1

Setting the Scene

This chapter falls into two unequal parts. First, there is an extended prologue which highlights (partly in tabular form) several important developments that have occurred in heterogeneous catalysis since the mid-1990s. Second, there follows (seriatim), with certain updated items and some omissions, the sequence of topics that were covered in Chapter 1 of the first edition.

1.1

Prologue: Advances since the Early 1990s

Apart from recent significant advances arising from the emergence of new experimental and theoretical techniques, many profound changes have occurred owing to a variety of both *external* and *internal* factors. Some external factors (Figure 1.1) are of a practical nature; many are of a societal-*cum*-cultural kind. In response to recent global trends of a political, legislative and environmental nature, the past decade has witnessed the arrival of new areas of scientific exploration that demand the development of new catalysts, particularly those capable of being recycled and/or reactivated.

In addition, we continually see the key role that internal factors – those that stem from the development of powerful new techniques of investigation (see Figure 1.2) – exert upon modern heterogeneous catalysis. Thus, quite dramatic discoveries have recently been made concerning the mode of operation of noble metal catalysts under working conditions, and these have already led to an overthrow or a re-examination of earlier descriptions and theories about the surface reactions on such ostensibly simple catalysts (e.g. palladium and platinum in their putative role in facilitating the oxidation of CO to CO_2). It transpires (see Hendriksen (Hendriksen, Bobaru and Frenken, 2004)) that, contrary to what experiments conducted with ultra-high vacuum equipment had led us to believe, under atmospheric pressure of reactant gases (as in an auto-exhaust catalytic system) the metal surface has a veneer of a PdO or a PtO_2 phase and this catalyses the oxidation of CO to CO_2 by the classic sacrificial (Mars – van Krevelen) mechanism (see Figure 1.22 below), and not the long-assumed Langmuir – Hinshelwood one (Figure 2.1). In other words this important catalytic reaction (of vital concern in environmental protection) proceeds by utilization of structural oxygen from

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- The attractions of (a) the hydrogen-economy and (b) the methanol economy[i]
- Fuel cells in general and the challenges posed by the direct methanol and direct ethanol fuel cells
- The production of bioethanol, biodiesel and biofuels in general with specific reference to (a) obtaining renewable liquid alkanes from aqueous-phase processing of bio-mass derived carbohydrates, (b) devising new ways of utilizing the fatty acid methyl esters (i.e. biodiesel) derived from sunflower, coriander and soybean, and (c) developing microbial catalysts for use in conjunction with inorganic solid catalysts so as to derive chemical building blocks from plant sources[ii]
- The need to harness solar energy and the consequential emphasis on photocatalysis and photoelectrochemistry[iii]
- The need to expand solvent-free, single-step processes[iv]
- Water remediation, especially the elimination of organo-chloro impurities[v]
- The gas-to-liquid (GTL) challenge, especially the conversion of natural gas into useful fuels and chemicals
- Coal gasification for chemicals and power. Polygeneration
- Need for improvements and new catalysts to effect:
- Fischer–Tropsch synthesis
  - hydrodesulfuration and hydrodenitridation
  - oxydesulfurization[vi]
- New challenges associated with automotive pollution control including elimination of particulates from diesel exhausts[vii]
- The exigent need to replace stoichiometric (ecologically harmful) oxidants in chemical synthesis and manufacture by oxygen, H_2O_2 or ‘safe’ solid oxidants that can liberate oxidizing agents *in situ*[viii]
- Advances in chemical engineering (catalytic reactor) practiced involving
  - periodic operation processes[ix]
  - process intensification
  - cascade reactions
  - use of membrane reactors[x]
- Ammonia-mediated hydrogen economy[xi]
- Reveres-flow membrane reactors[xii]
- Greater exploitation of microchannel reactors[xiii]
- Catalysts for the complete oxidation of volatile organic compounds[xiv]
- Catalytic Green Production of vitamins and fine chemicals[xv]
- H_2 production from ethanol[xvi]
- Acid-catalysed esterification of lactic acid[xvii]
- Selective hydrocracking of waxes (to produce diesel)[xviii]
- Replacement (solid) acid catalysts for Friedel–Crafts acylations[ixx]
- Conversion of starch into diesel and gasoline substitutes[xx]
- Synthetic enzymes by Darwinian evolution (e.g. for production of isobutanol as substitute gasoline[xxi]
- Strategies for production of fuels from ligoncellulosic biomass[xxii]
- Glucose production from saccharides using new solid acid catalysts[xxiii]
- Biodiesel from marine microalgae[xxiv]
- The catalytic activation of CO_2[xxv]

Figure 1.1 External factors that impinge upon the use and development of new solid catalysts.

i. Olah, Geoppert and Surya Prakash (2006); Olah (2013)
ii. van Bekkum and Gallezot (2004); Xu and Davis (2003)
iii. Lewis (2007), Vesborg and Jaramillo (2012)
vi. Thomas *et al*. (2001)
v. Gallezot (2005)
vi. Wachs (1997)
vii. Kruse *et al*. (2004)
viii. Some traditional oxidants used by organic chemists. for example the Jones reagent, which is CrO_3 dissolved in sulfuric acid, are now environmentally unacceptable. They may be replaced by benign reagents (e.g. transition-metal-exchanged micro-porous aluminophosphates and air) to effect a large variety of selective oxidation (primary alcohols to aldehydes and secondary alcohols to ketones). Often, highly selective oxidation, such as the Baeyer-Villiger reaction that converts cyclic ketones into lactones, may be effected by powerful oxidants generated *in situ* – see ten Brink and Arends (2004) and Raja and Thomas (2005). A recently reported powerful solid oxidant APB (acetyl peroxyborate) which, *inter alia*, releases peracetic acid and H_2O_2 on contact with a Mn^{III} ALPO catalyst, is a highly selective reagent (see Thomas in (Raja *et al*. (2006)). More recently (Thomas in Raja *et al*. (2008)) a facile green method of producing niacin (vitamin B_3) using APB. In the quest to replace stoichiometric reactions, two useful indices have entered the literature of catalysis in particular and clean technology in general: *atom efficiency* and the *E-factor*. The atom efficiency is the molecular weight of the desired product divided by the molecular weight of all products; and the E-factor is the weight of waste or undesirable by-product divided by the weight of the desired products. In the petrochemical industry E-factors are often as low as 0.1, in fine-chemical manufacture they fall in the range 5 to 50, and in the pharmaceutical industry reactions often have E values of 50–100
ix. *See* Chapter 7
x. Maschmeyer and Cornelius Jansen (2004)
xi. Christensen *et al*. (2006)
xii. Matros and Buninovich (1996)
xiii. Kiwi-Minsker and Renken (2005)
xiv. Taylor (2009)
xv. Raja (2009)
xvi. He *et al*. (2009)
xvii. Domen (Takagaki, *et al*., 2009)
xviii. Liu *et al*. (2009)
xix. Cejka (Procházková *et al*., 2009)
xx. Schmidt and Dauenhauer (2007); Dumesic (Roman-Leshkov *et al*., 2007); Dumesic (Chheda, Roman-Leshkov and Dumesic, 2007)
xxi. Arnold (Alcalde, Farinas and Arnold, 2004; Bastian *et al*., 2011; Keasling, 2010)
xxii. Huber and Dumesic (2006)
xxiii. Domen (Takagaki, Tagusagawa and Domen, 2008)
xxiv. Anon (2009); (King, 2013); (simon.evans@endsreport.co.uk)
xxv. Freund and Roberts (1996): Rodemerck and Baerns (Rodemerck. *et al*., 2013)

Figure 1.1 (*Continued*)

the surface oxide, not by interaction of adsorbed oxygen and CO at the exterior surface of the metal.

