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Supported Metal Catalysts: Some Unsolved Problems

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1 Historical Prologue

Almost 40 years have passed since the publication of my first contribution[1] to this journal, or, to be precise, to its antecedent. I was then at the start of my career, and it is appropriate now to review what progress has been made in the intervening years in understanding the subject that has occupied so much of my attention. Reflection on the research carried out in the field of heterogeneous catalysis over these four decades will however show not so much a catalogue of problems solved as of problems shelved. The title of my earlier article[1] was 'The Mechanism of Catalytic Hydrogenation and Related Reactions' and it mirrored the interest which continued to be shown through the '50s and '60s in the kinetics and mechanisms of catalysed reactions. These approaches were pursued because the appropriate techniques (such as the use of isotopic tracers) were available, and they generated a substantial and useful body of knowledge on the exchange of alkanes and other molecules with D_2 and on the hydrogenation of alkenes, alkynes, and alkadienes.[2] At the same time there was much research conducted on the presumption that an *electronic factor* played a prime role in determining the catalytic activity of metals and alloys;[3] the extensive experimentation of Schwab,[4] Rienäcker,[5] Eley,[6] and others seemed to show beyond doubt that activity for reactions involving H_2 was firmly connected to the presence of an incomplete *d*-band or unfilled *d*-orbitals. Unfortunately the collective electron model that at one time seemed to explain the various activity–composition relationships so satisfactorily has proved untenable,[7] at least for pairs of elements whose band structures differ radically, and as we shall see later many of the catalytic properties of alloy surfaces are best understood simply in terms of either the surface concentration, or the size of the available ensembles, of the active atom.

From the mid-60s onwards there was a major change of direction in catalysis research, and the advances accounting for this are readily identified. The realization that the average size of supported metal particles could be readily

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[1] G. C. Bond, *Quart. Rev. Chem. Soc.*, 1954, **8**, 279.
[2] G. C. Bond and P. B. Wells, *Adv. Catal.*, 1964, **15**, 92.
[3] G. C. Bond, 'Catalysis by Metals', Academic Press, London, 1962.
[4] G. M. Schwab, *Adv. Catal.*, 1978, **27**, 1.
[5] G. Rienäcker and G. Vornum, *Z. Anorg. Chem.*, 1956, **283**, 287.
[6] A. Couper and D. D. Eley, *Discuss. Faraday Soc.*, 1950, **8**, 172.
[7] H. C. de Jongste and V. Ponec, *Bull. Soc. Chim. Belg.*, 1979, **88**, 453.

deduced from the simple and inexpensive measurement of an H_2 chemisorption isotherm[8,9] opened the way to a much more quantitative assessment of catalytic activity. The general availability of the transmission electron microscope (TEM)[10] and the gradual development of a whole range of physical techniques enable us now to address questions which 40 years previously we did not even know how to ask. If progress is to be measured by the increased sophistication of the questions that can be posed, there has indeed been great progress: but if it should be defined by the number of problems definitively solved, we have less cause to be satisfied with our efforts. I take no particular pride in the need which I feel, after 40 years of study, to write a report, the title of which stresses our failures rather than our successes.

The purpose of this review is then to survey the present state of our knowledge of the structures and activities of supported metal catalysts, and to highlight the gaps that remain in our understanding, so that future research may be directed the more effectively to filling them.

2 Rationale of the Use of Supported Metals

A. The Concept of Degree of Dispersion.—Since catalysis is a phenomenon exclusively due to the reactivity of atoms on the surface, those which are not there are wasted and their fraction must be minimized by using the metal in the form of extremely small particles having a high surface:volume ratio. This is particularly so for the noble Group VIII metals. The fraction of atoms at the surface is defined by the degree of dispersion, D (sometimes called the fraction exposed, FE[11]). Model calculations show[12–16] that, depending on the metal and on the assumed particle shape, a dispersion of 50% is only achieved with particles containing about 500 atoms and being about 2 nm in size (Figure 1). We shall be chiefly concerned with particles between 1 and 5 nm in size, having dispersions from 100 down to about 20%. This zone, in which the characteristics of the elements change from those of single atoms to those of the bulk material,[14] has fascinated scientists of many disciplines, not just those interested in catalysis.[17] Other important branches of technology (*e.g.* photography) also rely on finely divided metals. This zone has been termed the *mitohedrical region*[13] (*i.e.* the face-edge region, where the proportions of atoms in faces and on edges undergo rapid change) and also the *mesoscopic region*[18] (*i.e.* that which lies between the macroscopic and the microscopic).

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[8] G K Boreskov, M G Slinko, and V S Chesalova, *Zh Fiz Khim*, 1956, **30**, 2787

[9] L Spenadel and M Boudart, *J Phys Chem*, 1960, **64**, 204

[10] T Baird, in 'Catalysis', ed G C Bond and G Webb, A Specialist Periodical Report, The Royal Society of Chemistry, London, 1982, vol 5, p 172

[11] R L Burwell, Jr, *Adv Catal*, 1977, **26**, 351

[12] R van Hardeveld and F Hartog, *Adv Catal*, 1972, **22**, 75

[13] O M Poltorak and V S Boronin, *Russ J Phys Chem*, 1966, **40**, 1436

[14] R Burch, in 'Catalysis', ed G C Bond and G Webb, A Specialist Periodical Report, The Royal Society of Chemistry, London, 1985, vol 7, p 149

[15] G C Bond, *Surf Sci*, 1985, **156**, 966

[16] M Che and C O Bennett, *Adv Catal*, 1989, **36**, 55

[17] W Romanowski, 'Highly Dispersed Metals', Ellis Horwood, Chichester, 1987

[18] H Muller, C Optiz, and L Skala, *J Mol Catal*, 1989, **54**, 389

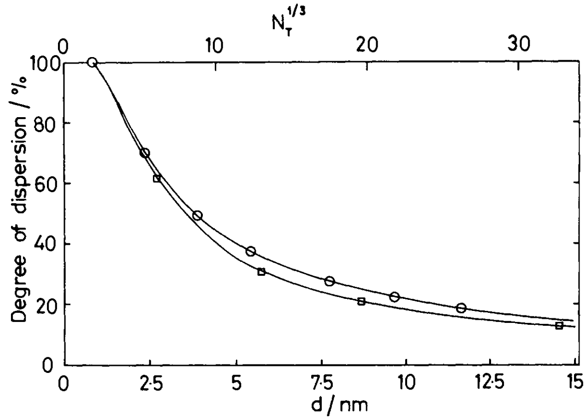

Figure 1 *Degree of dispersion D as a function of particle size d and of* $N_T^{1/3}$, *where* N_T *is the total number of atoms. The calculations, which are for* Pt, *are based on* (*a*) *the uniform sphere model*[15] (□) *and* (*b*) *the uniform cubo-octahedron model*[12,14] (○), *for which* $d = \sqrt{2} \times$ *edge-length* (*see Figure* 3)

B. Use of Supports to Stabilize Small Metal Particles.—These simple geometrical considerations at once give rise to the following questions. How can such particles be made? Will they be stable? Will they have characteristic metallic properties? They can indeed be made quite easily, and in a way which guarantees a high level of stability. They may be formed on the surface of a *support* to which they are more or less firmly anchored, and on which they are effectively separated from each other. This last consideration is important because there is a powerful thermodynamic driving force towards particle aggregation and growth, which is equal in magnitude to the work that had to be done to sub-divide the metal in the first place. Particle growth or *sintering* will therefore always occur providing suitable mechanisms are available, although in the design of an ideal catalyst they would of course be eliminated.

The average distance between particles will depend on the metal content, the particle size, and the surface area of the support. To achieve adequate separation, metal loadings usually lie between 0.3 and 3 wt.%, although higher and lower values find some application, and surface areas for supports are typically in the range 50 to 500 $m^2 g^{-1}$. Such high surface areas normally imply the presence of micropores, although low area non-microporous materials (such as TiO_2, α-Al_2O_3, and quartz) have their uses. A wide range of chemical substances have been used as supports, those most favoured being oxides (γ-Al_2O_3, SiO_2, zeolites *etc.*), although carbon (as very high area activated carbon or low area graphite) and metal salts (*e.g.* $CaCO_3$, $BaSO_4$ *etc.*) find application in specific areas. For further description of the great body of science and practical experience (mixed with some mythology) relating to catalyst supports, the reader is referred to the prior literature.[19–23] Much of the work treated in this review will concern the use of SiO_2, γ-Al_2O_3, and TiO_2 as supports; they are the most often used in academic research and exhibit significantly different properties.

C. Preparation of Supported Metal Catalysts.—It is beyond the scope of this article to describe in detail the various methods that have been and are used to create small metal particles on supports, and once again the reader has to be directed to other publications.[16,19–24] Since it is however well-established that the materials and methods employed in some way influence the behaviour of the finished catalyst, it is necessary at least to list the methods most often used. (i) If the support is microporous, it will soak up a solution of a metal salt (typically the chloride is used); drying, calcination (optional), and reduction will generate small particles of metal. This is the *impregnation method.* (ii) Hydroxyl groups at the surface of oxidic supports may undergo either anion or cation exchange, depending on the electronegativity of support cation:

$$S^+ + OH^- \rightleftharpoons S{-}OH \rightleftharpoons S{-}O^- + H^+$$

Exchange with a suitable metal ion complex, followed by washing, drying, and reduction also gives small particles of metal: this is the *ion exchange method.* (iii) Controlled precipitation of a hydroxide or other insoluble compound of the metal onto the support suspended in a liquid medium, followed by filtration, washing, drying, and reduction, is also effective in generating well-dispersed metal. This is the *deposition–precipitation method.* Numerous other procedures and variants on these methods have been described.

Depending on the envisaged application, the support may take the form of either a fine powder readily suspended in a liquid, or coarse particles up to about 1 cm in size, suitable for use in a fixed-bed reactor. These metal-support systems possess other useful features. (i) The location of the metal within the support particle is in principle controllable,[19,20] although this dimension is rarely exploited in academic work. (ii) Further components, variously described as modifiers, promoters, or selective poisons, can be incorporated, and two or more metals can be used to make (with luck or skill) supported alloys or bimetallic clusters (see Section 3.F). All in all, we have a device by which the catalytic properties of a metal can be honed and tuned to make it suitable for any one of a range of uses.

D. Characterization of Supported Metal Particles.—For many years the techniques needed to reveal the physical structures of supported metals either did not exist or were not widely available, and these materials were therefore not considered fit subjects for academic study. However the discovery,[8,9] already mentioned, that

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[19] G C Bond, 'Heterogeneous Catalysis Principles and Applications', 2nd edn, Oxford University Press, Oxford, 1978

[20] J R Anderson, 'Structure of Metallic Catalysts', Academic Press, New York, 1975

[21] G J K Acres, A J Bird, J W Jenkins, and F King, in 'Catalysis', ed D A Dowden and C Kemball, A Specialist Periodical Report, The Royal Society of Chemistry, London, 1981, vol 4, p 1

[22] C N Satterfield, 'Heterogeneous Catalysis in Practice', McGraw-Hill, New York, 1980

[23] N Pernicone and F Traina, in 'Applied Industrial Catalysis', ed B E Leach, Academic Press, London, 1984, vol 3, p 1

[24] A T Bell, in 'Catalyst Design Progress and Perspectives', ed L L Hegedus, Wiley, New York, 1987, p 103

H_2 would chemisorb selectively on the surface of the metallic component, thus directly titrating the metal atoms on the surface and giving the degree of dispersion, opened the way to expressing activities on the basis of unit area or as a turnover frequency (TOF), *i.e.* rate per surface metal atom. The subsequent use of CO, O_2, and other molecules as titrants, and of the titration of chemisorbed O atoms with H_2,[25] or of H atoms with alkene, [26,27] further extended the scope of the technique. The simultaneous wider use of TEM[10] (Section 3.F) and spectroscopic methods of various kinds[14,28,29] enabled much fuller physical characterization of supported metals to be undertaken. Once again, limitation of space restricts what can be said about the power and scope of these techniques, and only some aspects of the results obtained can be described. The facility which these methods afford to define (at least partially) the physical structure of catalysts has led not only to the change of emphasis in research, as noted above, but has attracted a larger number and a greater diversity of scientists to their study. Honesty, however, requires us to accept that the scientific interest of these materials could not of itself sustain the attention they have received, were it not for the fact that they are vital components of major industrial processes. There is now a vast literature on the Pt/Al_2O_3 catalysts and its congeners and modified forms,[30,31] for which their use in petroleum reforming is almost wholly responsible. More recently the use of supported Group VIII metals in a number of environmental control situations has occasioned the wider study of other metals (*e.g.* Rh and Pd) in supported form.[32]

E. Strong Metal–Support Interactions.—One discovery, seemingly of no practical use, has in particular stimulated research on supported metals through the past decade. The observation that reducing TiO_2-supported metals in H_2 at about 773 K causes them to lose much if not all of their capacity to chemisorb H_2 and CO (Table 1) has more than anything else fired the curiosity of catalytic scientists, and the so-called *strong metal–support interaction* (SMSI), described in what must surely be the most cited papers[33,34] in the literature of catalysis, has had a knock-on effect of no mean proportions. The discovery was made at a time when the physical methods were poised to tackle just such a problem, and it is fair to say that the main outlines of the explanation for the effect are now

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[25] J. E. Benson and M. Boudart, *J. Catal.*, 1965, **4**, 704; G. P. Valença and M. Boudart, *J. Catal.*, 1991, **128**, 447.

