarbons, proceeding in the gas phase.

The Objectives of Research on Supported Metal Catalysts

There are basically two types of objectives for research on supported metal catalysts: (i) the discovery of improved catalysts and (ii) the better understanding of phenomena already known. The purpose of the first type is to make, initially on a laboratory scale, catalysts which are more active, stabler, more resistant to poisoning, cheaper, and in particular more selective toward the desired products of the reaction. Work of this type is mainly the province of industrial scientists: it is unclear exactly how useful is fundamental theory to realizing a particular target, but empirical experimentation and extrapolation from known facts certainly still play a part and major discoveries continue to arise from the fortunate or fortuitous observation.

The second type of research is curiosity-driven and is chiefly the province of academics: we recall the old adage that "Scientific research is a means of satisfying one's curiosity at the public expense." It seeks an atomic–molecular description of events occurring during catalysis, the construction of conceptual models hopefully having predictive value, and a specification of a "reaction mechanism". This work addresses in the main known reactions and established catalysts, or relatively simple extensions of what is currently known. It is indeed disturbing that there is so little work in academic institutions that is designed to expand our knowledge of descriptive chemistry, that is, to discover quite new reactions and catalysts. In my experience, in the United Kingdom, grant-awarding bodies are reluctant to fund speculative work, preferring rather the safe if unadventurous path.

The problem of specifying a satisfactory mechanism for a heterogeneously catalyzed reaction is altogether more difficult than for a reaction proceeding homogeneously in either the gas or liquid phase, for reasons which will become clear. Indeed there is no agreement as to what it is that needs to be specified, or (based on

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(1) Bond, G. C. *Chem. Soc. Rev.* **1991**, *20*, 441–475.

some papers I read) whether anything needs to be specified at all. Some years ago we attempted[2] to define the minimum information required in the case of hydrogenation reactions; if I were to repeat the exercise now, the result might be somewhat, but not greatly, different. Some guidelines concerning discussion of reaction mechanisms will be suggested later.

Difficulties in the Development of Theoretical Models

The difficulty of devising comprehensive and comprehensible theoretical models to rationalize experimental observations arises chiefly from the sheer complexity of every catalytic system (that is, the catalyst–reactant–product combination) and from the variety of scientific inputs which need to be applied. Thus the preparation of a supported metal catalyst involves inorganic chemistry; the reaction may be organic in nature; it is studied by kinetic methods, which are in the sector of physical chemistry, the results of which may require sophisticated mathematical modeling; complex problems of analysis may arise, and the science of the solid state is relevant to the understanding of the catalyst's mode of action. Indeed there are few parts of physical science which one can confidently say are irrelevant to the phenomenon of heterogeneous catalysis.

Variable Factors in Catalyst Preparation: Their Causes and Consequences

The complexity shows itself in the extreme sensitivity of the catalyst to all facets of its preparation and pretreatment. Let us suppose that the quantity we wish to specify is the rate given by a unit amount of catalyst for a given reaction under clearly determined conditions of temperature, reactant concentration, etc. Let us further define the catalyst in question as Ru/TiO$_2$, one which has been quite thoroughly studied.[3-5] Now a partial list of the factors which will affect the measured rate would contain the following items: (i) the weight of catalyst used, (ii) the metal concentration in the catalyst, (iii) the Ru compound used in the preparation, (iv) the phase of the support (anatase/rutile), (v) its surface area and pore size distribution, (vi) its chemical purity, (vii) the method and scale of preparation used, (viii) conditions for drying the precursor, (ix) whether it is calcined or not, (x) the method of reduction (reductant, temperature, flow rate, etc.), and finally (xi) the conditions under which it is brought to the reaction temperature. Most of these factors have been established to apply to Ru/TiO$_2$;[5] all are known to require control on occasion, although not all factors are equally important to all catalysts. Ru catalysts do seem for example to be more temperamental than Pt catalysts.[6]

However, the exercise of a reasonable degree of control over all these variables is still no guarantee that reproducible rates will be obtained. Sample-to-sample variability due to lack of full control over pretreatment and reduction of the precursor can be considerable, even when care is exercised over gas purity, flow rates, and heating rates. Different laboratory-scale preparations show an even greater range of activities, especially when different operators are involved.[5] It is in this regard that the intrinsic sensitivity of a catalytic system manifests itself.