Several other internal factors have exerted their impact, notably the deployment of other new tools and techniques of an experimental nature, and the now almost routine recruitment of computational and modelling approaches utilizing density functional theory (DFT), molecular dynamics and variants thereof. These will be discussed in later chapters. Furthermore, there are sound reasons for believing that widely applicable strategies exist for the design of new

A. Non-invasive Methods Suitable for Studies Involving Pilot-plant-scale Catalytic Reactors
   1. Magnetic resonance imaging (MRI)
   2. Positron-emission tomography (PET)
   3. Positron-emission profiling (PEP)
   4. Synchrotron-based micro (X-ray) tomography
   5. Synchrotron-based micro (X-ray) fluorescence

B. *In siru* techniques for practical and model catalysts
   1. Scanning tunnelling microscopy (STM) and scanning tunnelling spectroscopy (STS)
   2. Atomic force microscopy, fluorescence microscopy
   3. X-ray absorption fine structure (XAFS), embracing near-edge (XANES) and extended-edge (EXAFS)
   4. Combined XAFS and X-ray diffraction (XRD)
   5. Sum frequency generation
   6. Environmental electron microscopy

C. *Ex siru* techniques
   1. Electron microscopy (encompassing TEM, STEM. high-angle-annular dark field (HAADF) imaging and tomography. coupled with
      (a) electron-simulated X-ray emission analysis, and
      (b) electron-energy-loss spectroscopy (EELS) and energy filled imaging and tomography
      (c) 4D-electron microscopy
      (d) rotation electron diffraction (RED)
   2. Electron crystallography

Figure 1.2 A selection of some of the powerful new techniques available for the non-invasive or *in situ* study of solid catalysts.

heterogeneous catalysts based, paradoxically perhaps, as much on the precepts of solid-state chemistry as on the lessons learned from surface science. The surface science approach relies heavily on the reductionist view that if all the key factors affecting individual discrete steps – such as rate of adsorption, surface diffusion and reorganization, poisoning at steps and surface desorption – are fully evaluated, one ought to be better placed to design superior catalysts. There are indeed some striking increases, registered by Nørskov, Besenbacher and their Danish colleagues, where the reductionist approach centred on scanning tunnelling microscopy (STM) has led to the design of viable, industrially important new (or improved) catalysts. But, in practice, it is not usually the reductionist argument, but the so-called 'emergent' one (which brings together all the relevant quantitative and intuitive factors and which is at the heart of the solid-state chemist's lines of argument) that succeeds in arriving at altogether new catalysts. The large, and ever-growing, class of single-site heterogeneous catalysts (SSHCs described later) testify to the validity of this view, and has led to the confluence of heterogeneous and homogeneous catalysis.

Another noteworthy chemical engineering trend is the use of micro-kinetic modelling procedures. In addition, it is a feature of present-day catalyst practice that the chemical and control-engineers who use robotic devices and a diversity of programmed logic controls as well as finite-element-analyses packages, can

1 Materials – chemical aspects of the preparation, characterization and properties of new types of heterogeneous, solid catalysts:

- Nanoporous (i.e. micro- and meso-porous) solids, C
- Zeolites (natural and synthetic) C; alumino-phosphate-based microporous solids, C; metal-organic frameworks, A; amorphous silica, C
- Microwave-assisted syntheses, A
- Perovskites, spinels, defective fluorite, pyrochlore complex oxides, C
- Layered double hydroxides, hydrotalcites, synthetic clays, A
- Heteropolyacids and other solid acids and polyoxometalates, C
- Monometallic nanoparticles, C; bimetallic nanoparticles, C; and bi- and tri-metallic clusters; A; nanogold catalysts, B
- Skeletal catalysts (mainly Ni and Cu), B
- Molecular precursors to single-site nanoporous catalysts, A
- Silsesquioxanes, A
- Dendrimers, A

2 Immobilized asymmetric transition-metal complex or organometallic catalysts, B

3 Immobilized enzymes, B; microbial catalysts, C, and imprinted solids, A

4 Ceramic and metallic monoliths, C

5 Cascade reactions, C; chemo-enzymatic catalysts, A

6 Process intensification, C

7 Autothermal reactors, B

8 Photocatalysts and electrocatalysts, C; electrochemical promotion, A

9 High throughput experimentation, C; combinational chemistry, C

10 Fluctuations and bistabilities, C

11 Microreactors and microfluidics, C. Robotic test rigs, B

12 Polygeneration (chemicals and electricity), B

13 Exergy analysis, B

14 Darwinian evolution, A

15 Atom efficiency, E-factor, C[i]

16 Selective catalytic reduction (SCR), C

17 Storage reduction catalyst (SRC), C

18 Sabatier principle, A; Brønsted-Evans-Polanyi (BEP) plots, A[ii]

19 Pareto-optimal catalysts, A

20 Single-site heterogeneous catalysts C[iii]

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[i] The E-factor is a useful measure of the environmental acceptability of a chemical process. E is the weight of waste or undesirable by-product divided by the weight of the desired product. It is a little unrealistic as it does not take account of water (used or generated) in the process. There is increasing environmental concern about the supply, utilization and purity of water

[ii] The Sabatier principle is in effect the well-known volcano plot. Sabatier was among the first to realize that if adsorption of a reactant on a catalyst is very weak, the catalyst has little effect (e.g. in dissociating the molecule), but if adsorption is too strong, there is difficulty in effecting desorption. These two extremes results in small rates of catalytic turnover (see Section 1.4.2)

[iii] See Thomas (2012)

(Some terms and topics occur mainly in academic or laboratory-scale activity; these are labelled A. Some refer mainly to pilot-plant and industrial-scale operations; these are labelled B. Those that fall in both categories are labelled C)

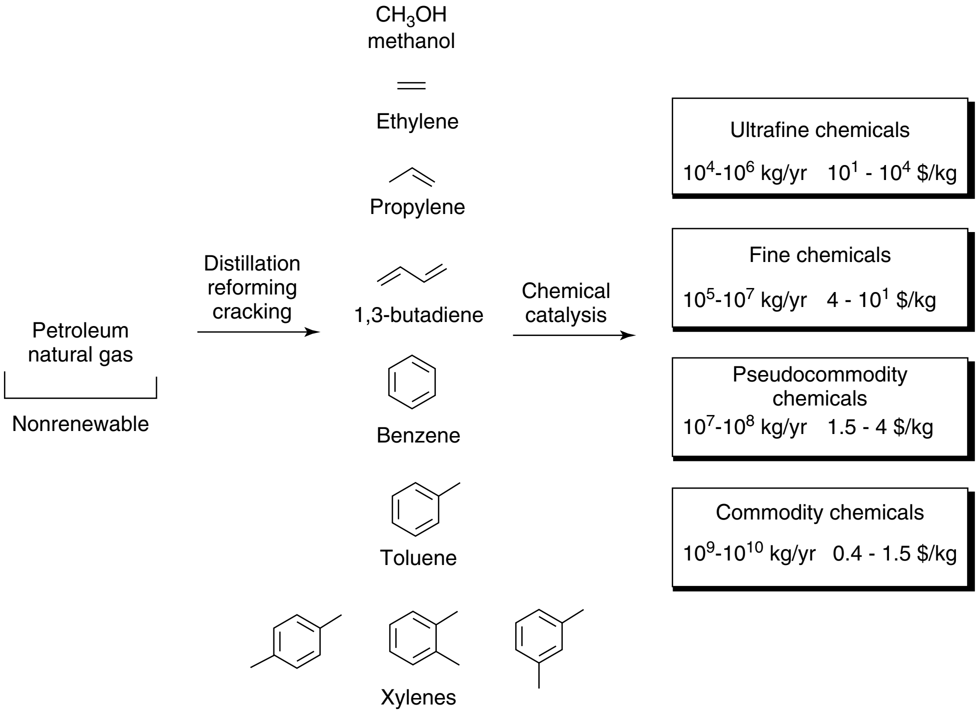
Figure 1.3 Glossary of terms and processes reflecting the changing face and current practice of heterogeneous catalysis.

nowadays set up precisely arranged catalytic reactors fine-tuned to maximize efficiency of chemical production.

Before we proceed to elaborate the nature of these external and internal factors that have led to the changing face of heterogeneous catalysis in the course of the past decade, it is prudent to tabulate a glossary of terms that have come into prominence in the past decade see (Figure 1.3). This is by no means a comprehensive list; and many of the terms were in use decades ago, but those have gained renewed relevance.