[26] G. C. Bond and P. A. Sermon, *J. Chem. Soc., Faraday Trans. 1*, 1976, **72**, 745.

[27] E. Choren, J. O. Hernández, A. Arteaga, G. Arteaga, H. Lugo, M. Arraez, A. Parra, and J. Sánchez, *J. Catal.*, 1990, **126**, 388.

[28] J. Evans, in 'Catalysis', ed. G. C. Bond and G. Webb, A Specialist Periodical Report, The Royal Society of Chemistry, London, 1989, vol. 8, p. 1.

[29] H. E. Rhodes, P. K. Wang, H. T. Stokes, C. P. Slichter, and J. H. Sinfelt, *Phys. Rev. B*, 1982, **26**, 3559.

[30] H. Charcosset, *Internat. Chem. Eng.*, 1983, **23**, 411.

[31] J. Biswas, G. M. Bickle, P. G. Gray, D. D. Do, and J. Barbier, *Catal. Rev. Sci. Eng.*, 1988, **30**, 161.

[32] B. Harrison, M. Wyatt, and K. G. Gough, in 'Catalysis', ed. G. C. Bond and G. Webb, A Specialist Periodical Report, The Royal Society of Chemistry, London, 1982, vol. 5, p. 127.

[33] S. J. Tauster and S. C. Fung, *J. Catal.*, 1978, **55**, 29.

[34] S. J. Tauster, S. C. Fung, R. L. Garten, *J. Am. Chem. Soc.*, 1978, **100**, 170.

Table 1 *Strong metal support interaction dependence of chemisorption stoicheiometry on reduction of temperature*[33,45]

Metal	*Support*	T_{red}/K	*H/M*	*CO/M*
Ru	TiO_2	433	0.75	
Ru	TiO_2	758	~0	
Ir	TiO_2	473	1.60	1.19
Ir	TiO_2	733	0	0
Ir	V_2O_3	476	0.84	
Ir	V_2O_3	774	0.05	

clear,[16,24,35,39] although many of the kinetic aspects are still virtually unexplored In a sense, the study of supported metals came of age and achieved academic respectability as a consequence of the work that the discovery of SMSI has stimulated This demonstrated that scientists now had the tools and the concepts to make sense of even the most complex and sensitive of systems

F. Bimetallic and Modified Catalysts. –It is an undoubted advantage of using metals in the supported state that interesting and sometimes beneficial alterations to the chemical composition of the system are readily made These may be classified as follows[40]

(i) Creation of bimetallic and alloy particles from pairs of elements showing substantial or complete miscibility (*e g* Ni–Cu,[41] Pd–Au,[42] Pt–Au[7] *etc*), the preparation and characterization of such systems present very real difficulties, which cannot however be treated in this review (but see Section 4 A)

(ii) Formation of bimetallic clusters from pairs of elements showing almost no mutual solubility (*e g* Ru–Cu,[43] Pt–Re, Pt–Sn,[31] Ru–Ge[44] *etc etc*), the problems of preparation and of characterization are equally great (Section 4 B)

(iii) Incorporation of a third component as a promoter or modifier, that component being unlikely to be reduced to the zero-valent state but nevertheless coming into contact with the metal particle (*e g* Pt–MoO_3/SiO_2, Ru–

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[35] G L Haller and D E Resasco *Adv Catal* 1989 **36** 173

[36] G C Bond and R Burch in Catalysis ed G C Bond and G Webb A Specialist Periodical Report The Royal Society of Chemistry London 1983 vol 6 p 27

[37] S J Tauster *Acc Chem Res* 1987 **20** 389

[38] Metal Support Interactions in Catalysis Sintering and Redispersion ed S A Stevenson J A Dumesic R T K Baker and E Ruckenstein Van Nostrand-Reinhold New York 1987

[39] Strong Metal–Support Interactions ed R T K Baker S J Tauster and J A Dumesic A C S Symp Ser 298 American Chemical Society Washington 1986

[40] G C Bond M R Gelsthorpe R R Rajaram and R Yahya in Structure and Reactivity of Surfaces ed C Morterra A Zecchina and G Costa Elsevier Amsterdam 1989 p 167

[41] W M H Sachtler *Vide* 1973 **164** 67

[42] G C Bond and E G Allison *Catal Rev* 1972 **7** 233

[43] J H Sinfelt *J Catal* 1973 **29** 308 *Acc Chem Res* 1977 **10** 15 *Internat Rev Phys Chem* 1989 7 281

[44] B Coq A Bittar and F Figueras in Structure and Reactivity of Surfaces ed C Morterra A Zecchina and G Costa Elsevier Amsterdam 1989 p 327 *Appl Catal* 1990 **59** 103

TiO_2/SiO_2[45,46] *etc.*); in this way, phenomena akin to the SMSI are the more readily studied (Section 4.C).

(iv) Addition of a third component that chiefly or exclusively interacts with the support (*e.g.* $Rh/La_2O_3–Al_2O_3$ *etc.*), in a way which modifies the metal–support interaction or interferes with bifunctional catalysis.[47]

(v) The deliberate addition or adventitious presence of other species, often electronegative in character, which act as selective or non-selective temporary or permanent poisons (*e.g.* Cl^-, S^{2-}, C *etc.*: see also Section 4.C).

The inclusion of such additional components can effect a number of practical benefits to a catalyst's behaviour. These include: selective elimination of undesired side-reactions, including coke formation; improved selectivity to the desired product; improved mechanical strength; decreased tendency to sintering; and greater ease of reactivation. Some attention will be paid to how these changes are brought about later on in this review (Section 4.C).

Considerable interest also attaches to the use of intermetallic compounds as catalysts,[48,49] but these are normally prepared by fusing the components and are not available in a dispersed form on a support. Intermetallic PtTi compounds have been considered[36,37] as possible agents for the effects of SMSI, although this view is not now widely held.

G. Changes in Physical Properties in the Mesoscopic Region.—For reasons other than their practical utility, metal particles which contain only a few tens or hundreds of atoms have attracted the attention of chemists, physicists, materials scientists, and especially theoreticians. It is of course important to know whether catalytic properties are enhanced or diminished as particle size is decreased, and whether there is an effective limit to the degree of dispersion that should be sought. As the size is decreased, the fraction of coordinatively unsaturated atoms on the surface will increase[12-16] (Figure 1) and these will play an increasingly important part in determining the physical properties of the particle. Consequential changes in melting temperature, interatomic distances, band structure, and many other physical properties have provided a happy hunting-ground for both experimentalists and theoreticians.[14,17,18] It has even been questioned whether very small particles always possess the crystal structure of the metal in bulk.[50] There have been a number of TEM observations of particles apparently having pentagonal symmetry (*e.g.* icosahedra),[50-53] although it is

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[45] G. C. Bond, R. R. Rajaram, and R. Burch, in 'Proc. 9th Int. Congr. Catal.', ed. M. J. Phillips and M. Ternan, Chem. Inst. Canada, 1988, vol. 3, p. 1130.

[46] J. P. S. Badyal, R. M. Lambert, K. Harrison, C. C. A. Riley, and J. C. Frost, *J. Catal.*, 1991, **129**, 486.

[47] E. K. Poels and V. Ponec, in 'Catalysis', ed. G. C. Bond and G. Webb, A Specialist Periodical Report, The Royal Society of Chemistry, London, 1983, vol. 6, p. 196.

[48] A. Bahia, J. M. Brown, I. T. Caga, I. R. Harris, C. E. King, and J. M. Winterbottom, *J. Chem. Technol. Biotechnol.*, 1990, **48**, 351.

[49] K. S. Sim, L. Hilaire, F. le Normand, R. Touroude, V. Paul-Boncour, and A. Percheron-Guegan, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 1453.

[50] J. J. Burton, *Catal. Rev.-Sci. Eng.*, 1974, **9**, 209.

[51] S. Fuentes, F. Madera, and M. J. Yacamán, *J. Chim. Phys. Phys.-Chim. Biol.*, 1983, **80**, 379.

[52] M. J. Yacamán and A. Gomez, *Appl. Surf. Sci.*, 1984, **19**, 348.

[53] M. J. Yacamán, *Appl. Catal.*, 1984, **13**, 1.

now thought[14] that these occur only infrequently in supported metal catalysts and that when they do they relax to the normal structure when chemisorption takes place.

Our principal task in this review is to investigate how the variables of a catalyst's preparation determine, through the chemical composition and physical structure of the finished catalyst, the activity and product selectivities which it exhibits. Previous reviews, of which there have been a number,[14–16,54,55] contain much of the basic information on which the statements made here can be shown to rest. We will, however, make use of some of our own recent work to illustrate the problems that are as yet unsolved.

3 The Evaluation of Particle Size Effects

A. A Geometric Basis for Particle Size Effects.—Attempts to determine how catalytic activity depends upon the size of metal particles in supported catalysts have been made for more than three decades, but since all this work has achieved nothing approaching consensus, either in terms of theoretical models or even of experimental results,[16] we must try to analyse the nature of the problem. Either the wrong questions are being asked or the wrong methodology is being used: or perhaps both.

Before the end of the 1960s, it had become clear that the rates of some catalysed reactions, expressed per unit area or as a TOF, were almost independent of metal particle size, while in other cases some form of dependence was observed.[8,13,16,56,57] Reactions of the former type, such as the hydrogenation of cyclopropane, were at first described[56] as *facile*, and those of the latter type, such as the hydrogenolysis of alkanes, were called *demanding*. At least three ways in which areal rate or TOF might vary with particle size were recognized[58] (Figure 2), and these (and others) have subsequently been seen experimentally.[16] Stimulated by the observation[59] that the ratio of the rates of neopentane hydrogenolysis and isomerization could be altered by thermally treating a Pt catalyst in a way that did not change its dispersion, the attention of catalytic chemists focused on the importance of surface morphology. The idea that every demanding reaction required a very specific grouping or ensemble of surface atoms was introduced by H. S. Taylor in 1925,[60] and was later developed and applied by Kobozev[61] and Balandin[62] in the U.S.S.R. To emphasize the supposed role of surface morphology in determining catalytic properties, the terms facile and demanding were later replaced by *structure-insensitive* and *structure-sensitive*.[57]

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[54] J R Anderson, *Sci Prog (Oxford)*, 1985, **69**, 461

[55] K Foger, in 'Catalysis--Science and Technology', ed J R Anderson and M Boudart, Springer-Verlag, Berlin, 1984, vol 6, ch 4

[56] M Boudart, A Aldag, J E Benson, N A Dougharty, and C G Harkins, *J Catal*, 1966, **6**, 92

[57] M Boudart, *Adv Catal*, 1969, **20**, 153

[58] G C Bond, in 'Proc 4th Int Cong Catal', Akademiai Kaido, Budapest, 1971, vol 2, p 266

[59] M Boudart, A W Aldag, L D Ptak, and J E Benson, *J Catal*, 1968, **11**, 35

[60] H S Taylor, *Proc R Soc London, Ser A*, 1925, **108**, 105

[61] N I Kobozev, *Uspek Khim*, 1958, **25**, 545

[62] B M W Trapnell, *Adv Catal*, 1951, **3**, 1

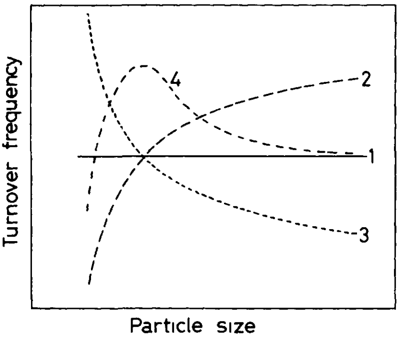

Figure 2 *Possible forms of dependence of activity expressed per surface metal atom (turnover frequency) on particle size*[58]

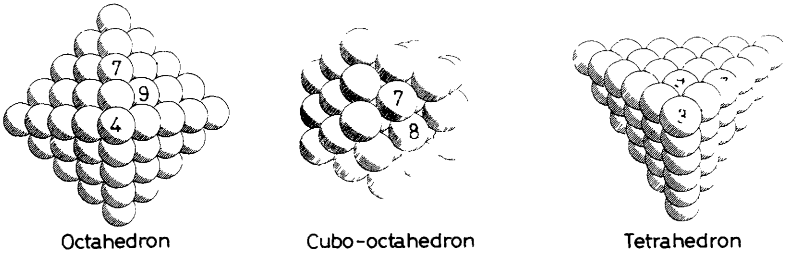

Figure 3 *Models of small (i) octahedron, (ii) cubo-octahedron, and (iii) tetrahedron the numbers are the coordination numbers of the atoms indicated*

It was fortunate that a comprehensive set of models became available to provide a framework for discussing the geometry of the surfaces of small particles. The calculations performed by van Hardeveld and Hartog[12] on the variation in the populations of atoms of specified coordination number with size of particle for a number of perfect crystal forms (octahedra, tetrahedra, cubo-octahedra, see Figure 3) were attractive because of their simplicity and ease of use, and have had a marked (and perhaps a disproportionately large) influence over the thinking about particle size effects. An example of their calculations is shown in Figure 4.