We must now ask why and how these variables affect the outcome. (A) First, an elementary point: the catalyst must operate under chemical control, i.e. the reaction must not be mass-transport limited (items i and v are relevant). Such limitation can operate either without or within the support's pore structure; if with a given catalyst the latter is suspected, it is necessary to lower either the rate of the surface reaction or the particle size of the catalyst.[7] If this is inconvenient, the choice of support must be altered to one having a larger mean pore radius and the location of the metal moved so that it is more accessible to the reactants. Preparation methods (item vii) can be fine-tuned to give the best concentration profile for any particular circumstance.[8] (B) The measured rate is at least partly determined by the exposed Ru surface area, i.e. by the number of Ru atoms available for catalysis (viz. the *fraction exposed* or the *degree of dispersion*): items ii, iii, v, and vii–x all bear on this. (C) The number of effective Ru atoms may be diminished by the presence of adventitious poisons: Cl$^-$ is especially troublesome, if RuCl$_3$ is the source of the metal,[9] and S^{2-}, if the support is prepared by a sulfate route[10] (items iii, vi, ix, and x are relevant).

If these were the only factors needing to be monitored, our problems would be comparatively straightforward. However, when all the necessary corrections have been applied (for example, by quoting the rate per exposed metal atom, i.e. as a turnover frequency), there can still remain substantial differences between one catalyst sample and another,[5] and these concern not only rates but also activation energies and product selectivities.[5,11] In fact, turnover frequency is only expected to be constant where the active center[12] comprises a single metal atom, i.e. where the number of surface metal atoms counted for example by titration with H$_2$ in a selective chemisorption procedure equates to the number of points at which the reaction can proceed.[13] While there are a number of cases where this appears to be true, for example, in simple C–H bond-making and bond-breaking processes as in alkene hydrogenation and alkane dehydrogenation, there are also well-established instances where the active center must contain several metal atoms (N_B), so that the number of centers (N_c) will be less than the total number of free surface atoms (N_t). The ratio of the number of active

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centers to the total of surface atoms has been called the Taylor ratio r_T;[14,15] thus

$$N_c/N_t = r_T$$

However the relationship

$$r_T = N_B^{-1}$$

only holds if all titrated atoms participate in active centers; commonly there will be some single metal atoms, or small groups, which cannot contribute to the ensemble of atoms which make the active center. Variations in particle morphology (i.e. shape and surface roughness) can therefore contribute to apparent variability of rates and other kinetic parameters; these factors are however not easily validated by independent methods. Indeed the number of active centers in a working catalyst can only be obtained by inference: reliable methods to estimate their number are sorely needed.[16]

Systematic Variation of Structure and Composition: (i) Structure Sensitivity

The foregoing discussion does not embrace the deliberate and systematic variation of any of the parameters known to influence the catalyst's performance. Such studies are however commonly made and are informative: in particular the alteration of those items (for example, ii, ix, and x in the above list) likely to change the mean particle size and size distribution of the metal will reveal the presence or absence of a *particle size effect*, that is, a dependence or otherwise of the rate per unit of metal area or the turnover frequency on the size of the metal crystallites. Where a positive dependence is observed, it is commonly taken as evidence that N_B (which we may call the Balandin number) exceeds unity and therefore that the probability of finding an active center in a unit of metal area increases with particle size.[17] Reactions showing this behavior are termed *structure-sensitive*,[13] although it is probably better to reserve this term for situations where surface structure is altered either by annealing[18] or by taking planes of different Miller indexes through a single crystal of the metal.[19] When particle size in a supported metal is changed and this alters turnover frequency, we should perhaps speak of *particle-size sensitivity*.