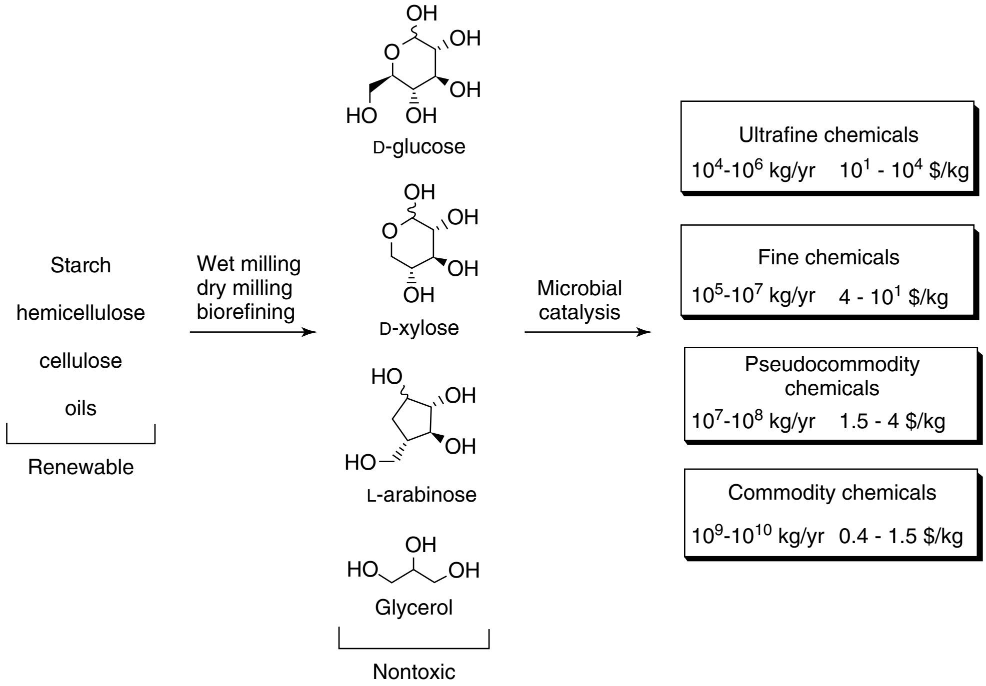
Catalysis is of great practical importance at present because of the need for sustainability of energy supplies (for fuel and transport), the quest for clean technology (with its goals of zero-waste and utilization or production of non-hazardous and ecologically non-harmful materials, and solvent-free processes) and the derivation of chemical building blocks from the plant kingdom and algae in place of non-renewable fossil sources. It is also vitally important in the context of powering the planet for the indefinite future: and all these issues are discussed in Chapter 9.

But a few comments on some of these issues, many of which are interrelated, are in order. Take, for example the fact that, at present, more than 90% of all organic chemicals are derived from just seven petrochemicals (Scheme 1.1): methanol, ethylene, propylene, butadiene, benzene, toluene and mixed xylenes.



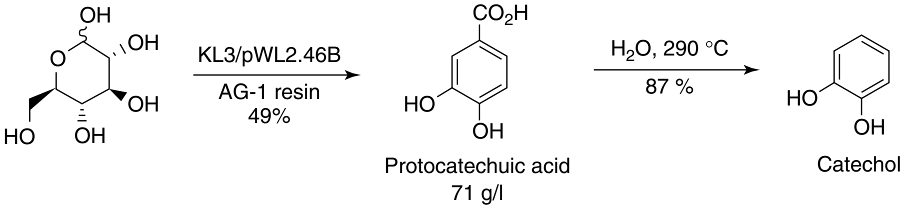
Scheme 1.1 Central importance of seven petrochemicals.

Whilst many commentators invariably highlight humankind's dependence on fossil sources for energy, few (until quite recently) faced up to the pressing need to seek renewable (e.g. plant or marine organism) sources for these vital seven chemical building blocks. Already, there are ways of addressing this challenge, and the efforts of Frost in particular in Michigan have shown how four principal building blocks (D-glucose, D-xylose, L-arabinose and glycerol, all of which are non-toxic), readily derived from (renewable) starch, hemicellulose, cellulose and vegetable oils, may, in principle, satisfy humankind's future chemical needs (Scheme 1.2). To take a specific example, catechol, which is used extensively in pharmaceuticals, flavours, agrochemicals, antioxidants and polymerization inhibitors, has been synthesized from D-glucose, by Frost *et al.*, in a benzene-free fashion using his tailored microbial catalyst (Scheme 1.3). It is also possible readily to derive muconic acid by microbial catalysis, and it, in turn, by judicious use of a supported bimetallic catalyst, may be converted into adipic acid (see Thomas *et al.* (2003a)).



Scheme 1.2 Some important carbohydrates derived from starch and cellulose.

It is not only the academically orientated community that nowadays is paying serious attention to bio-generated fuel and chemicals. Very recently the Chief Scientist of one of the world's leading multinational oil companies drew attention to the fact that Rudolph Diesel's original vision (that vegetable oils would be a source of bio-diesel) is again being given serious consideration. There is substantial technology 'headroom' for advanced biofuels to enhance energy security,



Scheme 1.3 Benzene-free synthesis of catechol: interfacing microbial and chemical catalysis (Li, Xie and Frost, 2005).

reduce greenhouse gas and provide economical transport. (This last possibility is, however, debatable, as it will require careful analysis of land or sea areas to sustain the needs of transport fuel in developed countries.) This headroom exists largely because the world's scientific and engineering skills have not yet been focused coherently on the challenges involved.

The challenge of producing liquid alkanes from biomass-derived carbohydrates, for example shows clearly the need to combine the appropriate microbial and heterogeneous catalysts. Thus, Dumesic *et al.* in Wisconsin have recently shown that liquid alkanes with the number of carbon atoms ranging from C_7 to C_{15} are selectively produced from biomass-derived carbohydrates by acid-catalysed dehydration, followed by aldol condensation over solid base catalysts, thereby forming large organic compounds. (This theme is amplified in Section 9.6.) These, in turn, were converted into alkanes by dehydration – dehydrogenation over bifunctional catalysts that contain acidic and metal sites. The liquid alkanes generated in this manner are of appropriate molecular weight to be used as transport fuel components. Dumesic, Huber and co-workers have also demonstrated that it is possible to produce light alkanes by aqueous-phase reforming of sorbitol (which is readily derived from biomass by hydrogenating glucose). Considerable amounts of hydrogen are needed to accomplish this:

$$C_6H_1O_6 + 6H_2 \rightarrow C_6H_{14} + 6H_2O \tag{1.1}$$

But hydrogen can be produced in a catalytic processes at 500 K in water from biomass-derived polyols having a C : O ratio of unity as in sorbitol:

$$C_6H_{14}O_6 + 6H_2O \rightarrow 13H_2 + 6CO_2 \tag{1.2}$$

All this indicates that, in the presence of an appropriate catalyst, the hydrogen needed to produce the alkanes, should be available.

Another noteworthy facet of the use of carbohydrates as chemical raw materials is that this will create remarkable opportunities for the chemical processing industry. The use of carbohydrates as raw materials should eliminate the need for several capital-intensive, oxidative processes currently used in the petroleum industry. Biomass carbohydrates will provide a viable route to products such as alcohols, carboxylic acids and esters. These natural products are also stereo- and regio-chemically pure, thereby reducing dependence on expensive chiral catalysts and complex syntheses that are nowadays required to install (selectively) chemical functionality in petrochemicals. Such an approach, as well as others, have