It appears that much of the subsequent work relating to particle size effects was based on the expectation that significant changes in surface structure, or in the frequency with which specified groupings of atoms occurred, would attend a change in particle size: at least in many instances the results have been interpreted[16,51–53,63,64] with the aid of the van Hardeveld–Hartog models. Sober reflection suggests however the existence of a very large number of

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[63] D Farin and D Avnir, in 'Proc 9th Int Congr Catal', ed M J Phillips and M Ternan, Chem Inst Canada, Ottawa, 1988, vol 3, p 988

[64] D Farin and D Avnir, *J Am Chem Soc*, 1988, **110**, 2039, *J Catal*, 1989, **120**, 55

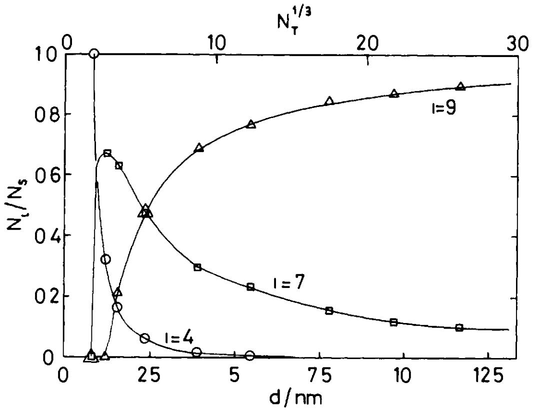

Figure 4 *Variation of the fraction of surface atoms of coordination number i as a function of particle size d and of $N_T^{1/3}$ for the uniform cubo-octahedron model*[12]

complicating factors which confuse the meaning of the experimental results, and their interpretation, in terms of surface structural models Ultimate progress depends on recognizing these factors, so that they can then be eliminated

B. Reproducible Activation of Catalysts.—Let us therefore begin by rehearsing some of the problems of an experimental nature Reference to the article by Che and Bennett[16] will produce numerous examples of discordant results on the same or similar systems it is unfortunate that the painstaking work necessary to ensure reproducibility of rates, and the routine measurements that have to be made to ensure comparability with other workers, are not prime candidates for research funding Experience shows that, even with the exercise of moderate care, the sample-to-sample variability of rates for a given batch of catalyst is at least a factor of two to three for 'well-behaved' systems, while for those that are less 'well-behaved' a factor of 10 has to be tolerated[65] This statement applies to industrial preparations made on a large scale, which are presumably very homogeneous in composition, reproducibility is generally worse with laboratory preparations, where homogeneity of composition may be a problem Batch-to-batch reproducibility of laboratory-made preparations, especially those made by different workers, is usually even more worrisome[66]

Some, perhaps much, of this variability can be attributed to differences in the active area, although it is not always totally removed by expressing rates on an areal or TOF basis We may guess that the number of exposed metal atoms will depend, critically in some cases, upon the precise schedule used for activation, the effectiveness of drying, calcination, and reduction will be determined by the times, temperatures, heating rates, and gas compositions used Ideally some estimate of

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[65] G C Bond and R H Cunningham unpublished work

[66] G C Bond R R Rajaram and R Yahya *J Mol Catal* accepted for publication

dispersion should be made with each sample of catalyst before *and after* use, in the same apparatus and under the same conditions as are used for the rate measurement, but this is rarely if ever done, because it would inevitably 'slow the pace of the research'. More haste can, however, sometimes lead to less speed.

Quite minor differences in the activation schedule can sometimes affect the degree of reduction of the precursor. Supported Ni catalysts are notoriously difficult to reduce completely,[67] after standard impregnation and ion exchange procedures; so is Re/Al_2O_3.[68] Much depends on the propensity of the precursor ion (Ni^{2+}, Re^{4+} *etc.*) to interact chemically with the support's surface, and in general few problems are met with the noble Group VIII metals. Even here, however, the temperature needed to achieve complete reduction will depend on the precursor to be reduced (oxide, ammine complex, chloro-complex *etc.*), on the metal loading, and on the support. A study of the precursor's reactivity by quantitative temperature-programmed reduction (TPR) is strongly to be recommended before reduction conditions are adopted, so that if possible they may bring about 100% reduction. Where this cannot be done, the degree of reduction attained needs to be estimated separately.

The dispersion and particle structure achieved depends on the nature of the precursor, and reactivation by oxidation and a second reduction does not necessarily reproduce the properties of the original catalyst; whether or not the precursor is calcined before reduction can also greatly affect a catalyst's behaviour.[45] In the case of Pt/Al_2O_3 catalysts for petroleum reforming, much attention has been given to means of reconstructing a deactivated catalyst, and Cl^- has been identified as having a major role in the redispersion of the metal.[69] These catalysts are often bimetallic, and it is even more difficult to obtain reproducibly activated samples (*e.g.* of Pt–Re/Al_2O_3) in the laboratory;[65] this is generally true of bimetallic and modified catalysts. The greater the number of possible configurations that the finished product can adopt, the greater the control that has to be exercised over the activation.

C. Effect of Altering the Metal Content.—A well-established procedure for altering the mean particle size is to change the metal content of the catalyst. When an impregnation method is used, the number of metal particles formed is approximately independent of the salt concentration used and their mean size therefore varies as the two-thirds power of the metal content.[70] However, the complex nature of many TPR profiles[71] reflects the complexity of the chemistry involved in the reduction of the precursor. There is now much evidence for two or more types of precursor species, *viz.* dispersed ions or complexes, perhaps arising from an ion exchange, and discrete microcrystals.[15,36] The proportions of

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[67] J. W. E. Coenen, *Appl. Catal.*, 1989, **54**, 59, 65.

[68] J. A. Moulijn and J. C. Mol, *J. Mol. Catal.*, 1988, **46**, 1.

[69] H. Lieske, G. Lietz, H. Spindler, and J. Völter, *J. Catal.*, 1983, **81**, 8.

[70] T. A. Dorling and R. L. Moss, *J. Catal.*, 1967, **7**, 378.

[71] Le Van Tiep, M. Bureau-Tardy, G. Bugli, G. Djega-Mariadassou, M. Che, and G. C. Bond, *J. Catal.*, 1986, **99**, 449.

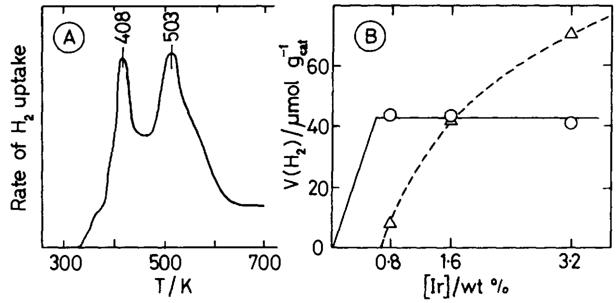

Figure 5 *Reduction of* $IrCl_6^{3-}/TiO_2$ *by* H_2 (*A*) *reduction profile for* 3 2% Ir; (*b*) *areas of first* (○) *and second* (△) *peaks, in* mol H_2 g_{cat}^{-1} *as a function of* Ir *content*[71]

the various forms differ with metal content and in reducibility (Figure 5); they give rise to groups of particles having different dispersions, and the possibility of having a binodal distribution of particle sizes therefore has to be faced. Where this is the case, measurement of dispersion or mean particle size by gas chemisorption would clearly be meaningless.

D. Impurities Associated with the Support.—This manner of effecting changes in mean particle size can create other difficulties as well. It is of course well known that some supports (particularly Al_2O_3 and TiO_2) can strongly hold Cl^- ions originally in the salt or complex ion used to make the precursor;[72] indeed the performance of Pt/Al_2O_3 catalysts for petroleum reforming depends on this fact. However, such Cl^- ions can also interfere seriously with the measurement of H_2 chemisorption isotherms,[45,72] hence leading to quite false estimates of dispersion and of the magnitude of particle size effects.[73] The use of a Cl^--free metal compound is only a partial solution, since changing the precursor may alter completely the initial interaction with the support, and all the subsequent chemistry through to the metal particle's size, shape, and surface morphology. Cl^- can, however, be removed after reduction by steaming, by NH_3, or simply by washing in hot water.[74] Some supports may also contain ions such as SO_4^{2-}, not removed during calcination, which on reduction give toxic molecules (*e.g.* H_2S);[75] again Al_2O_3 and TiO_2 are prone to this disadvantage. Al_2O_3 also dissolves at a pH below 3,[76] so that impregnation with acidic solutions (*e.g.* H_2PtCl_6) can give rise to Al^{3+} ions which may re-precipitate later, perhaps partially coating the metal in a kind of SMSI effect. Some of the effects of these accidental impurities on catalytic behaviour will be considered in Section 4.C.

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[72] G C Bond, R R Rajaram, and R Burch, *Appl Catal*, 1986, **27**, 379

[73] T A Dorling, M J Eastlake, and R L Moss, *J Catal*, 1969, **14**, 23

[74] G C Bond, M J Fuller, and L R Molloy, in 'Proc 6th Int Congr Catal' ed G C Bond, P B Wells, and F C Tompkins, The Chemical Society, London, 1977, vol 1, p 356

[75] S Fuentes and F Figueras, *J Chem Soc*, *Faraday Trans 1*, 1978, **74**, 174

[76] M S Heise and J A Schwarz, in 'Preparation of Catalysts IV', ed B Delmon, P Grange, P A Jacobs, and G Poncelet, Elsevier, Amsterdam, 1987, p 1

E. Measurement of Mean Particle Size.—First of all, the term 'size' has no unambiguous meaning when applied to very small particles. Thus a particle comprising a given number of atoms may exhibit very different degrees of dispersion, surface areas, and linear dimensions, depending on the form adopted. Any number of atoms can form a two-dimensional raft showing 100% dispersion. The projected areas and diameters of a sphere and a hemisphere on a support may be the same, but the number of atoms and the surface areas will differ twofold. One simplifying solution is to by-pass the concept of size, and to work only in terms of the number of surface metal atoms, equated to the number of H atoms chemisorbed at saturation. The ratio of H atoms to *total* metal atoms, H/M, gives some kind of measure of dispersion,[9] but it is clearly established (i) that the ratio of H atoms to surface metal atoms, H/M_s, can rise well above unity for very small particles, especially with Ir,[77] and (ii) that there may be no clearly defined point of saturation as the equilibrium H_2 pressure is raised.[78] Indeed in the case of Pt/SiO_2 (EUROPT-1), some of the H_2 taken up appears to be used in hydrogenating metal–oxygen–support bridges, since only in this way can the H_2 isotherm and the TEM results be reconciled.[78] With CO, the concentrations of the bridged and linear forms have to be established by spectroscopy before the CO/M_s ratio can be known, and with O_2 the ready occurrence of sub-surface sorption and of bulk oxidation[79] necessitates using sub-ambient temperature if meaningful results are to be obtained.[80] Despite the ease of measurement and the comparatively low price of the equipment needed, the use of selective chemisorption is unlikely to lead to much more profound understanding of particle size effects.

One further difficulty deserves mention. The selective chemisorption method requires an estimate of the total metal concentration, and this can present problems. Many catalysts are not easily dissolved completely, but Soxhlet extraction of the unreduced precursor with aqueous HCl has proved effective for low metal concentrations.[45] Since a typical concentration is 1 wt.%, a 1% accuracy in the estimation of dispersion (and it is generally quoted to this accuracy) requires the metal loading to be known to *at least* ±0.01 wt.%. It is more usual to express analytical figures (where they are given to all) to the nearest 0.1 wt.%. This is therefore probably the major source of error in estimating dispersion by gas chemisorption.