Much effort has been expended in attempting to use geometric models of small metal particles[20] to understand how the populations of various groups of surface atoms might change with particle size (Figure 1) and thus to explain variations in turnover frequency. This approach, while simple and aesthetically satisfying, is limited in its usefulness by the breadth of particle size distributions and by the possibility that the surfaces of some metals, especially those having somewhat low melting points, may at high temperatures be in semifluid states and therefore lacking in definite structure;[21]
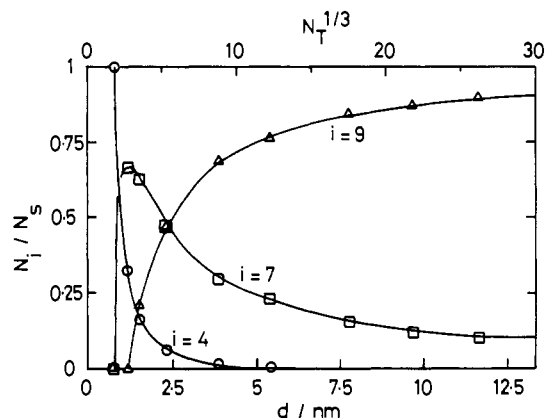
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Figure 1. Variation of the fraction N_i/N_s of surface atoms of coordination number i as a function of particle size d and of $N_T^{1/3}$ for the uniform cuboctahedron model.[20]

electronic effects may yet need to be invoked. Electron bandwidth increases with particle size and with temperature,[17] so both geometric and electronic explanations may be needed, according to the circumstances.

Reactions whose turnover frequencies are unresponsive to particle size or surface structure have been termed *structure-insensitive*,[13] but it is by no means clear that every reaction should be deemed to fall into one category or the other. Just as one cannot say that all people are either tall or short, so it may be that catalyzed reactions show various *degrees of structure sensitivity*. This concept reflects Taylor's original idea that "the fraction of surface utilised depends on the reaction being catalysed" and has been quantified by David Avnir[22] who, using fractal theory, has defined a *reaction dimension* D_R as rate $= kR^{D_R-3}$ where R is the mean particle radius and k is a constant. This approach has been criticized[14] but at least has value in recognizing that shades of grey are possible and that the degree of structure sensitivity will reflect the stringency with which atoms composing an active center have to be chosen. Broadly speaking, the greater the number of atoms in the center, the higher will be the degree of structure sensitivity.

(ii) Metal–Support Interactions

When the gross chemical composition of the catalyst is changed by use of a different support, the activity of the metal may be greatly varied. Some of the effect may be due to the different physical structure and chemical purity of the new support (items iv–vi in the above list), so that the particle size of the metal may consequentially alter. The possibility of epitaxial growth of the metal particles on the support may provide a reason for invoking shape and morphology factors.[23] Reducible supports (especially TiO_2 and V_2O_3) are well-known to induce a *strong metal–support interaction* (SMSI); the very great volume of work generated by the original observations[24] seems to suggest that there may be two different effects at work. First, partial reduction of the surface of the support by hydrogen spillover leads to formation of anion vacancies and Ti^{3+} or V^{2+} ions, which affect particle morphology and electron density within the metal particle M, by

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processes such as $Ti^{3+} + M \rightarrow Ti^{4+} + M^-$ etc. Secondly, there is good evidence that the partial reduction of the support mobilizes the surface, so that species TiO_x or VO_x migrate onto the metal, leading to partial (sometimes selective) or complete inactivation.[25] However, not dissimilar phenomena have also been found with MgO,[26] ZrO_2,[27] Nb_2O_5,[28] and Al_2O_3;[11] only in the case of Nb_2O_5 is reduction by molecular H_2 thermodynamically favored, any reduction of cations in the other cases requiring H atoms generated by spillover.