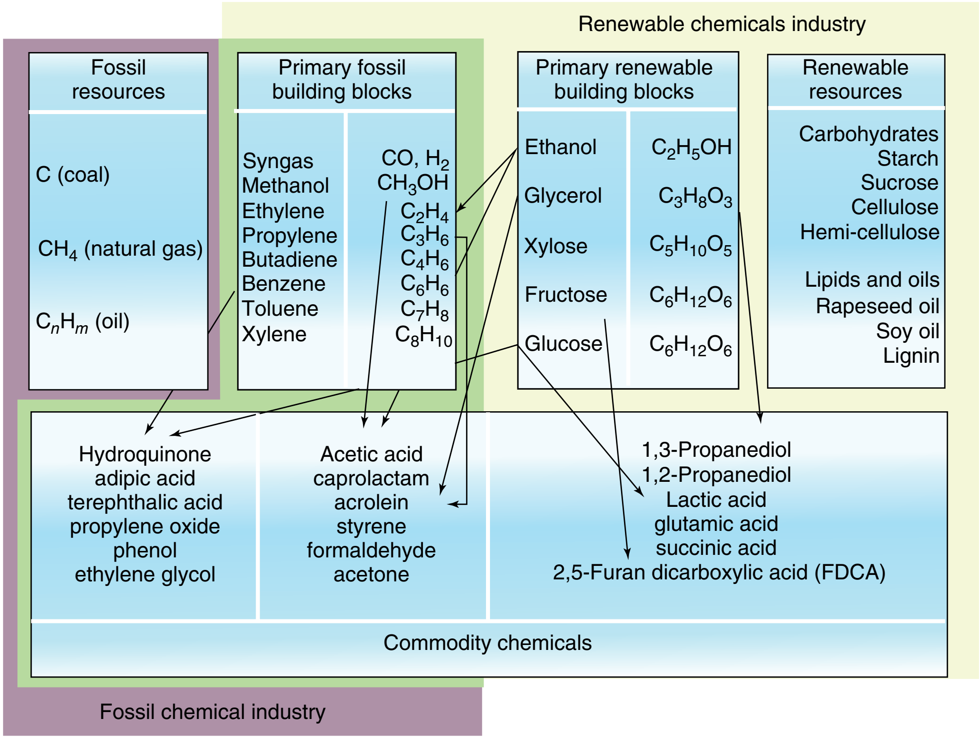
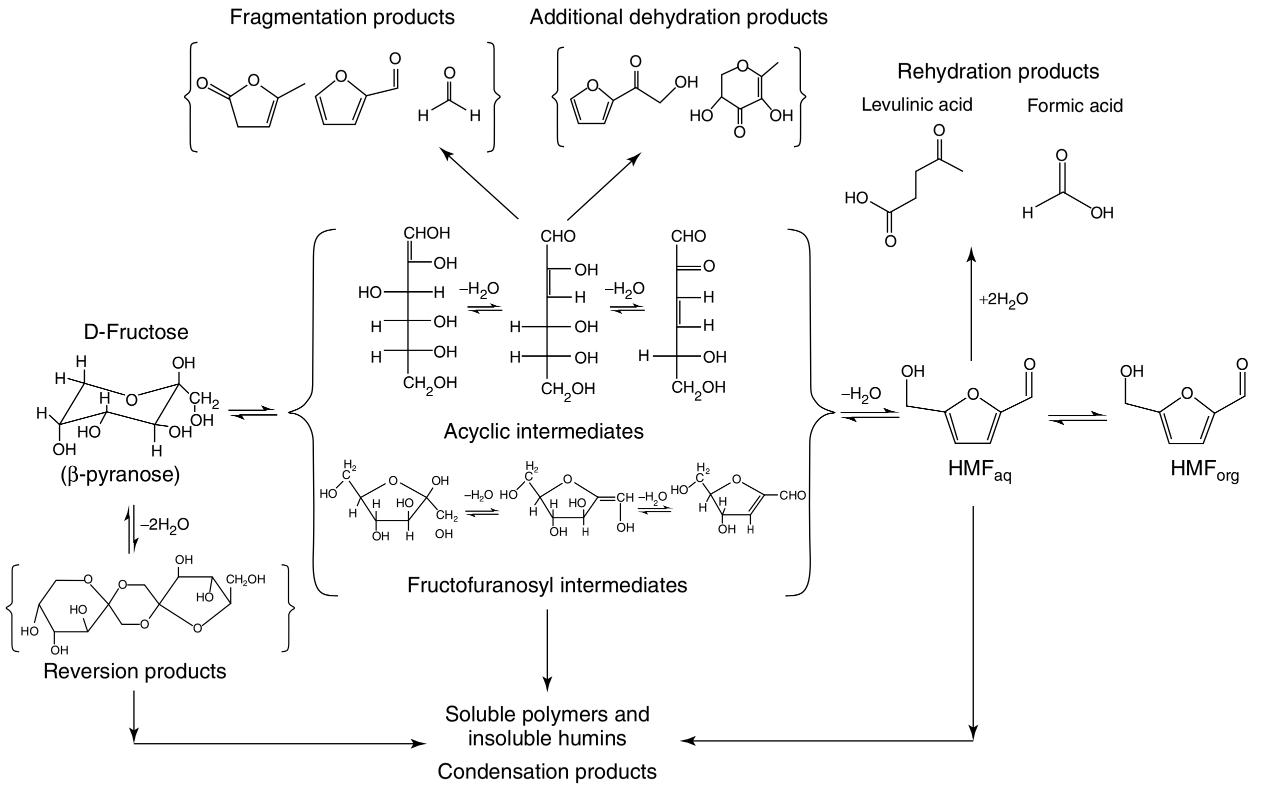


Figure 1.4 Strategies for producing commodity chemicals from biomass. The part set on a grey background shows some of the currently most important commodity chemicals produced from fossil resources. By strategy 1, these same chemicals are produced from renewable building blocks. Strategy 2 covers the idea of producing alternative chemicals, which potentially can substitute some 'old' chemicals. Together strategies 1 and 2 cover the parts shown on the green background. (With permission from Wiley-VCH (Christensen *et al.*, 2008).)

been advanced by Christensen *et al.*, in Denmark and Figure 1.4, taken from his work, portrays a comparative account of the strategies for producing commodity chemicals.

To take a specific example, D-fructose may now be catalytically converted into 5-hydroxymethylfurfural (see Scheme 1.4, taken from Dumesic's work) which is a key intermediate for manufacturing polymers and pharmaceuticals; it is a good substitute for ethylene glycol and other linker molecules used in the manufacture of plastics and fibres. Derivatives readily made from 5-hydroxymethylfurfural including furan dicarboxylic acid, can be used in place of terephthalic acid (generated from fossil-derived petroleum) in the polymer industry.

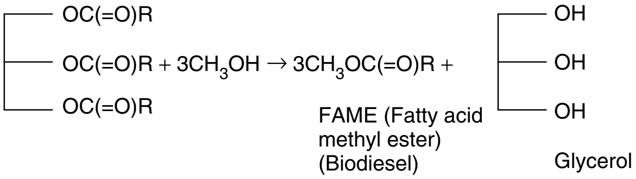
The production of diesel from vegetable oils requires an efficient solid catalyst to make the process fully ecologically friendly. Esterification of higher fatty acids by liquid acids (e.g. H_2SO_4) is intrinsically inferior to the use of solid acids. Nafion®,



Scheme 1.4 Schematic representation of reaction pathways for acid-catalysed dehydration of fructose. Structures in brackets correspond to representative species (Román-Leshkov, Chheda and Dumesic, 2006).

for example is a useful catalyst for this purpose, but a cheaper, superior solid catalyst is one prepared by sulfonating partially carbonized sugar, starch or cellulose, as recently demonstrated by Domen *et al.* in Japan.

Returning to the two products of transesterification of triglycerides (from soybean, sunflower or rapeseed), considerable practical scope exists for the catalytic exploitation of both the glycerol and the FAME (the biodiesel, see Scheme 1.5).