F. Measurement of Particle Shape and of Size Distribution.—Transmission electron microscopy (TEM) takes pride of place amongst the available physical methods of characterization for the wealth and immediacy of the information it provides.[10] Instruments using 200 keV electrons and having a resolving power of better than 1 nm are now widely employed, and automated methods for counting particles in discrete size ranges facilitate measurement of particle size distributions.

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[77] B. J. Kip, F. B. M. Duivenvoorden, D. C. Koningsberger, and R. Prins, *J. Catal.*, 1987, **105**, 26.

[78] A. Frennet and P. B. Wells, *Appl. Catal.*, 1985, **18**, 243.

[79] P. B. Wells, *Appl. Catal.*, 1985, **18**, 259.

[80] S. K. Masthan, K. V. R. Chary, and P. K. Rao, *J. Catal.*, 1990, **124**, 289.

Use of higher energy electrons[81] gives information on the structure and shape of metal particles, including lattice parameters (measurable with the help of Moire fringes to an accuracy of 0 005 nm[82]), but has not revealed the oxidic overlayers thought by some to be responsible for the SMSI[83] No method is without its limitations however, the chief for TEM being the concern[14] that extremely small clusters may escape detection amongst many larger ones, although groups of a very few atoms are claimed to have been imaged[84] The worry that the use of UHV conditions might alter the equilibrium particle shape is now somewhat lessened, as observations can be made at pressures of up to 10^{-4} Torr This limitation does not of course apply to extended *X*-ray absorption fine structure (EXAFS) measurements,[28] with which, using the latest technology, dynamic information under realistic conditions of temperature and pressure can now be obtained on a millisecond time-scale[14] Both techniques are set fair to expand and develop, and to contribute usefully to our knowledge of small metal particles

Study of the vibrational spectra shown by chemisorbed CO is also able to reveal information on the nature of the exposed planes[85] and also incidentally on particle size[86] These effects have not yet been widely exploited, but have considerable potential value

G. Measurement of Catalytic Activity.—The next stage is the measurement of the catalytic activity, this is also a minefield In a continuous-flow mode, rates normally decrease with time-on-stream, at first rapidly and then more slowly, and especially where a hydrocarbon is involved here the activity loss is ascribed to poisoning by 'carbonaceous residues' or more simply 'coke' Occasionally, however, large *increases* in rate occur with continued use[87] Many authors unfortunately do not trouble to specify whether their results pertain to initial or steady-state performance of their catalyst, this complicates comparisons between different groups, and working with partially coked catalysts can generate spurious particle size effects, as large particles are more easily deactivated than small ones[88] Problems of deactivation are less evident in static or recirculatory reactors and in the pulse-flow mode, although they may still be present Slow activity changes can sometimes be due to sintering of the metal particles,[14] aided perhaps by mobile species formed in the catalysis or to modification of the particles' shape as they assume the configuration of minimum energy appropriate to their circumstances With bulk metals, surface mobility is considered[89] to start

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[81] M J Yacaman R Herrera S Tehuacanero A Gomez and L Beltran del Rio *Ultramicroscopy* 1990 **33** 133

[82] J Woltersdorf A A Nepijko and E Pippel *Surf Sci* 1981 **106** 64

[83] J H A Martens R Prins H Zandbergen and D C Koningsberger *J Phys Chem* 1988 **92** 1903

[84] E B Prestridge and D J C Yates *Nature* 1971 **234** 345

[85] J Pritchard T Catterick and R K Gupta *Surf Sci* 1975 **53** 1

[86] F J C M Toolenaar G J van der Poort F Stoop and V Ponec *J Chim Phys* 1981 **78** 927

[87] T R Baldwin and R Burch *Appl Catal* 1990 **337** 359

[88] E H van Broekhoven J W F M Schoonhoven and V Ponec *Surf Sci* 1985 **156** 899

[89] M S Spencer *Nature* 1986 **323** 685

above the Huttig temperature (*i.e.* one-third of the melting temperature), so that most metals are used (or at least have been reduced) above this temperature and hence have thermally equilibrated surfaces: only the most refractory metals will have metastable surfaces having a high concentration of defects.

It is self-evident that, if one wishes to study particle size dependence, one should employ a reaction which only proceeds on the metal and not on the support as well. There are at least two pit-falls here. First, the catalyst may be bifunctional, as with Pt on acidic Al_2O_3 and its congeners when used for petroleum reforming:[30,31] the metal provides a hydrogenation–dehydrogenation function while the carbocations needed for efficient skeletal isomerization are formed and discharged on the support. Bifunctional behaviour which, as here, employs gas-phase migration of intermediates will only be found at quite high temperatures, but the second pit-fall can be encountered under much milder conditions. This is the possibility of *spillover catalysis*, so called because it works by *surface* migratory steps of adsorbed molecules and intermediates.[90] This kind of cooperation between metal and support is now well-established in hydrogenations,[90] in oxidations where a reactive support (*e.g.* SnO_2) is used,[74] and in NO–CO reactions.[91] In such cases the role of the metal particle size is not readily identified. It has also been seriously suggested[92] that reactions such as alkene hydrogenation may proceed on top of a carbon deposit over the metal particles, with the carbon acting as an H-transfer agent from metal to alkene; the concept is still being debated, but if true it would obviously mask any underlying particle size effects.

H. Measurement of Reaction Kinetics.—Of course the rate given by a catalyst under specified conditions of temperature and reactant pressures provides only a fraction of the potentially available information. Since different catalytic systems exhibit different apparent activation energies, the hierarchy of activities shown in a family of catalysts can be inverted by choosing another temperature at which to compare rates.[93] Precise reproducibility of activation energy is a more exacting manifestation of experimental control than is reproducing the rate at a single temperature. With the kind of automated test equipment now available in many laboratories, repeated measurement of kinetic parameters based on a large number of data-points presents no difficulty, so that activation energies can and should be quoted to high precision. The frequent observance of a 'compensation effect' between activation energy and pre-exponential factor (*i.e.* between enthalpy and entropy of activation) (Figure 6) has occasioned much discussion,[93,94] and had tended to diminish the significance of the activation energy. However, in at least one case, a 'compensation effect' has been shown[95] to be an artefact of a

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[90] G. C. Bond, in 'Spillover of Adsorbed species', ed. G. M. Pajonk, S. J. Teichner, and J. E. Germain, Elsevier, Amsterdam, 1983, p. 1.

[91] F. Solymosi, L. Völgyesi, and J. Sárkány, *J. Catal.*, 1978, **54**, 336.

[92] S. J. Thomson and G. Webb, *J. Chem. Soc., Chem. Commun.*, 1976, 526.

[93] G. C. Bond, *Z. Phys. Chem. N.F.*, 1985, **144**, 21.

[94] W. Linert and R. F. Jameson, *Chem. Soc. Rev.*, 1989, **18**, 477.

[95] P. K. Tsjeng and R. B. Anderson, *Can. J. Chem. Eng.*, 1976, **54**, 101.

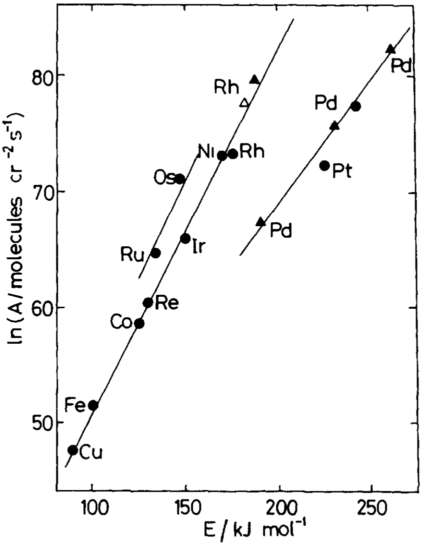

Figure 6 *Compensation plots of E* vs. ln *A for hydrogenolysis of ethane on* SiO_2*-supported metals.*[93] *Circles, see J. H. Sinfelt, Catal. Rev.,* 1969, **3**, 175; *triangles, see G. C. Bond and G. Hierl, J. Catal.,* 1980, **61**, 348

particular kinetic model and to disappear with a true activation energy is extracted through the use of the appropriate Langmuir–Hinshelwood rate expression. However even apparent activation energies have an empirical value and deserve to be measured wherever possible.

If for a series of related catalysts the orders of reaction, or the constants of the kinetic equation, differ, then the activity sequence they show will in principle depend on the partial pressures used to measure the rate. The proper basis for comparison then has to be the rate coefficients derived from a kinetic equation based on the Langmuir–Hinshelwood formalism. Perhaps the ultimate criterion for reproducibility and for identifying the catalytic finger-print of a material lies in the measurement of orders of reaction at several temperatures, and the discovery of a rate-expression, derivable from a sensible mechanism, which well describes the results and which generates logical values of true activation energy and of adsorption enthalpies through the temperature-dependence of the relevant constants.[96] Work of this nature is usually thought to lie within the province of chemical engineers, but we must remember that kinetic analysis is the *only* method giving direct access to the composition of the transition state for the rate-determining step and hence to the heart of the reaction mechanism. With hydrocarbon reactions, kinetics and mechanism may change as the catalyst

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[96] M Boudart and G Djega-Mariadassou, 'Kinetics of Heterogeneous Catalytic Reactions', Princeton U P, Princeton, N J, 1984

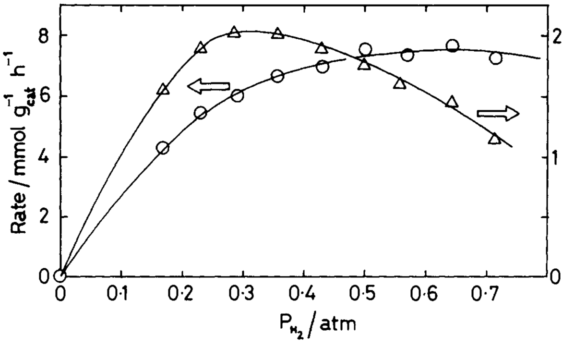

Figure 7 *Variation of the rate of n-butane hydrogenolysis with* H_2 *pressure on clean* (○) *and coked* (△) 0.3% Pt/Al_2O_3[65]

deactivates through coke formation. We have recently been able to record the kinetics of alkane hydrogenolysis on clean Pt/Al_2O_3 catalysts (by using very short H_2-alkane pulses) as well as on their coked counterparts; significant differences in reaction orders are observed (Figure 7).

I. Effect of Particle Size on Enthalpies of Adsorption.—The following predominant factors determine the activity of a supported metal catalyst under specified conditions: (i) the number of active centres, reflecting the degree of dispersion; (ii) the probability of finding an active centre at any particular dispersion, reflecting the geometric constraints that the reaction suffers; and (iii) the energetics of chemisorption of the reactants. In the simplest cases, the free energies of adsorption control the occupancies of the adsorption sites, and the enthalpies of adsorption decide the height of the energy barrier to the transition state, *i.e.* the enthalpy of activation or the true activation energy. The formalism of the Absolute Rate Theory does not however allow the entropy of activation to be readily distinguished from the other temperature-independent terms.[3] Enthalpies of adsorption, as we have just seen, can be obtained under reaction conditions from the temperature dependence of the adsorption coefficients, although their validity hinges on the correct choice of rate equation; alternatively they can be measured calorimetrically[97] or by temperature-programmed desorption (TPD).[98] The former method was widely employed from the '30s through to the early '60s, especially on wires and condensed metal films, but spurious results are easily obtained with supported metal catalysts, especially where the support is microporous, because uniform distribution of the adsorbate over the whole surface cannot be achieved at low pressure. Recently however reliable results have been obtained with a modified differential-scanning calorimeter.[99] The TPD

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[97] M. W. Roberts and C. S. McKee, 'Chemistry of the Metal–Gas Interface', Oxford University Press, Oxford, 1978, p. 37 ff.

[98] M. W. Roberts and C. S. McKee, reference 97, p. 264 ff.