The Importance of Kinetic Measurements

If we simply measure the rate of the chosen reaction under one specific set of conditions, we deprive ourselves of much valuable information. Knowledge of the manner in which rates and product selectivites vary with temperature and with reactant concentrations is essential for the complete description of the reaction and its mechanism. While it has long been appreciated that it is virtually impossible to derive a mechanism from purely kinetic evidence, it is important to recognize that no proposed mechanism passes the test of acceptability until it has been shown to be consistent with the observed kinetics. With hydrocarbon reactions, it is vitally important to know the state of cleanliness of the surface, as most hydrocarbons more or less readily form a partial layer of dehydrogenated "carbonaceous residues" which not only lower the rate but can affect other kinetic parameters as well.[29] Thermal cycling procedures, involving accelerated aging at high temperature, reveal how important this is,[30] and it is only by the use of short reaction pulses (1-2 min)[31,32] that effects due to "carbon" deposition can be minimized and kinetics results pertaining to a substantially clean surface obtained.

Kinetic studies embracing effects of reactant concentrations and temperature can however assume an importance beyond that of simply validating a possible mechanism. Much interest continues to surround reactions of hydrocarbons on metal catalysts[1] and the dependence of "catalyst activity" on measurable parameters of the catalyst. However, use of a single set of reaction conditions, giving a single rate measurement, is without significance, as the relative activities of two catalysts can vary depending on the reactant pressures and temperatures used. If the form of the rate variation with reactant pressure is itself temperature-dependent, then the activation energy will also vary with the reactant pressures used (Figure 2).[33] The true activation energy may be greater or less than that derived from temperature dependence of the rate, according to whether the concentration of the adsorbed species involved in the rate-determining step falls or rises as temperature is increased.

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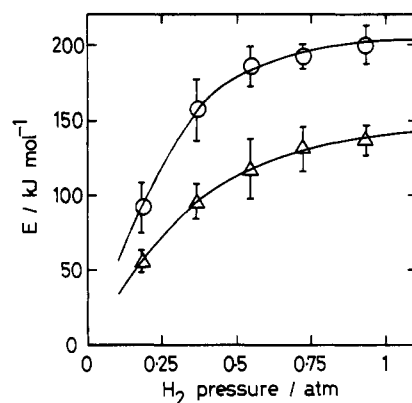(33) Cunningham, R. H. Ph.D. Thesis, Brunel University, 1992.

Figure 2. Variation of the apparent activation energy with H_2 pressure for hydrogenolysis of propane (O) and of *n*-butane (A) over 0.3% Pt/Al_2O_3.[33]
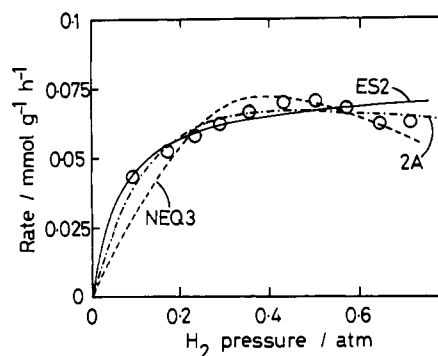

Figure 3. Dependence of the rate of *n*-butane hydrogenolysis with H_2 pressure on coked $Pt-Re/Al_2O_3$: congruence of results with alternative rate equations.[31]

The only sure basis of comparison would seem to be the full rate expression, which should yield the true activation energy and pre-exponential factor. It is however not always easy to decide which of several alternative rate expressions best fits the results. In complex hydrocarbon reactions (e.g. hydrogenolysis of alkanes), quite radically different rate equations can give approximately equal qualities of fit by adjustment of the variable terms (Figure 3).[32,33] This reinforces the old belief that kinetics cannot discriminate effectively between mechanisms, although one postulates a mechanism in the absence of kinetic information at one's peril.

Degree of Structure Sensitivity

Notwithstanding all these constraints and uncertainties surrounding what is reported in the literature, there is nevertheless sufficient reliable information available to attempt some generalizations.