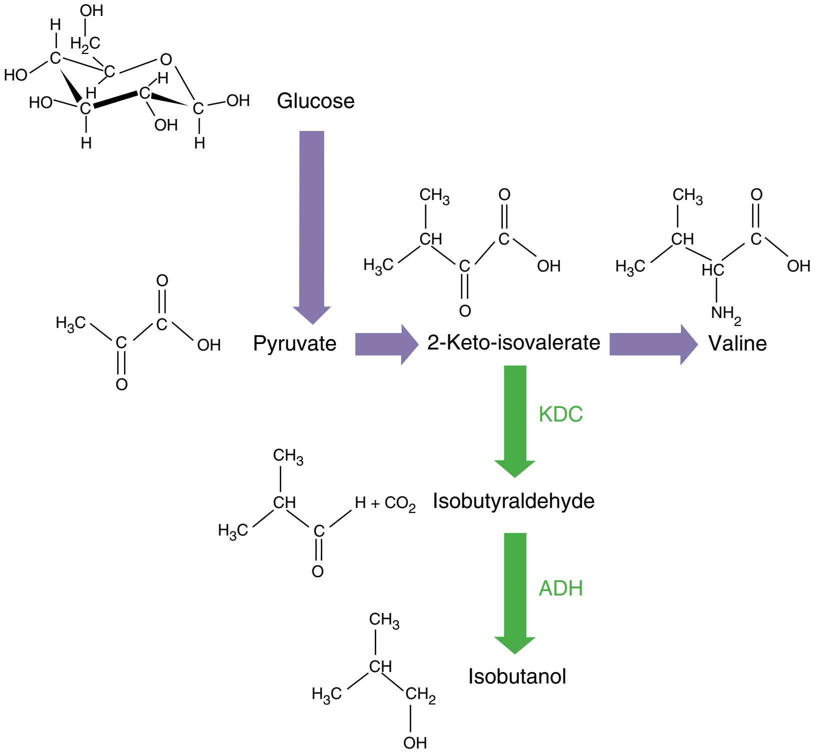
Scheme 1.5 Transesterification of triglycerides.

The crude glycerol, produced as a by-product in the production of biodiesel, is itself insoluble in the biodiesel. For blending into the diesel, glycerol has to be converted into a product boiling in the diesel range, and in addition, be freely soluble. Recently Ratnasamy in India has developed appropriate solid acid catalysts (aluminosilicate and silicoaluminophosphate microporous materials) that effectively etherify the glycerol, thereby solving a practical problem and altering the economics of the manufacture of biodisel.

It is known that glycerol can be converted over platinum-based catalyst into gas mixtures of CO and H_2 (syngas) at temperatures from 498 to 620 K, these being much lower than those for conventional gasification of biomass (e.g. 800 – 1000 K). Syngas can be used to produce fuels and chemicals. The endothermic conversion of glycerol into syngas may be combined with the exothermic Fischer – Tropsch and methanol synthesis to provide low-temperature and energy-efficient routes for the production of these compounds. This heat-intensive catalytic process could become a less energy-intensive alternative to current methods of converting carbohydrates into fuel-grade ethanol. Major advances are currently (2013) being made in converting plentiful biomass feedstock to bio-oil. Maschmeyer and colleagues, in association with the Licella Company, take low cost waste such as saw dust that is then effectively converted into a grade of bio-oil that can be subsequently processed in a conventional oil refinery, a catalytic hydro-thermal reactor being used for this purpose (see Maschmeyer (Fabos *et al.*, 2012)).

Another recent development exploits the possibility of selectively oxidizing, with the right choice of catalyst, the constituents of biodiesel (e.g. methyl oleate), derived from soybean. These constituents may be converted into valuable olefins and olefinic esters in an autothermal catalytic reactor, where the heat is supplied by the exothermic oxidation reactors, not by external heaters. A rhodium and cerium catalyst, supported on alumina, when used with a ratio of biodiesel to oxygen (C/O) in the feed stream of about 1.3, yields about 25% ethylene and smaller concentrations of propylene, 1-butene and 1-pentene.

Bioethanol, which now seems much less attractive than it did even a few years ago as a versatile sustainable chemical feedstock and as a ‘green’ fuel additive, is losing favour to isobutanol, a more acceptable fuel. Isobutanol, can, by Darwinian evolution of the right enzyme (as shown by Arnold *et al.* in the USA), be readily (biocatalytically) generated from glucose (Scheme 1.6). It is less corrosive than ethanol (for transport fuel) and has a good octane value. Isobutanol made this way (see Section 9.6) is also a source of isoprene, which is formed by dehydration; and hence of polyisoprene polymers. Nevertheless, as Christensen *et al.* have recently shown, with appropriate catalysts, biomass, via ethanol, has potential as a fuel and as a feedstock for important chemicals.



Scheme 1.6 *Escherichia coli* has a series of catalytic steps that turns pyruvate into an amino acid called *valine* (Alcalde, Farinas and Arnold, 2004).

It is known that nanoparticles of gold (3–6 nm size range), supported on a porous $MgAl_2O_4$ support, catalytically convert ethanol to acetic acid in aqueous acidic media using modest pressures of air as an oxidant at about 150 °C. Yields of up to 90% are achieved, with CO_2 as the only major by-product. This simple process, which presents room for improvement, is to be contrasted with the current main means of producing bulk quantities of acetic acid – the carbonylation of methanol, which in turn is derived from natural gas (or other fossil sources).

There is clearly much scope for catalytic development using nanoparticles of gold supported on various solids, as demonstrated by Haruta, Hutchings, Goodman, Freund and Corma and their co-workers in Japan, the UK, the US, Germany and Spain respectively.

Compared with existing crops grown for biofuels, marine microalgae appear to offer many advantages: they do not require freshwater, nor do they require farmland, so there is no need to sacrifice food-growing land nor to push further the trend towards deforestation. Moreover, microscopic algae, which harness sunlight, can consume flue-gas CO_2 from power plants, steelworks and cement factories. In 2006, the US company Valcent published results that revealed astonishingly high yields of biodiesel: up to 1.4 million l per ha per annum, compared with 470 l per ha from Soya grown biodiesel. In 2008, the UK government-backed Carbon Trust launched its Algae Biofuel Challenge to help develop open-pond algae cultivation, since algae has received far less attention than lignocellulosic ethanol. Initially, at least the pursuit of this type of sustainable chemistry will rely more on biological phenomena – strain selection (there are tens of thousands of distinct species of algae) for maximum productivity as well as resistance to viruses – than on heterogeneous catalysis. But, as with the materials derived from the plant kingdom, the feedstocks from algae will also require powerful catalysts. One major company, Exxon-Mobil, in association with a Craig Venter Company had, by 2013, invested some $600 million on algaeculture required to make such an industry viable. But the Exxon-Mobil CEO in 2013 stated that algae fuel is still some 25 years away from commercial viability. Another US-based company, Algenol, however, has claimed to produce 9000 gal of ethanol (by biocatalytic, algae-assisted combination of CO_2 and H_2O) and hope to be fully commercial in their production in 2014 (see Section 9.7.2 for more details).

1.2
Introduction

The phenomenon of catalysis is so intricately woven into the fabric of chemistry, and the recognition of its nature and importance is so intimately associated with the pioneering endeavours of the founders of modern chemistry and physics – Berzelius, Davy, Faraday, Nernst, Kirchhoff and Ostwald – that it hardly seems necessary to recall what the term '*catalysis*' signifies. To be sure that there is no misunderstanding, we define a catalyst as a substance that increases the rate of attainment of chemical equilibrium without itself undergoing chemical change. We shall consider later whether the catalyst suffers any change, transitory or permanent. But it follows from this definition that if the rate of a forward reaction, for example hydrogenation, is speeded up in the presence of a particular catalyst, the reverse reaction, dehydrogenation, will likewise be facilitated to the same degree.

Heterogeneous catalysis is perennially relevant, it is endlessly fascinating, and it continues to be deeply enigmatic. More than 90% of the chemical manufacturing processes in use throughout the world utilize catalysts in one form or another: much of the food we eat and the medicines we take, many of the fabrics and building materials that keep up warm, and almost all the fuels that transport us by road, sea or air are produced by heterogeneously catalysed reactions. The current world production of ammonia, required principally as an agricultural fertilizer, is about 150 million tons per annum. Owing to the expanding need to feed mankind, this figure is increasing at some 3% per annum. The science and technology of catalysis are therefore of central practical importance. However, when we recall that, until recently, the majority of commercially significant catalysts were discovered and developed principally by empirical methods, we appreciate how much more remains to be learned about the principles and manifestations of catalysis. Rational design of certain kinds of catalyst and chemical engineering process, thanks to very recent advances, is now a reality.