[99] M. A. Vannice, B. Sen, and P. Chou, *Rev. Sci. Instrum.*, 1987, **58**, 647; P. Chou and M. A. Vannice, *J. Catal.*, 1987, **104**, 1.

method suffers from interpretational problems, and absolute values of adsorption enthalpies are not easily extracted from the results [100]

It is therefore not surprising, although nevertheless unfortunate, that there is so little information available on how enthalpies of adsorption vary with particle size For Pd on various supports they have been reported to be independent of particle size for H_2 and for CO, down to 3 nm, but below this both values rise rapidly [99] The H_2 adsorption enthalpies parallel the enthalpies of formation of the β-hydride phase, but are some 50% higher Trends in activation energy of desorption estimated from TPD measurements on the H_2/Pt [101] and O_2/Pt [100] systems are in opposite senses, the results for the latter indicating strongest adsorption on small particles Calorimetric measurements [102] confirm this trend, enthalpies of O_2 chemisorption being respectively about 211 and 286 kJ mole $^{-1}$ on large and small Pt particles The amount of weakly adsorbed H relative to strongly adsorbed H increases with increasing dispersion of Pt on carbon supports [103] The amount of published information is clearly insufficient for firm conclusions to be drawn It must be remembered that the chemisorption of small molecules is unlikely to be *structure*-sensitive, and any changes that are established to occur will reflect a change in metallic character or in the mean coordination number of surface atoms

J. Structure-sensitivity of Catalysed Reactions.—We have seen that catalysed reactions have been classified as being either structure-sensitive or structure-insensitive, thus if one wishes to explore the phenomenon of structure-sensitivity, the choice of reaction or reactions will clearly be important We shall return to the question of insensitive reactions later (Section 3 Q) As for structure-sensitive reactions, there are two types of parameter that can be measured (i) the rate, expressed in some absolute units, and (ii) product selectivities, where more than one product is possible In the absence of cogent reasons to the contrary, it is preferable to select a reaction that can give a variety of products, since the *relative* rates of the competing processes may also be subject to structural influences Thus in reacting alkanes with H_2, ethane gives only one product, propane forms methane and ethane, n-butane gives all three lower alkanes plus isobutane by isomerization, whereas pentane and higher alkanes can additionally undergo cyclization, ring-expansion, and dehydrogenation If a reaction from this family is to be selected as a probe for surface structural features, a reasonable compromise is to select the most complex molecule for which a simple but comprehensive kinetic model is available

It may of course be overly simplistic to seek to categorize all reactions as being either sensitive or insensitive to surface structure As Figure 2 shows, there can be different *forms* of sensitivity, and there is no *a priori* reason why all 'sensitive'

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[100] N I Jaeger A L Jourdan and G Schulz Ekloff *J Chem Soc Faraday Trans* 1991 **87** 1251

[101] Y Takasu M Teramoto and Y Matsuda *J Chem Soc Chem Commun* 1983 1329

[102] B Sen and M Vannice *J Catal* 1991 **129** 31

[103] C Prado Burguete A Linares Solano F Rodriguez Reinoso and C Salinas Martinez de Lecea *J Catal* 1991 **128** 397

reactions should show the same degree of sensitivity. H. S. Taylor, in his perspicacious paper[60] on active centres in catalysis, stated that the fraction of a catalyst's surface that is active depends upon the reaction being catalysed. Although the perception of the likely nature of surface heterogeneity has changed with the passage of time, the concepts he introduced to describe the topology of surfaces provided a framework for understanding different degrees of structure-sensitivity. Avnir[63,64] has attempted to quantify this idea by applying fractal analysis, and has defined a *reaction dimension* D_R as

$$\log(r/t^{-1}) = \log k + (D_R - 2)\log R$$

or

$$\log(r/\text{mol}\ t^{-1}\ \text{g}^{-1}) = \log k' + (D_R - 3)\log R$$

where r = rate, t = time, k and k' are constants and R = mean particle radius. An extensive analysis of the literature[64] has shown convincingly linear plots of these equations, and the derived, frequently integral, reaction dimension is then interpreted in terms of the involvement of a specific class of surface atom (edge, corner, or plane), as expounded by van Hardeveld and Hartog.[12] Occasional non-integral values are explained by the active site comprising atoms from more than one such class. While the utility of this approach has been seriously questioned,[104] it has been of value in attaching shades of grey to a concept that was previously seen only in black and white.

It is not the purpose of this review to describe or even to try to summarize the results of research on variation of rates with particle size, as this has been comprehensively done in the recent past by Che and Bennett,[16] and in a number of earlier reviews.[14,15,54,55] Indeed, because of the lack of concordance in the results, already alluded to, such a compilation would made depressing reading. It seems more useful to try to construct some general theoretical framework into which results of proven validity might be fitted, and in doing so to stress what is not yet known and what has not yet been done, as much as what has been achieved and what is understood. The structure-sensitivity of product selectivity will receive particular notice.

We have seen that it is of limited use to classify a reaction as being either sensitive or insensitive to surface structure or particle size, since it is more likely that every reaction will show *some* degree of sensitivity, large or small, depending on the stringency of its requirements for an active centre. Furthermore particle size sensitivity is not an attribute of a reaction, nor does one metal show such sensitivity for all reactions. The manner in which the rate of a reaction varies with particle size on a given metal is characteristic of the reaction–metal combination, that is, of the *catalytic system*, and may even be specific to a particular shape of particle as determined by the support, the method of preparation and the pretreatment. A most striking example of the importance of the metal is provided by the reaction of cyclopropane with H_2. Over Pt catalysts, one of the earliest studies of particle size effects concluded[56,57] that the areal rate

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[104] C O Bennett and M Che, *J Catal*, 1989, **120**, 293

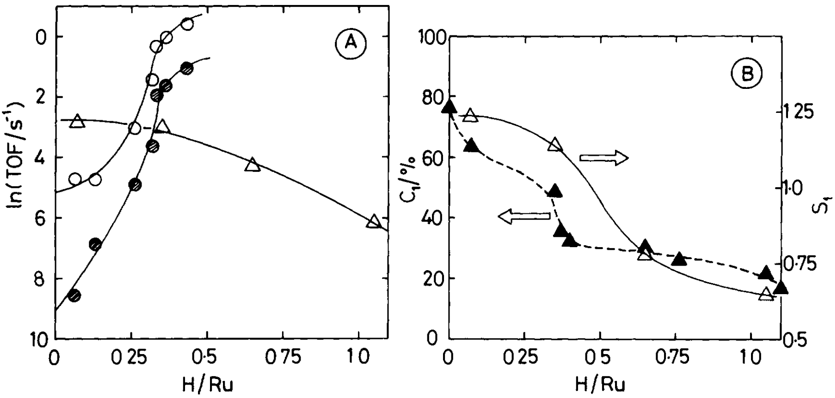

Figure 8 *(A) Turnover frequencies for the hydrogenation* (○) *and hydrogenolysis* (●) *of cyclopropane on various* Ru *catalysts at* 330 K[105] *and for hydrogenolysis of n-butane on* Ru/Al_2O_3 *at* 433 K (△), *as a function of* H/Ru_{tot} *ratio.*[106] *(B) Methane selectivity in the hydrogenolysis of n-butane at* 433 K[106] (△, S_1) *and of n-hexane at* 458 K[44] (▲, $C_1/\%$) *on* Ru/Al_2O_3 *catalysts, as a function of* H/Ru *ratio*

of the reaction (which was purely hydrogenation to propane) was effectively independent of size; more recently, the same reaction over Ru catalysts (giving methane and ethane as well as propane) was shown[105] to have much higher TOFs on small particles ($D \cong 50\%$) than on large ones (Figure 8). A clear particle size effect in the opposite sense is shown[44,106] by Ru/Al_2O_3 catalysts for alkane hydrogenolysis (see also Figure 8), but differences in supports and preparative methods mean that the two sets of results are not strictly comparable.

It is possible for a given catalytic system to show a particle size effect in only a small range of particle size. Good examples of such behaviour are the hydrogenation of benzene and of cyclopropane on Ni catalysts, where variation of areal rate only appears at sizes below about 1 nm.[107] A system cannot therefore be classified as 'size-insensitive' unless catalysts having dispersions of up to almost 100% have been tested; the studies of allegedly insensitive reactions do not always cover the higher range of dispersion.[108]

K. Turnover Frequencies, Active Centres, and the Taylor Ratio.—It is the view generally but not universally held that the active centre for a structure-sensitive reaction comprises a number of atoms, probably exceeding two, held in an arrangement peculiarly effective for the reaction in question. The introduction of the concept of turnover frequency (TOF) as the number of reactions per site in unit time under defined conditions has not in fact greatly advanced the science. A

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[105] J Schwank, J Y Lee, and J G Goodwin, *J Catal*, 1987, **108**, 495

[106] G C Bond, R Yahya, and B Coq, *J Chem Soc Faraday Trans*, 1990, **86**, 2297

[107] J W E Coenen, W M T M Schats, and R Z C van Meerten, *Bull Soc Chim Belg*, 1979, **88**, 435

[108] J Barbier, A Morales, P Marecot, and R Maurel, *Bull Soc Chim Belg*, 1979, **88**, 569

TOF is only a rate expressed per surface metal atom as estimated by H_2 chemisorption or other means, and hence is only useful in cancelling the effect of dispersion on rate in the case of insensitive reactions. For sensitive reactions, the true TOF *per site* will exceed that based on the total number of surface atoms by a factor R_T^{-1}, where R_T is the Taylor ratio,[16,104] *viz.* the ratio of the number of sites to the number of surface atoms. With alkane hydrogenolysis, where as is usually the case the values of TOF are far from constant,[45] the most likely explanation lies in a value of R_T considerably less than unity. It should in theory be possible to extract a value of R_T from the variation of TOF with dispersion, but to do so would involve the unproven assumptions that R_T is indeed constant, *i.e.* that only one type of site, comprising a set number of atoms and showing a fixed activity, is operational. We shall shortly encounter evidence that these assumptions may well be unfounded. If in fact alternative site geometries are possible, we might wonder whether the composition of the transition state for the rate-determining step is in all cases the same. There is as yet little to indicate whether kinetic equations are subject to particle size effects.[108]

There is one general principle that seems to emerge from the welter of observations relating to the nature and size of active centres. Where a reaction has a choice of paths, the one preferred will be that which is able to utilise the largest possible ensemble of atoms as its active centre. Thus on clean Ru particles of moderate size, hydrogenolysis of alkanes predominates over dehydrogenation and isomerization,[45,106] but when the surface is modified to diminish the number of large ensembles those reactions needing only smaller ensembles can then take place.[109] This is only true of course if the larger ensembles possess the necessary electronic attributes to give the required transition state.

L. Product Selectivities in Structure-sensitive Reactions.—It appears to be a characteristic of reaction systems showing structure sensitivity that product selectivities can also exhibit marked variations. Very clear examples of this are provided by the hydrogenolysis of propane, n-butane, and n-hexane over Ru/Al_2O_3 catalysts,[44,106] where the larger and more active particles show higher selectivities to methane (Figure 8), this being due with n-butane both to a shift towards statistical probability of breaking the C–C bonds and towards a stronger adsorption of the adsorbed C_3 intermediate as particle size increases.[106] There may well be a causal connection between TOF and selectivity, perhaps arising from the existence of two or more different kinds of site being available in different sizes of particles. It is a question not much discussed in the literature, whether a given reaction can proceed on a variety of types of active centre, each having its characteristic TOF and product mix, but there is no reason in principle why this should not be so. Mechanistic analysis is hampered by our current inability to estimate the number of operational active centres, but the use[44,110] of carefully selected reactants (*e.g.* 2,2,3,3-tetramethylbutane, which can

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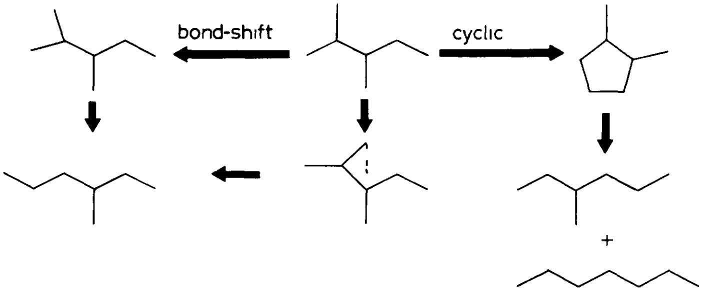
[109] G C Bond and R. R. Rajaram, unpublished work.