There is no reason to believe that a given reaction will exhibit the same degree of structure sensitivity on all catalysts: the data available are insufficient, but there are well-established cases when a reaction is highly structure-sensitive on one metal, but is structure-insensitive on another. One clear example is the hydrogenation of cyclopropane, which on Pt catalysts is insensitive but on Ru catalysts is highly sensitive to particle size variation.[1] It is therefore preferable to speak of the sensitivity shown by a *catalytic system*, i.e. the combination of reaction plus catalyst.

The extent to which reactions of different types respond to variations in particle size with Ru catalysts of similar type is well-illustrated by (i) alkane hydro-

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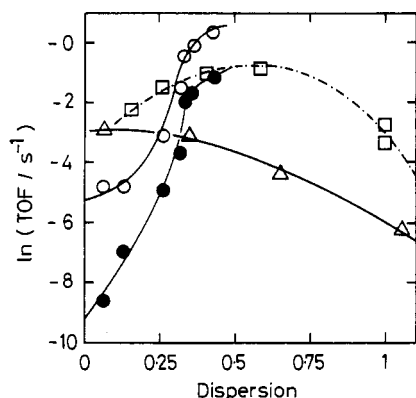
Figure 4. Variation of the turnover frequency with metal dispersion. Hydrogenation (O) and hydrogenolysis (●) of cyclopropane on various Ru catalysts.[1] Hydrogenolysis of n-butane on Ru/Al$_2$O$_3$ catalysts (△).[1] Hydrogenation of benzene on Ru/SiO$_2$ catalysts (□).[34]

genolysis (TOF increases with size),[1] (ii) cyclopropane hydrogenation (TOF decreases with increasing size),[1] and (iii) benzene hydrogenation (TOF passes through a maximum) (Figure 4).[34]

It is interesting to speculate exactly how specific are the requirements for the active center in a particular catalytic system. It seems probable, and in harmony with some of the earliest thinking on the subject, that molecules may react at different rates on different types of centers; in some cases,[1] the products formed change markedly with particle size, presumably as alternative sites become available and operational. With alkane reactions, the process requiring the larger active center is preferred where possible, probably because it has the more favorable kinetic parameters.

Generalizations are always dangerous, but are a necessary step in the clarification of ideas. In systems of high structure sensitivity, reactions appear to proceed only at high temperatures (>375 K) and to show high activation energies (>75 kJ mol⁻¹): hydrogenolysis of alkanes on most metals (but not curiously enough cyclopentane and its homologues[17]) and reactions of CO with H$_2$[35] are good examples. In systems of low structure sensitivity, on the other hand, reactions often show low activation energies (<60 kJ mol⁻¹) and proceed at low or even subambient temperatures: hydrogenation of alkenes and exchange of alkanes with D$_2$ are examples of this class.[16,36] Space limitations forbid any fuller review of the pertinent literature, so the interested reader is referred to recent reviews.[1,17]

In view of the evidence favoring energetically-inhomogeneous surfaces in consequence of there being atoms of different coordination numbers, it is hard to understand why some reactions appear to show low or zero structure sensitivity. Among the explanations canvassed are the following. (1) All surface atoms are indifferently active for reactions of this type. (2) The surface is homogenized by the adsorbed reactants. (3) Most of the surface is covered by toxic species, only a small and uniform fraction remaining active. (4) In reactions of hydrocarbons, the surface is totally covered

by a carbonaceous layer on top of which the catalyzed reaction proceeds.[37] These last two points have been much debated,[16] but the issue remains unresolved; many obvious experiments have not yet been performed. It is true that alkenes react quickly and extensively with clean metal surfaces,[38] even at subambient temperatures: unfortunately degrees of dispersion are usually measured before the reaction rather than after, so that no direct estimate of the area of the surface free for reaction is made.