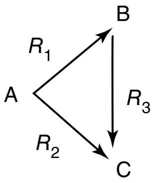
But it is not the industrial scientist alone who responds to the challenge of catalysis: the academic is also profoundly aroused. How is it that molecules impinging upon certain (catalytic) surfaces at velocities of typically $1600\,\mathrm{km\,h^{-1}}$ can be converted at that surface, with high efficiency and often with spectacular selectivity, into a desired product, whereas the same species impinging upon other (inert) surfaces merely rebound with more or less retention of translational, vibrational and rotational energy? This is one of the key questions we endeavour to answer in this book. In doing so, we invoke many other considerations, which span thermodynamics, kinetics and theories of bonding and crystal structure, and draw upon the panoply of techniques that have deepened our understanding of electron transfer and atomic transformations at solid surfaces.

1.2.1
Selectivity of Catalysts

A good catalyst must possess both high activity and long-term stability. But its single most important attribute is its selectivity, *S,* which reflects its ability to direct conversion of the reactant(s) along one specific pathway.

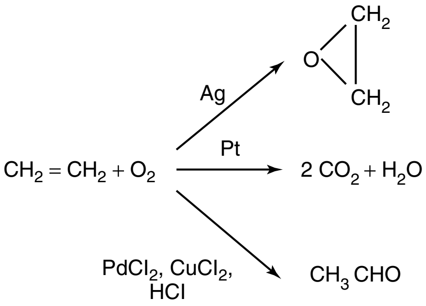
When a reactant A can be transformed into either B or C at rates R_1 and R_2 (Scheme 1.7), respectively, the selectivity S is calculated as shown in Scheme 1.7. It is also sometimes convenient, when R_3 is zero, to define another index of selectivity, $p = R_1/R_2$.

$$S = \frac{R_1 - R_3}{R_1 + R_2}$$



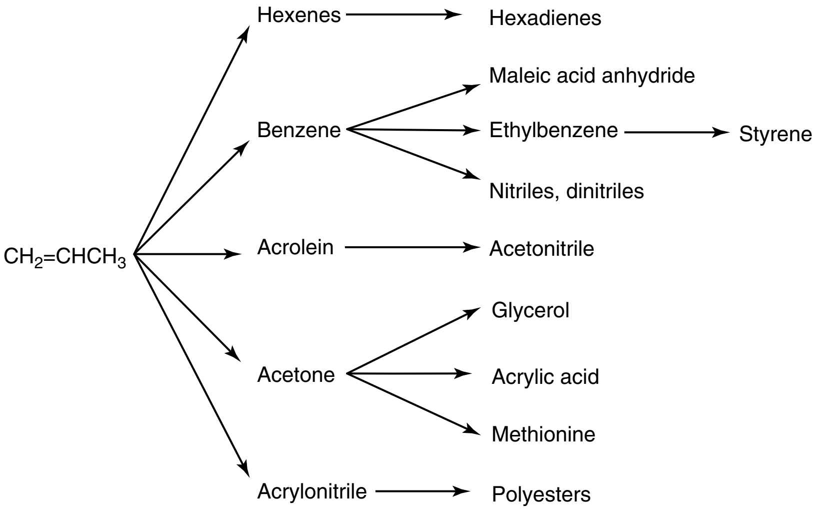
Scheme 1.7

Over a silver catalyst, ethylene (ethene) is selectively converted into ethylene oxide an important precursor in the manufacture of ethylene glycol which, in turn, is required for the production of polyester fibres and antifreeze agents – in preference to the other two possibilities represented in Scheme 1.8. Finely dispersed platinum, as in an auto-exhaust catalyst, selectively favours the total combustion of ethylene. The oxidation of ethylene to acetaldehyde is best performed homogeneously in the presence of aqueous palladium chloride and copper ions, this being the essence of the industrial Wacker process.



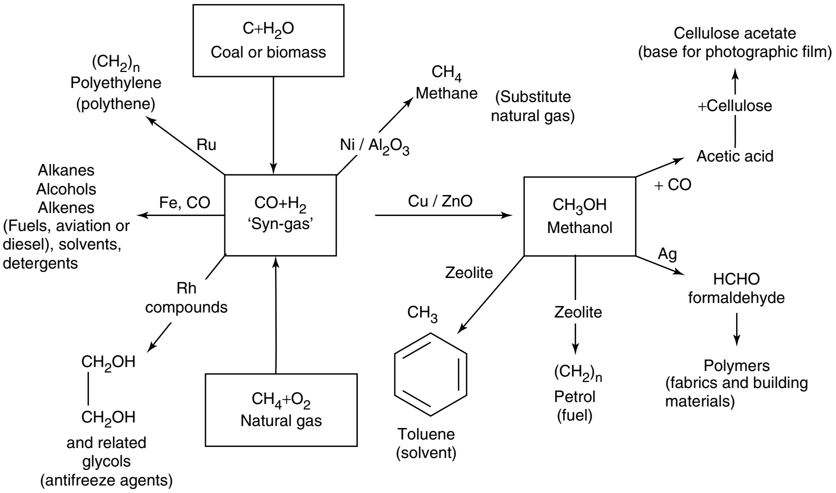
Scheme 1.8

Depending upon the solid catalyst employed, one or other of the products shown in Scheme 1.9 can be selectively generated from propylene (propene). From a mixture of carbon monoxide and hydrogen, also known as '*synthesis gas*' or '*syn-gas*', produced either by the older method of gasification of coal by steam ($C + H_2O \rightarrow CO + H_2$) or by the newer method of partial oxidation and 'steam reforming' of methane from natural gas



Scheme 1.9

($2\,CH_4 + O_2 \rightleftharpoons 2\,CO + 4\,H_2$ and $CH_4 + H_2O \rightleftharpoons CO + 3\,H_2$), many commercially important products can be prepared with high efficiency (Scheme 1.10).



Scheme 1.10 Synthesis gas (abbreviated 'syn-gas') is a mixture of carbon monoxide and hydrogen and may be produced either by oxidizing coal with steam, or by burning methane or biomass. A wide diversity of products can be generated from 'syn-gas', using the appropriate catalyst, as shown here.

1.3
Perspectives in Catalysis: Past, Present and Future

Berzelius, who in 1836 first introduced the terms '*catalysis*' (meaning 'loosening down' in Greek), endowed catalysts with some mysterious quality – he talked of a recondite catalytic force – and only in comparatively recent times has the aura of the occult been finally exorcized from discussions of the subject. The phenomenon of catalysis has been extensively studied since the early decades of the nineteenth century, and used unconsciously for a much longer period: it may not, like Melchizedek, have existed from eternity, but it was certainly harnessed by the ancients in the pursuit of some of their primitive arts.

In 1814, Kirchhoff noted the catalysed hydrolysis of starch by acids, a classic example of homogeneous catalysis. Then in 1817 Humphry Davy discovered that the introduction of hot platinum into a mixture of air and coal gas led to the metal becoming white hot. In 1824, Henry reported the first example of poisoning of a catalyst: ethylene inhibited the reaction between hydrogen and oxygen on platinum. He also noted selective oxidation in the reaction between oxygen and a mixture of hydrogen, carbon monoxide and methane. At about that time Döbereiner introduced his remarkable 'tinderbox' (*Feuerzeug*), which consisted of a miniature generator of hydrogen and spongy platinum. The box, which was commercialized for the purpose of lighting fires and smoking pipes, contained a small Kipp's apparatus with zinc and dilute sulfuric acid. A jet of hydrogen produced by this means was directed on to the supported platinum where it catalytically combined with oxygen to yield a gentle flame. It has been said that over a million tinderboxes were sold in the 1820s.

In 1834, Michael Faraday examined the power of platinum plate to effect the recombination of gaseous hydrogen and oxygen, which he had produced by the electrolysis of water. Grove in 1845 demonstrated that a hot platinum filament was equally good as a catalyst for the decomposition of water vapour into hydrogen and oxygen. Like Henry, Faraday observed that certain other gases, notably carbon monoxide and ethylene, suppressed the catalytic activity of the metal. A few decades later, another English scientist, Phillips, patented the use of platinum for oxidizing sulfur dioxide to sulfur trioxide with air. He also noted that the loss of catalytic activity arose because the surface of the metal was poisoned by other reactants. In 1871, an industrial process (the Deacon process) for the oxidation of hydrochloric acid in air to chlorine (used for making bleaching powder) was developed. The catalyst was a clay brick impregnated with cupric salts. (Inspired application of the principles of solid-state chemistry by Pérez-Ramírez and coworkers has led recently to a viable new catalyst that enables the environmentally responsible process to be resurrected. The catalyst is closely related to the mineral delafossite (see Amrute *et al.* (2013)).