[110] B Coq, A. Bittar, and F Figueras, *Appl Catal*, 1990, **59**, 103



Scheme 1 *Mechanisms for metal-catalysed skeletal isomerization of 2 3 dimethylpentane*

undergo either demethylation or cracking to isobutane) serves to confirm the existence of sites of different structure

The reactions of C_5, C_6, and C_7 alkanes with H_2 have been much studied, especially over Pt catalysts, because of their obvious relevance to petroleum reforming, here however we are concerned only with *metal*-catalysed reactions Their intrinsic complexity also reveals aspects of structure sensitivity not exposed by the study of simpler molecules It is now well-established that dehydrogenation and isomerization are broadly speaking insensitive reactions, while hydrogenolysis is structure sensitive by proceeding preferentially on small particles, *i e* by employing atoms of low corodination number in the active centre[111] Two routes to skeletal isomerization are recognized (see Scheme 1) the bond-shift mechanism (where a cyclopropane intermediate may exist) and the cyclic mechanism, where a cyclopentane intermediate is stipulated[112] [113] In a number of elegant papers,[112] [114] the late François Gault and his associates distinguished these routes by using ^{13}C-labelled molecules (see Scheme 2), and showed that the cyclic mechanism rose in importance with particles smaller than about 1 nm The products of hydrogenolysis of methylcyclopentane have often been used[113] [116] as a means of exploring surface morphology on small particles (<2 5 nm), the three possible products are formed in their statistical proportions, whereas on larger particles n-hexane is not formed These findings exemplify Taylor's prophecy[60] that the fraction of surface that is active depends upon the reaction being catalysed, and they illustrate too that the path a reaction follows is conditioned by the available types of active centre

Unfortunately the differences in product selectivities are often caused by the presence of adventitious impurities (Cl , S, coke *etc*) rather than by changes in

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[111] F Rodriguez Reinoso I Rodriguez Ramos C Moreno Castilla A Guerrero Ruiz and J D Lopez Gonzalez *J Catal* 1987 **107** 1

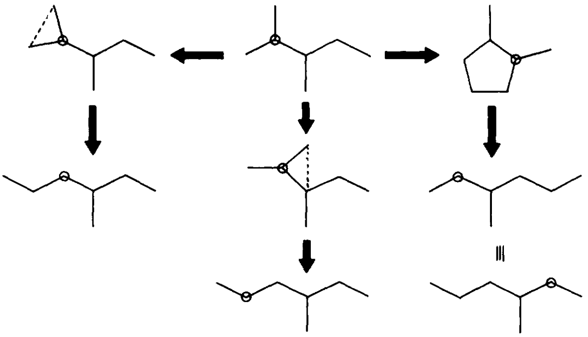
[112] J M Dartigues A Chambellan and F G Gault *J Am Chem Soc* 1976 **98** 856

[113] F G Gault V Amir Ebrahimi F Garin P Parayre and F Weisang *Bull Soc Chim Belg* 1979 **88** 475

[114] F G Gault *Adv Catal* 1981 **30** 1

[115] R Kramer and H Zuegg *J Catal* 1983 **80** 446 1984 **85** 530

[116] P Villamil J Reyes N Rosas and R Gomez *J Mol Catal* 1989 **54** 205



Scheme 2 *Use of 2,3-dimethyl-[2-^{13}C]pentane to distinguish bond-shift and cyclic mechanisms for skeletal isomerization*

the architecture of the active centre; examples of this, and of effects arising from the deliberate modification of the surface structure (by alloying, SMSI *etc.*) will be mentioned later (Section 4.C). There is however one case we can cite where conditions of pretreatment affect selectivities but probably not through impurity levels. We have studied[45] n-butane hydrogenolysis on Ru/SiO_2 catalysts prepared from $RuCl_3$, using both direct reduction of the chloride to Ru^0, and pre-calcination (*i.e.* $RuCl_3 \longrightarrow RuO_2 \longrightarrow Ru^0$). There is a good deal of evidence[72] to show that Cl^- is not strongly retained by SiO_2 and that it therefore does not affect the results. Each sample was first reduced at 758 K (HTR1), then oxidized (623 K) and reduced at 433 K (LTO/R), and finally reduced again at 758 K (HTR2). The results (Table 2) show that values of TOF vary only by a factor of three, while product selectivities, especially for the pre-calcined catalysts, vary enormously. The results quoted were obtained at the same temperature and at conversions that only ranged from 1 to 5%. We can merely conclude that HTR of the pre-calcined precursor leads to a surface structure on which deep hydrogenolysis to methane is the preferred route.

M. A Critique of the Surface Geometry Model.—From what has been said above, it will be clear that most of the studies on particle size effects have employed the van Hardeveld–Hartog models[12] to interpret the results. Unfortunately this procedure has one very substantial but rarely recognized flaw. Most of the calculations pertain to crystals having *exactly* the number of atoms to form a perfectly regular and symmetrical shape, *i.e.* having complete outer shells. Such a particle is statistically improbable in a practical catalyst having even the narrowest of size distributions; the majority of real particles will therefore be imperfect and will have atoms in a greater variety of coordination number than would a perfect particle. Calculations have been performed[117] to show how the populations of any class of atom might vary as the next outer layer of atoms is built up, and it is evident that any real particle size distribution, spanning at least

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[117] O. L. Pérez, D. Romeu, and M. J. Yacamán, *App. Surf. Sci.*, 1982, **10**, 135.

Table 2 *n-Butane hydrogenolysis on* 0.5% Ru/SiO_2 *catalysts at* 433 K[45]

Precursor	*Reduction*[a]	*H/Ru*	r/mmol g_{Ru}^{-1}h^{-1}	10^3 *TOF*/s^{-1}	S_1[b]	S_2	S_3
$RuCl_3/SiO_2$	HTR1	0.42	634	42.4	1.17	0.86	0.37
	LTO/R	0.46	644	39.3	1.22	0.76	0.42
	HTR2	0.18	137	21.9	1.99	0.81	0.13
RuO_2/SiO_2	HTR1	0.21	364	47.8	3.57	0.17	0.03
	LTO/R	0.38	874	63.8	1.52	0.85	0.26
	HTR2	0.10	158	46.6	3.41	0.19	0.07

[a] HTR1 and HTR2: high temperature reductions (758 K); LTO/R: oxidation at 623 K and reduction at 433 K.

[b] Selectivities S_1–S_3 are defined such that $S_1 + 2S_2 + 3S_3 = 4$, the subscript numeral giving the number of carbon atoms.

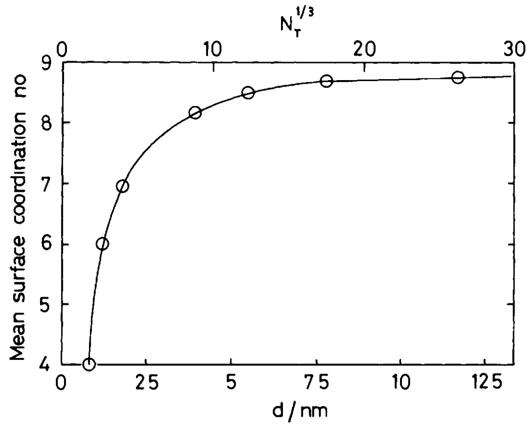

Figure 9 *Variation of mean surface coordination number with particle size for octahedra*[12] *(for description of scales see Figure* 1)

the range equivalent to the two atomic diameters (~0.5 nm) by which the size would increase on adding an extra shell, would contain such a range of surface structures as to render simple statistics inapplicable. The *only* geometric quantity that will change smoothly as the size of a particle is increased by addition of further atoms is the mean coordination number of all surface atoms, which will rise asymptotically towards a value of 9 (for fcc and cph structures) as the particle grows (Figure 9).

This criticism of a purely geometric approach must however be qualified on two scores. First, van Hardeveld and Hartog realized[12] that an active centre might comprise two or more atoms in a specific geometric relationship, and that the population of such sites might not vary monotonically with size. For example, the so-called B_5 site (Figure 10) was selected for attention, and it was shown that the maximum fraction of surface atoms that could form such sites on particles having a single incomplete outer shell passed through a maximum with increasing particle size. However particles of this type are no more probable than

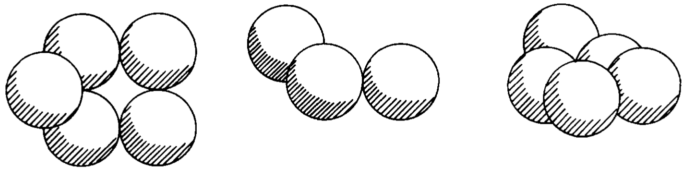

Figure 10 *Diagrammatic representations of a* B_5 *site at a step on a* (100) *fcc surface*

those having a complete outer shell, and so the case for the relevance of the B_5 site to catalysis is subject to the same strictures as that for the role of single atoms of any coordination class. A second qualification would apply if there were any factor which favoured particles having complete outer shells rather than incomplete ones. One such factor might be the surface free energy, since the average number of bonds per atom will be a maximum for a complete outer layer and hence the surface free energy will be a minimum. For this to be a practical possibility we have to suppose a mechanism whereby atoms can move during the reduction, so that only minimum energy configurations prevail. A recent study[118] of the 6% Pt/SiO_2 catalyst EUROPT-1 by Debye function analysis of its *X*-ray diffraction pattern has indicated that most of the particles are present as 55-atom cubo-octahedra; but an EXAFS study[119] of the same catalyst, although giving about the same number of atoms per particle, has suggested a quite different shape. At least one of the methods of analysis is wrong: perhaps both are.

N. Surface Mobility.—The foregoing considerations are predicated on the assumption that atoms in the outer layer of a particle will remain frozen in position during use, or at least that the amplitude of their vibrational motions will be so low that movement from one location to another can be neglected. There is however little direct evidence to support this assumption. The Huttig temperature for bulk Pd is however as low as 610 K[89] and the melting temperature of Au particles of 1 nm size is some 500 K below the bulk value.[120] This suggests that surface mobility may be commonplace between 300 and 500 K. Chemisorption will tend to weaken the attachment of surface atoms to those beneath, and the exothermic nature of many catalysed reactions will provide an additional source of energy. It therefore seems likely that the surfaces of metal particles in many operating conditions may be semi-fluid rather than static;[89] and indeed the outer layers of metal particles sometimes appear disordered, as if a fluid phase had on cooling formed a glass-like phase.[121]

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[118] V. Gnutzmann and W. Vogel, *J. Phys. Chem.*, 1990, **94**, 4991.

[119] S. D. Jackson, M. B. T. Keegan, G. D. McLellan, P. A. Meheux, R. B. Moyes, G. Webb, P. B. Wells, R. Whyman, and J. Willis, in 'Preparation of Catalysts V', ed. G. Poncelet, P. A. Jacobs, and B. Delman, Elsevier, Amsterdam, 1991, p. 135.

[120] M. Takagi, *J. Phys. Soc. Jpn.*, 1954, **9**, 359; P. Buffat and J.-P. Borel, *Phys. Rev. A*, 1976, **13**, 2287.

[121] P. Ratnasamy, A. J. Leonard, C. Rodrigue, and J. J. Fripiat, *J. Catal.*, 1973, **29**, 374.

More far-reaching effects on particle integrity can be obtained with molecules that interact strongly with the surface, and especially those, such as CO, that can form compounds with the zero-valent metal. It is well-known that Ni can be removed from a catalyst as $Ni(CO)_4$ on treatment with CO at high temperature; more recently the disruption of Rh particles by CO, with the reversible formation of adsorbed $M(CO)_x$ species, has been recorded.[122] The non-rigid nature of small particles is also well-demonstrated by the observation[123] that CO can draw Pd to the surface of Pd–Ag bimetallic particles because it interacts much more strongly with Pd than with Ag.

O. An Electronic Basis for Particle Size Effects.—In the face of these concerns about the usefulness of geometric models, we have now to consider whether particle size effects may find their origins in the changing electronic properties which small metal particles experience as they grow. Evidence for these changes comes both from theory and experiment.[14,17,18] There have been numerous calculations of various degrees of sophistication, most of which have addressed the band structure,[14] since band widths increase with size as the number of electrons to be accommodated increases. The spacing δ between electron energy *levels* is inversely proportional to the number of atoms in the particle, n:[16]

$$\delta \cong \varepsilon_F / n$$

where ε_F is the Fermi energy. As this spacing becomes larger than the thermal energy kT on lowering particle size, the levels cease to overlap and the particle loses its metallic character. With a Fermi energy of ~10 eV, this occurs at room temperature when n falls below about 400. Calculations of band width and position, and results obtained by photoelectron spectroscopy, photoionization mass-spectrometry and other methods, agree within broad limits that metallic character requires at least 100 to 150 atoms in a particle.[16] Although these various lines of argument and evidence do not agree precisely, it may be safely concluded that particles larger than 2 nm in size will be metallic in character at and above ambient temperature, those between 1 and 2 nm in size may have metallic properties only at high temperature, or may show an intermediate behaviour, while those below 1 nm in size will always be non-metallic.