Reactions capable of yielding a variety of products are paradoxically often more informative than their simpler counterparts.[2] Thus, in reactions of the n-butenes with H$_2$, one may observe hydrogenation, double-bond migration, and cis–trans isomerization. R. L. Augustine[39] has applied his STO (single turnover) technique in an effort to identify what different sites are responsible for each: 1-butene reacts with an H-covered surface to give n-butane and butene isomers, but some butyl radicals remain and are reacted off with more H$_2$. The experiments certainly reveal significant differences between formally similar catalysts: unfortunately, not being a steady-state technique, it cannot be said to estimate the number of active centers.

It appears to be a feature of reactions of low structure sensitivity that product selectivities are almost independent of a catalyst's detailed structure and composition. Thus almost any Pd catalyst will hydrogenate an alkyne or an alkadiene to the alkene with a selectivity approaching 100%, while with Pt, Ir, and other metals, the selectivity will be much lower.[2] Pd also efficiently catalyzes double-bond migration in alkenes, whereas Pt does not.[2] Such uniformities are harder to discern in reactions of high structure sensitivity, as might be expected, although certain common features do emerge. In alkane hydrogenolysis, for example, on Pt and Pd, only one bond is broken in a single residence; with others (Ru, Ni, Re, etc.), multiple bond breaking occurs.[40] On some metals (Ni and Pd), fission of the terminal bond is preferred, while the Pt[3,30] and Ru,[3–5] all bonds are comparably reactive (Figure 5). Relative rates of hydrogenolysis and skeletal isomerization can however be very variable on different Pt catalysts; on some (e.g. Pt/Al$_2$O$_3$), isomerization is usually slight (<2%),[30] while on others (e.g. Pt/SiO$_2$[6] and Pt/MgO), it is much greater (∼50%). These observations are cited to indicate what common tendencies there are which reflect the essential catalytic character of an element and what aspects reflect the structure sensitivity of the system. Further careful work and thoughtful analysis of the results will be needed before all becomes clear.

Criteria for the Validation of Reaction Mechanisms

As noted above, one of the principal objectives of academic research on metal catalysts has been the construction of a "reaction mechanism", i.e. a model expressed in atomic–molecular terms representing the pathways by which reactants are converted into products. The achievement of such a model, explaining most if not all the experimental observations, denotes a

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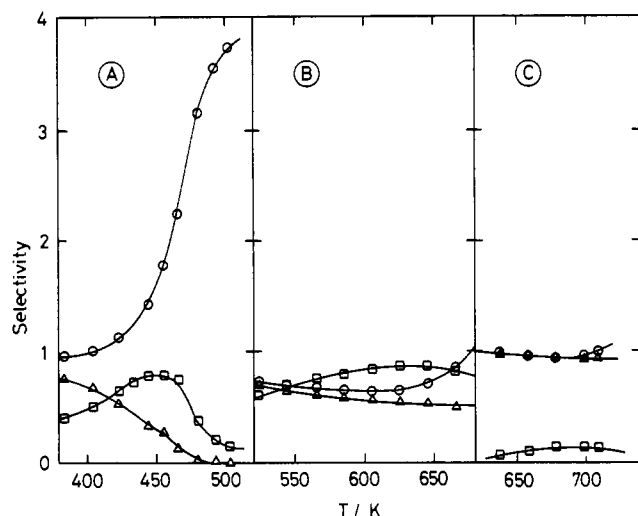
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Figure 5. Dependence on temperature of product selectivities in hydrogenolysis of *n*-butane (H_2:*n*-butane = 10:1): O, CH_4; □, C_2H_6; △, C_3H_8. A: 0.9% Ru/Al_2O_3. B: 6.3% Pt/SiO_2 (EUROPT-1).[6] C: 1% Pd/Al_2O_3.

satisfactory degree of understanding of how the system operates and, by identifying the rate-determining step, can sometimes point the way to the development of a better catalyst. The literature reveals mechanistic statements of various degrees of sophistication; this is because progressive conceptual refinement is always possible, leading to an ever more detailed specificiation (ultimately in quantum-mechanical terms) of what is going on. In this sense, discussion of the mechanism resembles more the skinning of an onion than that of an orange: at no point does the inner truth stand revealed in all its glory.