A few years later (in 1877), Lemoine demonstrated that the decomposition of hydriodic acid to hydrogen and iodine reached the same equilibrium point (19%) at 350 °C, irrespective of whether the reaction was carried out homogeneously and slowly in the gas phase or rapidly and heterogeneously in the presence of platinum sponge. Bertholet, in 1879, working on the acid-catalysed esterification of organic acids and hydrolysis of esters, confirmed that the catalyst did not influence the position of equilibrium, a key observation in our understanding of the nature of catalysis.

The introduction of catalytic hydrogenation is rightly associated with the work of the French chemist Paul Sabatier, whose insight into the nature of surface phenomena was exceptional. A German contemporary, Wilhelm Normann, also played a crucial role in establishing catalytic hydrogenation, using finely divided nickel powder, as a means of converting oils, fats and waxes into edible foodstuffs and other products. Normann, in 1901, described how he converted oleic acid (*cis*-9-octadecenoic acid, $C_{17}H_{33}COOH$), a liquid, into its saturated analogue, stearic acid ($C_{17}H_{35}COOH$), which is crystalline. Reactions of this kind carry an echo of the remarkable accomplishment of Hipployte Mège-Mouries, the Frenchman who invented margarine (in 1869 he won a prize offered by Napoleon III for a satisfactory substitute for butter). Catalytic hydrogenation of oils and fats is still of major importance for the production of foodstuffs, vitamins, medicines, soap, perfumery, paints, varnishes, lubricants, polishes, candles and chocolate. Remarkably, metallic nickel remains the preferred catalyst in these hydrogenations.

A landmark in the history of applied catalysis was 2 July 1909. On that day in Karlsruhe Fritz Haber succeeded in preparing copious quantities of ammonia from nitrogen and hydrogen in the presence of a reduced magnetite (Fe_3O_4) catalyst using a high-pressure apparatus. This catalyst was to be perfected by Bosch and Mittasch at the laboratories of Badische Anilin und Soda Fabrik (BASF) in Oppau, Germany, in the years preceding World War I (Section 8.3). But already, in 1903, Ostwald had shown that ammonia could be catalytically oxidized over a platinum gauze to yield oxides of nitrogen which, in turn, were converted into nitric acid. The first synthetic methanol plant, also utilizing high-pressure reactors, was commissioned by BASF in 1923. The process operated at about 400 °C and 200 bar using a zinc oxide–chromium oxide catalyst (Section 8.1). Shortly afterwards, also in Germany, the Fischer–Tropsch process, which converts syn-gas into hydrocarbons and alcohols, became operational using cobalt or iron catalysts (Section 8.2). In due course, it became feasible to produce on an industrial scale formaldehyde, phthalic anhydride and maleic anhydride by the selective oxidation of methanol, naphthalene and benzene, respectively. By 1937, the Union Carbide company had commercialized the selective, silver-catalysed oxidation of ethylene to ethylene oxide.

In the late 1930s, catalytic cracking, which refers to the rupture of C–C bonds in order to convert large petroleum molecules, such as those that occur in gas oil, into small hydrocarbons of the kind found in fuel, first came into prominence. Alkanes are ‘cracked’ to give alkenes and smaller alkanes; alkenes yield smaller alkenes; and alkyl aromatics undergo dealkylation. For cracking, the most popular catalyst was initially acid-treated clay of the montmorillonite type, although many years earlier Friedel–Crafts catalysts, consisting of aluminium trichloride ($AICI_3$), had been used for this purpose. As a consequence of ingenious chemical engineering, in particular the optimization and regeneration of deactivated catalysts, Houdry devised fixed-bed catalytic cracking reactors; and from such units came most of the aviation fuel (gasoline) consumed by the Allies in the Battle of Britain. In 1941, fluid-bed or fluidized catalytic cracking (FCC) became a commercial reality, the culmination of revolutionary engineering design work by the American workers Lewis and Gilleland. In FCC units, fine particles of catalyst are maintained in suspension in a stream of vaporized (heavy) hydrocarbon that is blown through the so-called transfer-time reactor and subsequently passed through the regenerator. Thus contact times can readily be adjusted, thereby offering greater control in optimizing product yield. In fluidized reactors, catalyst lifetime depends upon the mechanical or attritional resistance of the fine particles.

Another important development that gained rapid momentum in the 1930s was the work of Ipatieff and Pines in the oligomerization of gaseous alkenes with ‘silicophosphoric’ acid, sometimes designated ‘solid phosphoric acid’ (SPA). This solid acid catalyst is made by taking phosphoric acid, a liquid which is awkward to handle on a commercial scale because of its corrosiveness, and mixing it with kieselguhr (diatomaceous earth) to form a plastic composite calcinable at 200–300 °C. The final acid (composition 60% P_2O_5 and 40% SiO_2) can be readily fashioned into granular or cylindrical pieces of acceptable physical strength at the temperatures required for catalysis (300–500 °C). Iso-octane was produced by oligomerization of lower olefins, followed by hydrogenation. This became an industrial reality following Ipatieff's work. Ipatieff also discovered paraffin alkylation in which isobutane was reacted with butenes or propylene, the initial catalyst being those first used by F. C. Whitmore for alkene isomerization: mineral acids.

1.3.1
Applied Catalysis since the 1940s

After World War II, acid-treated clays for catalytic cracking became unpopular because of their lack of long-term stability. They were gradually supplanted by amorphous synthetic silica – alumina catalysts, which were more stable under regeneration conditions: they also gave better product distributions.

Synthetic zeolite catalysts were first reported to be especially active and selective for isomerizing hydrocarbons by Rabo *et al.* in 1960. Shortly after Milton (USA) and Barrer (UK) had independently shown that zeolites could readily be synthesized, considerable effort was made to explore the reactions they catalyse. We now know that a bewildering variety of reactions are catalysed to a greater or lesser degree by zeolites. But it was Plank and Rosinsky who demonstrated the remarkable performance of synthetic zeolites as cracking catalysts in 1964. Synthetic zeolites were later used also for hydrocracking, and for shape-selective conversions, thanks to the pioneering work of Weisz *et al.* at the Mobil Company Laboratories. In shape-selectivity, advantage is taken of the convenient fact that the intracrystalline space available to reactant and product molecules has dimensions comparable with those of the molecules themselves. Highly branched hydrocarbons cannot, therefore, enter the internal volume of the zeolite, where most of the 'surface' area resides and where the active sites (Figure 1.5) are situated. Monobranched or linear molecules like the *n*-alkanes, on the other hand, can readily diffuse into zeolite catalysts, which, consequently, can be used in selective oxidation of linear hydrocarbons without converting the branched or aromatic ones. Since 1974, a series of novel catalytic processes based on the unique properties of a synthetic zeolite called *ZSM-5* has been introduced. This catalyst has pore openings of about 5.5 Å (Figure 1.6) and exhibits shape-selectivity as well as acid

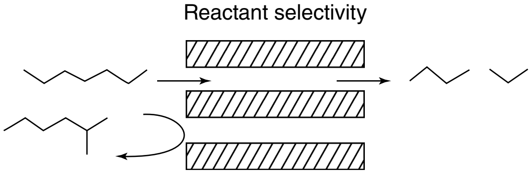


Figure 1.5 A shape-selective catalyst, such as a synthetic zeolite with cylindrical pores of about 5.5 Å in diameter, permits ready ingress of straight-chain reactant alkanes (e.g. *n*-heptane) but not of branched isomers (e.g. 2-methylhexane). The acid centres lining the pores can therefore catalyse the cracking of the *n*-heptane but not of the branched hexane. For similar reasons, in the acid-catalysed disproportionation of toluene to xylene and benzene, production of the *p*-xylene is favoured.