It is of course conceivable that properties other than the strictly geometric or electronic, although perhaps associated with or derived from them, may play a vital role in catalysis. Factors concerning lattice dynamics spring to mind. However a large number of physical properties show monotonic trends with particle size and are well modelled[18] by expressions of the kind

$$G(n) = G(\infty) \pm c/n^{1/3} = G(\infty) \pm k/R$$

where $G(n)$ is the value of a property for a particle having n atoms, $G(\infty)$ is its

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[122] H F J van't Blok, J B A D von Zon, T Huizinga, J C Vis, D C Konigsberger, and R Prins, *J Phys Chem*, 1983, **87**, 2264, see also T Mizushima, K Tohji, Y Udagawa, and A Veno, *J Phys Chem*, 1990, **94**, 4980

[123] W M H Sachtler, *Catal Rev-Sci Eng*, 1976, **14**, 193

bulk value, R is the particle radius (if it can be taken as spherical), and c and k are constants. It is therefore difficult to account in this way for maxima or minima in the variation of rate with particle size. Effects shown only at very small size (< 1 nm) may however arise from the transition to non-metallic character. It is also possible that *both* surface geometry or morphology *and* electronic character may affect different aspects of a reaction, the former determining the *structure* of chemisorbed intermediates and the latter their *reactivity*.

There has also been much discussion as to whether the mean electron/atom ratio in a small particle may be changed by electron transfer to or from the support. This possibility motivated the early work[36] on metal–support interactions, the worth of which is now uncertain, but the transfer of a single electron in either direction would create an image charge which would inhibit further movement, and so the scope for change in the electron/atom ratio is now felt to be small. Small metal particles in zeolite cavities are however clearly electron deficient,[124] due to some transfer of charge to neighbouring highly acidic protons.

P. Summary of the Possible Factors Responsible for Particle Size Effects.—If we may for a moment dismiss the various worries we have expressed concerning the validity of rate measurements and of particle size estimates, and accept that there is evidence for monotonic or non-monotonic variations of rate with particle size, we should now try to summarise the possible lines along which explanations are to be sought.

(i) The electronic/dynamic properties of an assembly of atoms in the form of a small *metallic* particle will change monotonically with particle size in the range 2 to 10 nm; a marked change in character in the 1 to 2 nm range may signify transition to a non-metallic phase.
(ii) The *average* electronic/dynamic properties of a *surface* atom will not change much with size if there are more than 25 to 30 atoms in the particle ($\sim$0.8 nm in size).[14]
(iii) Average surface coordination number and population of atoms in a specified coordination number in the surface change only slowly when the size exceeds 2 nm (Figures 4 and 9).
(iv) Large ensembles of atoms in specified geometry cannot be found in very small particles: this fact will account for particle size effects on rate when *structure* sensitivity is clearly operative.
(v) Changes of activity with particle size should originate from differences in the energetics of adsorption, but where there can be a multiplicity of adsorbed states (as with alkenes, alkanes, CO *etc.*) thermochemical evidence is almost entirely lacking.
(vi) Differences in particle shape, in exposed planes or in surface roughness may

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[124] Z. Karpinski, *Adv. Catal.*, 1990, **37**, 45.

be brought about by changing the support, since particles may exhibit epitaxial effects or may be affected by the presence of a 'chemical glue' between the metal and the support.

Q. The Origin of Structure Insensitivity.—In view of the substantial changes which surface atoms suffer, either singly or collectively, as particle size is increased, the existence of a size effect on the rate in some sense or other is hardly surprising. What is in fact more difficult to understand is structure- or size-*insensitivity*, which implies that single atoms or very small ensembles in a variety of situations all behave in much the same way catalytically. It was at one time suggested[125] that this could be explained by a high degree of surface mobility, but it is worth noting that insensitive reactions generally proceed under mild (even sub-ambient) conditions where surface mobility is improbable. Moreover, work at the Institut Français du Pétrole has recently confirmed[126] that alkene hydrogenation is indeed insensitive to particle size variation with Pd, while hydrogenation of the more strongly adsorbing 1,3-butadiene is strongly size-dependent.[126,127] We have already noted the idea[92] that some insensitive reactions (such as alkene hydrogenation) may proceed on carbon-coated particles; this is a possible basis for explaining the lack of a particle size effect. It seems safe to say that what is at first blush the simplest situation has received least theoretical attention and may prove the hardest to explain.

It is possible to take the discussion one stage further. Although the term 'structure-insensitive' was first devised[57] to describe a lack of dependence of TOF on dispersion, the internal structures of reactions of this type, as revealed by product selectivities, are often surprisingly independent of dispersion and other variables of the catalyst preparation, including the presence of poisons and of alloying elements, and are characteristic only of the metal. Thus, for example, Pd nearly always shows very high selectivity to alkene in the hydrogenation of alkynes and dienes, marked tendency to give double-bond migration during alkene hydrogenation, and efficient alkene exchange in reactions of alkenes with D_2.[2] The contrast with for example Pt is very obvious, and is consistently shown, so we have here a further criterion by which reactions can be classified. While the factors responsible for the distinguishing characteristics of metals for this family of reactions are understood, at least in broad terms,[2,126] equally marked differences are shown by similar metals in alkane–D_2 exchanges,[128] for which there is as yet no logical explanation. The principles governing the formation of reactive intermediates from hydrocarbons are by no means yet fully elucidated.

It is however possible to discern minor but probably significant variations in

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[125] G C Bond, in 'The Physical Basis of Heterogeneous Catalysis', ed E Drauglis and R I Jaffee, Plenum, New York, 1975, p 53

[126] J P Boitiaux, J Cosyns, and S Vasudevan, in 'Preparation of Catalysts III', ed G Poncelet, P Grange, and P A Jacobs, Elsevier, Amsterdam, 1983, p 123

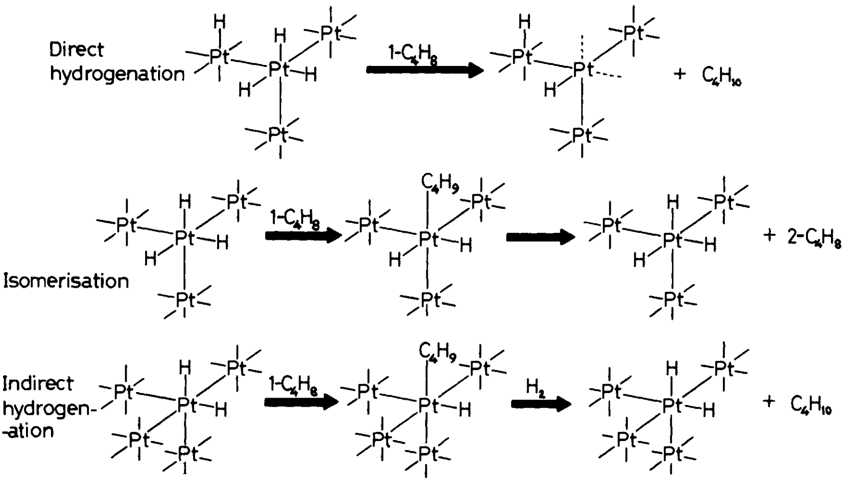
[127] B Tardy, C Noupa, C Leclercq, J C Bertolini, A Hoareau, M Treilleux, J P Faure, and G Nihoul, *J Catal*, 1991, **129**, 1

[128] R Brown, C Kemball, and I H Sadler, in 'Proc 9th Int Congr Catal', ed M J Phillips and M Ternan, Chem Inst Canada, Ottawa, 1988, vol 3, p 1013

Table 3 *Products of the reaction of ethene with* D_2 *on various* Pt *catalysts*[129,130]

Support	% Pt	*Conditions*[a]	% $C_2H_4D_2$	M^b
Al_2O_3	1	A	30.8	1.60
Al_2O_3	0.1	B	41.7	1.82
SiO_2	1	A	46.6	1.93
SiO_2	0.1	B	43.3	1.90
SiO_2–Al_2O_3	1	A	33.8	1.61
SiO_2–Al_2O_3	0.1	B	44.8	1.99
MgO	0.1	B	40.3	1.67
TiO_2	0.1	B	59.9	1.64
pumice	5	A	31.8	1.91
Pt foil[c]	–	A	27.3	1.69

[a] A: 273 K, $P(C_2H_4) \cong P(D_2)$, 48 ± 5% conversion. B: 293 K, $P(C_2H_4) = P(D_2)$, 15 ± 2% conversion. [b] Mean number of *D* atoms per ethane molecule. [c] Pt deposited electrolytically on Pt foil.



Scheme 3 *Single turnover hydrogenation of* 1*-butene*

product selectivities within one supposedly insensitive reaction on a group of catalysts containing the same metal. For example, the $C_2H_4 + D_2$ reaction has twice been examined[129,130] on variously supported Pt catalysts, and on both occasions small differences were noted in the relative rate of alkene exchange and in the breadth of the deuteroalkane distribution (Table 3). Augustine and his collaborators have developed[131] a 'single-turnover' procedure which they claim distinguishes between sites at which, in alkene hydrogenation, there is (i) direct saturation, (ii) isomerization, and (iii) two-step saturation involving alkyl intermediates (Scheme 3). The hydrogenation of methylcyclopropane (to either n-

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[129] G. C. Bond, *Trans. Faraday Soc.*, 1956, **52**, 1235.

[130] D. Briggs, J. Dewing, A. G. Burden, R. B. Moyes, and P. B. Wells, *J. Catal.*, 1980, **65**, 31.

[131] R. L. Augustine, D. R. Baum, K. G. High, L. S. Szivos, and S. T. O'Leary, *J. Catal.*, 1991, **127**, 675.

or iso-butane) is also capable of making subtle distinctions between otherwise similar catalysts.[132] Regardless of whether the observations are being properly interpreted, and whether the significance currently assigned to them is correct, we may hope to see further refinement and extension of kinetic studies that can explore the finer aspects of surface structure.

4 Modification of the Catalytic Properties of Supported Metals

A. Modification by Metallic Species.—We have had to leave our review of supported monometallic catalysts in a somewhat unsatisfactory state, feeling that the distinction between surface geometric requirements and bulk electronic factors is less clear than we might have wished, and that the local electronic properties of the active centre may be inextricably interwoven with the spatial distribution of the participating atoms. We now enquire whether the inclusion of an additional component in the catalyst can paradoxically lead to some simplification.

We noted above (Section 3.F) that the early work on bimetallic alloys required reinterpretation once it became clear from photoelectron spectroscopy[7] that each type of atom retained its own band characteristics; the discovery of low-temperature solubility limits in the Ni–Cu phase diagram[41] also necessitated the development of new structural models. However it soon became clear that the surface of a bimetallic metal particle, the components of which were mutually soluble, would contain ensembles of the active atom, the mean size of which would decrease as the proportion of the inactive component was raised.[133] In this way a clear distinction at once became apparent between structure-sensitive reactions, whose rates decreased rapidly with increasing amount of the inactive metal, and structure-insensitive reactions, the rates of which were unaffected over broad ranges of composition.[134–136] Interpretation of the results was qualified by concerns about microscopic homogeneity and surface segregation, although photoelectron spectroscopy has helped to assess the latter. The quantitative relationship between rate and surface composition allows an estimate of the number of atoms in the active centre, although some estimates do appear to be unreasonably large.[137] H_2 chemisorption has been used to count the number of active surface atoms, although in the Ru–Cu system there is evidence[138] for spillover to the inactive atoms. Work with Pt–Au[139] and related catalysts has confirmed the sequence of structure sensitivity in the reactions of n-hexane as being: isomerization < dehydrogenation < hydrogenolysis. A quite definite

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[132] S S Wong, P H Otero-Schipper, W A Wachter, Y Inoue, M Kobayashi, J B Butt, R L Burwell, Jr, and J B Cohen, *J Catal*, 1980, **64**, 84

[133] D A Dowden, in 'Proc 5th Int Congr Catal', ed J W Hightower, North Holland, Amsterdam, 1973, vol 1, p 621

[134] J H Sinfelt, J L Carter, and D J C Yates, *J Catal*, 1972, **24**, 283

[135] J K A Clarke, *Chem Rev*, 1975, **75**, 291

[136] H D Lanh, Ng Khoai, H S Thoang, and J Volter, *J Catal*, 1991, **129**, 58

[137] G A Martin, J A Dalmon, and C Mirodatos, *Bull Soc Chim Belg*, 1979, **88**, 559

[138] D W Goodman and C H F Peden, *J Catal*, 1985, **95**, 321

[139] J W A Sachtler and G A Somorjai, *J Catal*, 1983, **81**, 77

conclusion from the large body of experimental work on bimetallic particles is that the electron density on the active atoms is affected at most only marginally by neighbouring inactive atoms, so that the geometric factor is isolated in a relatively pure form.