Future progress in our ability to manipulate the power of catalysis to our advantage depends not only on our practical skills in addressing the difficulties outlined above but also on our ability to hone and refine our theoretical tools to explain what we see. One of the most severe limitations is the lack of the flexible symbolism to represent our ideals: we need to be able to show locations and movements in real spaces, as well as changes in energy. No doubt molecular graphics will be of much help here.

One notable shortcoming in many discussions of reaction mechanisms is the failure to embrace all the relevant information. Partial truths are disastrous, as they bring a sense of well-being that is entirely misplaced. It is unscientific to propose a mechanism for the reaction of one molecule and to ignore totally what is known about the behaviors of its congeners and homologues. It would be invidious to cite specific papers which fall short of the highest standards of mechanistic discussion: they are however readily found.

The application of isotopic tracers has, from the earliest days of their use, enlarged our conceptions of the complexity of catalytic mechanisms, especially where hydrocarbons are involved. Recent publications[35,41] confirm that their usefulness is by no means exhausted.

Reference was made above to a previous attempt[2] to set down the minimal information that a mechanistic statement should aspire to. The salient points are these: (i) identification of the principal adsorbed species which mediate between reactants and products, i.e. the so-called masi (most abundant surface intermediates), (ii) specification of the principal routes by which they interact, and (iii) nomination of the rate-determining step. If this does not represent the beginning of the end, it is at least the end of the beginning.

Recommendations for Future Action

I am sorry if this review seems to strike so many negative notes. It is certainly not my intention to be dismissive of the great volume of work already in the literature; indeed, it is a triumph of scientific methodology that so much progress has been made in so difficult a field. This does not however mean that we must be uncritical; rather, we should inspect what has been done and try to learn from past mistakes how better to conduct our research in the future. Speaking as one close to the termination of his career, I can at least deploy a lifetime's experience. I often wish—as who does not—that I could have my time over again—with the knowledge I now have.

One clear impression I have is that we have tried to go too far too fast. We have left behind many problems unsolved, or only partially solved: we have made superficial studies of too many systems and in particular to a large extent each of us has made our own catalysts, using left-handed procedures on a very small scale, so that our work cannot always be reproduced or checked by others. In my opinion, the use of standard or reference catalysts, such as those developed by Burwell and his colleagues in the United States,[36] by the EUROCAT Group in Europe,[42] and by Japanese scientists, is a major step forward. The use where possible of such uniform materials or of industrial catalysts prepared on a large scale[30] is particularly desirable for mechanistic and basic studies: results obtained by different groups can then be compared with confidence.[42] I understand that, in the field of molecular biology, once a paper is published that contains information on specific genes or proteins, the authors are in duty bound to provide material from their laboratory, so that others can pursue the work. Those of us working on inorganic catalysts would do well to follow this practice.

A second impression, closely connected to the first, is that many of us perform our work for our own satisfaction, or for the glorification of our institution, rather than as an aid to the construction of a sound edifice of scientific understanding: this requires that all the components should interlock satisfactorily and that our own findings should always be compared and contrasted with those of others. Large cooperative programs such as those sponsored by the EUROCAT Group have been enormously beneficial in revealing inadequate experimental control, which could be rectified before false results appeared in the literature. Perhaps it is one of the tragedies of our times that our material well-being, our promotion prospects, and the health of our institutions depend much on the quantity and quality of our scientific output. The needs of the science itself sometimes seem to take second place.

(41) Goddard, S. A.; Cortright, R. D.; Dumesic, J. A. *J. Catal.* **1992**, *137*, 186–198.

(42) Bond, G. C.; Paál, Z. *Appl. Catal. A* **1992**, *86*, 1–35.