It is not of course necessary to confine our attention to pairs of elements demonstrating complete mutual solubility. Sinfelt has shown that bimetallic clusters can be formed from pairs of metals (*e.g.* Ru–Cu, Os–Cu[43]) where the solubility is very small, so that the structure of the cluster is best described as having a core of the active metal and a surface partially covered by the inactive atoms, to an extent depending upon the gross composition and the mean particle size. It has further become appreciated that, over and above the tendency for the component of lower surface energy to segregate to the surface, that component will prefer to occupy those positions on the surface where it can make the greatest contribution to decreasing the surface free energy, that is to say, the sites of lowest coordination number.[140] This realization is of considerable significance in advancing our understanding of structure sensitivity, since whole classes of surface sites can now be effectively eliminated in a controlled way by judicious incorporation of inactive atoms, with the retention of active atoms in only a restricted range of environments.[44]

The literature now contains a number of examples of the application of this concept. For example, the greater tendency of the Pt–Re/Al_2O_3 to effect central C–C bond fission in n-butane hydrogenolysis as compared to Pt/Al_2O_3 (Table 4) has been ascribed[141] to a Pt–Re active centre in which the Pt atom has a low coordination number and the Re atom a high number.

B. Modification by Non-metallic Species.—We believe that non-metallic species are equally capable of decorating the surfaces of metal particles in a controlled and selective way, although such is not always the case. We[45] and others[24] have recognized that the use of reducible supports as a source of species that can modify the surface of metallic particles through an SMSI is difficult to control, and that adding a small amount of reducible oxide or other intended modifier provides a better means of limiting the extent to which modification can take place. Moreover by applying the modifier to a preformed supported metal, its effect and the relative powers of different substances to act as modifiers, can be directly evaluated.[142,143] We have established that Ru on Al_2O_3, SiO_2, and TiO_2 can be modified by the presence of V_2O_3 under reducing conditions, and that oxidation (which converts V_2O_3 to V_2O_5) negates the effect; a second high-temperature reduction can restore it.[144] Ru/SiO_2 and Ru/Al_2O_3 are similarly affected by the presence of small amounts of TiO_2.[45] Modification of this sort

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[140] J. K. Strohl and T. S. King, *J. Catal.*, 1989, **116**, 540; M. W. Smale and T. S. King, *J. Catal.*, 1990, **125**, 335

[141] G. C. Bond and M. R. Gelsthorpe, *J. Chem. Soc., Faraday Trans.*, 1989, **85**, 3767.

[142] G. C. Bond and S. Flamerz, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 767

[143] G. C. Bond and Lou Hui, unpublished work.

[144] G. C. Bond and R. Yahya, *J. Mol. Catal.*, 1991, **69**, 75.

Table 4 *Kinetic parameters for the hydrogenolysis of n-butane on* Pt/Al_2O_3 *and* $Pt\text{–}Re/Al_2O_3$ *catalysts*[141]

Catalyst	*Stage*[a]	E/kJ mol^{-1}	r/mmol $g_{cat}^{-1}h^{-1}$	S_2	S_3	F[b]	T_3[b]
Pt	1	139	4.55	0.418	0.782	0.204	0.982
Pt	2	124	3.49	0.294	0.844	0.141	0.983
Pt–Re	1	139	9.60	0.794	0.534	0.383	0.865
Pt–Re	2	128	7.20	0.782	0.535	0.377	0.859

Rates and selectivities at 603 K for definition of S_2 and S_3, see footnote to Table 2

[a] In stage 1, temperature was raised stepwise from *ca* 530 to 660 K, in stage 2, the process was reversed

[b] Parameters F and T_3 are derived from S_2 and S_3, and describe respectively the fractional chance of the central C—C bond splitting, and the fractional chance of an adsorbed C_3 intermediate desorbing as propane

Table 5 *Effect of the addition of modifiers* (*M*) *on the kinetic parameters for n-butane hydrogenolysis shown by* Ru/SiO_2 *catalysts*[45]

Modifier	*M* Ru_{tot}	*wt.* % Ru	E/kJ mol^{-1}	r/mmol $g_{Ru}^{-1}h^{-1}$	10^3 TOF/s^{-1}	S_2	S_3	F	T_3
–	–	0.5[a]	134	364	47.8	0.17	0.03	–	–
TiO_2	3.3	0.5[b]	127	45	40.8	1.07	0.36	0.43	0.61
–	–	1[c]	137	3165	–	0.85	0.45	0.30	0.64
V_2O_5	0.55	1[d]	139	54	–	1.44	0.26	0.70	0.87

Rates and selectivities at 433 K, S_2, S_3, F, and T_3 defined as in footnotes to Tables 2 and 4

[a] Precursor calcined before reduction [b] Precursor calcined after addition of Ti compound [c] No calcination of precursor [d] V_2O_5 deposited on SiO_2 before impregnation with $RuCl_3$

changes product selectivities as well as rates (Table 5), and it is just becoming possible to propose[44] models to account for these changes, in terms of specific inactivation of certain types of surface site. Cations of electropositive elements (Ca, Sc) are less effective than those of the more reducible elements (V, Cr, Mn).[144]

The effect is not confined to reducible modifiers. Hu *et al.* have shown[145] that adding Al_2O_3 to Rh/SiO_2 poisons hydrogenolysis without affecting dehydrogenation, although adding TiO_2 or Al_2O_3 to Pt/SiO_2 depresses the rate of n-butane hydrogenolysis, without changing product selectivities in any significant way.[143] Ru/Al_2O_3 catalysts prepared from $RuCl_3$, and either reduced directly or precalcined, show a range of activities, TOF's and product selectivities in alkane hydrogenolysis;[45] these results suggest that one contributing factor may be some dissolution of Al_2O_3 in the strongly acidic $RuCl_3$ solution, followed by re-precipitation during subsequent processing of Al^{3+} ions, some of which decorate the Ru^0 particles. Al_2O_3 does not of course show a conventional SMSI.

Dramatic changes in activity, TOF, and product selectivities for n-butane hydrogenolysis also result from altering the pretreatment of $RuCl_3/TiO_2$ precursors.[45,146] Reduction at 758 K (HTR1) gives catalysts of moderate activity, showing high values of S_2 (see Table 6); they are believed to be substantially

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[145] Z Hu, A Maeda, K Kunimori, and T Uchijima, *Chem Lett*, 1986, 2079

[146] G C Bond and Xu Yide, *J Chem Soc*, *Faraday Trans 1*, 1984, **80**, 3103

Table 6 *Effect of pretreatment on the kinetic parameters of* 0.5% Ru/TiO_2 *catalyst for n-butane hydrogenolysis*[45]

Precursor	*Pretreatment*[a]	*H*/*Ru*	*E*/kJ mol^{-1}	*r*/mmol $g_{Ru}^{-1}h^{-1}$	10^3 *TOF*/s^{-1}	S_2	S_3	*F*	T_3
$RuCl_3/TiO_2$	HTR1	0.15	133	59	11.2	1.23	0.29	0.52	0.60
	LTO/R	0.62	106	1380	62.1	0.65	0.46	0.11	0.52
	HTR2	0.11	145	12	2.8	0.95	0.30	0.25	0.40
RuO_2/TiO_2	HTR1	0.07	97	71*	28.8	0.95	0.22	0.17	0.26
	LTO/R	0.75	124	1911	71.2	0.78	0.34	0.12	0.39
	HTR2	~0	165	0.01**	-	1.24	0.17	0.41	0.29

Rates and selectivities at 433 K except: * 443 K; ** 533 K. S_2, S_3, *F*, and T_3 defined as in footnotes to Tables 2 and 4.

[a] See footnote to Table 2.

poisoned by Cl^-, since oxidation at 623 K and reduction at 433 K (LTR) leads to very much higher rates and TOFs, and to high values of S_1. A second HTR (HTR2) gives very low activities characteristic of the SMSI state. Catalysts prepared from $IrCl_6^{2-}/TiO_2$ behave similarly, although Os/TiO_2 catalysts show highest activity after HTR1.[147]

It has been known since the work of Maxted[148] that a great many molecules and ions, usually having a lone pair of electrons, can chemisorb strongly on metals and thereby act as catalyst poisons. That not all reactions respond equally to the presence of a given toxin is evident from the fact that some, singly or in combination, can act as *selective poisons* by poisoning specifically some undesired reaction path. A well-known use of this principle is to improve the selectivity of a Pd catalyst for hydrogenation of poly-ynes to poly-*cis*-enes by addition of Pb^{4+} and quinoline (the Lindlar catalyst[3,124]). A complex pattern of behaviour is, however, revealed when a range of toxins is applied to both sensitive and insensitive reactions.[108] Some (*e.g.* thiophen, H_2S, SO_2 *etc.*) are classed as non-selective poisons, as they affect both classes of reaction indifferently; others (S^0, Pb^{4+}, Zn^{2+} *etc.*) are selective in that they poison the structure-sensitive reactions more effectively than the insensitive reactions. One must suppose that the latter group have a preference for attaching themselves to the larger active centres, in the same way that some of the Group IVB elements can show some topological specificity;[44] the detailed chemistry remains to be uncovered. It is noteworthy that by this criterion the hydrogenolysis of cyclopentane shows the features of structure *in*sensitivity.[108] The ability of dehydrogenated hydrocarbon species, precursors to the formation of coke, to poison larger metal particles more than small ones[88] has already been noted, but their presence also changes product selectivities in n-butane hydrogenolysis over Pt/Al_2O_3 (Table 4), because they prefer to attach themselves to atoms of high coordination number.[141]

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[147] G. C. Bond and R. Yahya, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 775.

[148] E. B. Maxted, *Adv. Catal.*, 1951, **3**, 129.

Many of the aspects of the modification of supported metals remain to be explored, and we are far from constructing a good theoretical model to describe the observations. It seems likely that this will be an important future avenue of research, holding out the prospect of permitting any catalysed reaction to be conducted effectively by use of one of a limited number of basic catalysts modified by a simple chemical operation to tailor it to that reaction's requirements. We think too it should ultimately be possible to draw all modifiers, selective poisons, promoters and indeed coke into a single comprehensive model of particle surface structure.

5 Conclusions

It seems certain that supported metal catalysts will continue to be employed in the chemical manufacturing industry, and in environmental control, for many years to come, and for that reason they will be the continued focus of research in which the question of particle size effects will be dominant. I hope it will not be considered presumptuous if I try to offer some advice to those who will bear the torch in the coming years. Much of this will be based on my own experience; some on the perceived inadequacies of certain published papers.

In every research publication in this field, there should be a reasonably detailed description of the preparation of the catalyst (or its origin stated), of the materials used in making it, the BET area of the support *and of the finished catalyst,*[149] its pretreatment(s) and as full a description as possible of the metal particles. Any characterization is better than none, and there is really no excuse today for not reporting at least a dispersion derived from an H_2 isotherm. It is often desirable to show the isotherm or at least to describe it, as its form can sometimes reveal information about the purity of the metal surface.[45,72] Procedures employed to give kinetic results also merit full description, especially where ageing effects may obtrude (especially in continuous-flow systems). The reporting of results obtained at various times-on-stream temperatures and reaction pressures is also to be encouraged.

A common fault (and here we have sinned as much as any) is to use poorly controlled methods to prepare a small amount of catalyst and then to spend weeks if not months in studying it. We are then disappointed (but should not be surprised) when another operator fails to reproduce in a second preparation the behaviour of the first.[66] A major stumbling block to progress has been the extent to which each research group has chosen (for sometimes quite parochial reasons) to prepare and characterize its own catalysts, rather than sharing them with other groups engaged in similar work. The greater use of standard catalysts such as EUROPT-1[79,80,149,150] has partially counteracted the trend to individual preparations, and steps to make available a much wider range of such materials would be very welcome. Their value as basic catalysts which can be modified in controlled ways has been noted. The further refinement of preparative methods

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[149] G. C. Bond and P. B. Wells, *Appl. Catal.*, 1985, **18**, 221.
[150] G. C. Bond, F. Garin, and G. Maire, *Appl. Catal.*, 1988, **41**, 313.

to produce materials more homogeneous in composition and having narrower particle size distributions would also be very desirable.

It is also possible to find that much labour (and money) can be spent in characterizing a catalyst, and that little if any thought is given to the choice of reaction to which it is applied. In alkane hydrogenolysis, it is as easy to study n-butane as ethane, and it gives much more information: hydrogenating 1-butene or ethyne is more informative than hydrogenating ethene, and if one must stick with ethene, its reaction with D_2 is more interesting (if somewhat more difficult to follow) than its reaction with H_2. An earnest plea is made to give thought and care to the choice of reactions.

Finally, there is a need for clearer thinking and deeper insight into the nature of the problems under study. Where there are so many factors that bear upon the outcome, it is necessary to evaluate them all, and to try to integrate them into simple but comprehensive models. The introduction of the concepts of TOF and of structure sensitivity seemed to provide clarification, but the effect was only temporary, and their limitations are now apparent. The continued development and testing of theoretical models is essential to progress in this field.

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