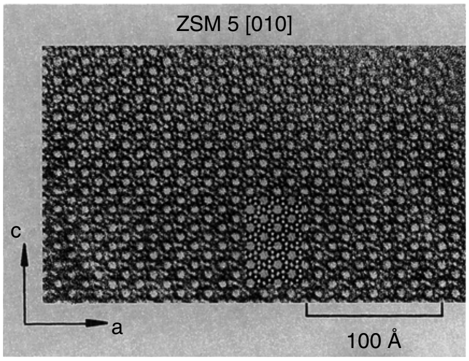


Figure 1.6 This high-resolution electron micrograph shows up the aperture openings (large white spots) of 5.5 Å diameter present in the shape-selective zeolitic catalyst ZSM-5. (The rectangular inset shows the calculated image).

activity, an unusual resistance to coking, and freedom from poisoning. ZSM-5 is nowadays a catalyst used to convert *m*ethanol in*to* petrol (*g*asoline) – the MTG process – and to effect xylene isomerization (so as to maximize production of *p*-xylene) and a number of other key industrial processes. Thanks to recent works on meso-structured Y zeolite (by Garcia-Martinez *et al.* (2014) and Pérez-Ramírez *et al.* Valtchev *et al.* (2013)) dramatic advances in FCC have been made.

Catalytic reforming, in particular naphtha reforming, which entails the isomerization of alkanes, the dehydrogenation of cyclohexanes, the dehydroisomerization of methylcyclopentanes (MCPs), as well as the aromatization of some alkanes and the hydrocracking of other hydrocarbons, serves to enhance the octane number of a fuel. In 1949, a new generation of reforming catalysts was introduced by Haensel at the United Oil Products Company. Such catalysts consist of finely dispersed platinum on an acidic support, generally γ-alumina (γ-Al_2O_3). The dual-function character of these reforming catalysts, possessing hydrogenative–dehydrogenative capabilities as well as acidic properties, was appreciated by Mills *et al.*, whose summarizing interpretation of the essence of the reforming (or 'platforming') process is shown in Figure 1.7. There is no doubt that alkenes play an important role here. In the period 1967–1971, two major improvements in reforming catalysts, one from the Chevron Oil Company, the other from the Exxon Company, were announced. The first used platinum–rhenium bimetallic particles as the catalyst, the second platinum–iridium. The improvement results because the second element (e.g. iridium) is much more active than platinum in effecting the hydrogenolysis (rupture of C–C bonds) of carbonaceous residues that tend to accumulate on the catalyst and poison its surface.

Hydrodesulfurization and, more recently, hydrodenitrification, which consists of removing the organic sulfur- and nitrogen-containing components from crude oil or from the products of cracking (such as hydrogen sulfide or ammonia, respectively) have become progressively more important catalytic reactions since about the early 1960s because of the increasing supply of 'high-sulfur' and

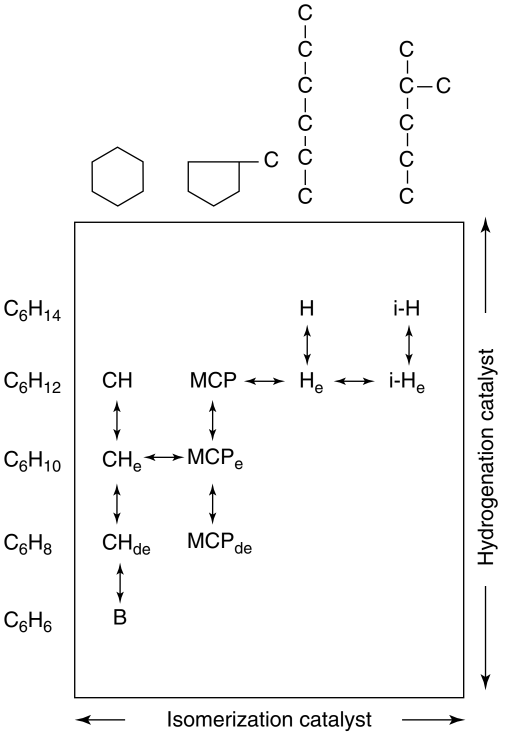
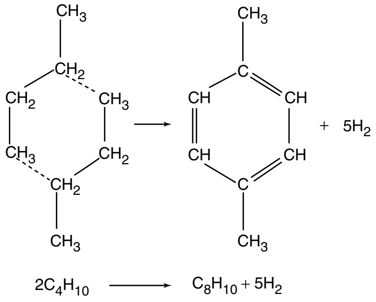


Figure 1.7 In a dual-function catalyst, such as finely dispersed platinum on an acidic Al_2O_3 support, the role of the acid support is principally to facilitate isomerization (e.g. methylcyclopentane (MCP) from *n*- or isohexane (H_e or i-H_e)) whereas the metal facilitates the dehydrogenation (of cyclohexane, CH, to cyclohexadiene, CH_{de}, to benzene, B). With permission from Mills (Heinemann *et al.*, 1953).

'high-nitrogen' crude oils, which tend to poison the catalysts that effect reforming, and the pressing environmental need to eliminate sulfur- and nitrogen-containing pollutants from the atmosphere. The most common catalysts are Co/MoS_2 and Ni/WS_2, which are often prepared on alumina supports.

Production of hydrogen, the preliminary step in so many major commercially significant catalytic systems, typified by the synthesis of ammonia and methanol and by the Fischer–Tropsch process, has undergone many changes since the early 1960s. Hydrogen currently comes chiefly from two sources: from naphtha (hydrocarbon) reforming mentioned above, and from the steam–hydrocarbon reaction. The second of these is also called *steam-reforming* and '*syn-gas*' ($CO + H_2$ mixture) is often produced by the steam-reforming reaction of natural gas (chiefly methane, CH_4). An important technical advance in the industrial production of hydrogen, and hence in the emergence of a new generation of ammonia plants, hinged upon the fact that the carbon–steam reaction ($C + H_2O \rightleftharpoons CO + H_2$) is greatly accelerated by the presence of alkali or alkaline earth elements added to the nickel catalyst normally used for this conversion. Much hydrogen in future could well come from natural gas and from propane and butane, especially in those parts of the world where liquefied petroleum gas (LPG) is plentiful. A high-activity zeolite catalyst recently developed by British Petroleum and United Oil Products (known as the *cyclar process*) converts propane and butane to monocyclic aromatics plus hydrogen (Scheme 1.11): shape-selective zeolites impregnated with tellurium or other elements are good for this purpose.



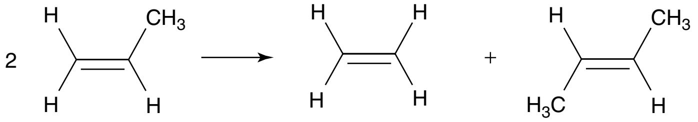
Scheme 1.11 A recently developed catalyst converts *n*-butane, present in natural gas, into xylene and hydrogen, both of which are desirable products.

Other important large-scale catalysed reactions that gained prominence in the mid-1960s included dehydrogenation of butane to butenes and/or butadienes, and of ethylbenzene to styrene monomer:

$$CH_3CH_2CH_2CH_3 \rightarrow CH_3CH_2CH = CH_2 \rightarrow CH_2 = CHCH = CH_2$$
$$C_6H_5CH_2CH_3 \rightarrow C_6H_5CH = CH_2$$

Both of these conversions are oxidative dehydrogenations, and are often quoted as examples of selective oxidation, which has an important commercial manifestation in the conversion of propylene into acrolein over a bismuth molybdate catalyst. Closely related to the latter is the production of acrylonitrile, CH_2=CHCN, from a mixture of propylene, ammonia and air, in the so-called ‘ammoxidation’ process of the Sohio Company. Multicomponent catalysts, containing iron, potassium and manganese and other additives to bismuth molybdate, are used for this purpose.

Disproportionation and polymerization of alkenes have also assumed industrial significance since the 1960s. Propylene, for example can be converted into ethylene and butene in the renowned triolefin process associated with the Phillips Company, a typical metathesis reaction using $Mo(CO)_6$ or $W(CO)_6$ supported on alumina (Scheme 1.12).



Scheme 1.12

The best examples of polymerization are Ziegler–Natta conversions, which permit the production of polyethylene and crystalline stereoregular polypropylene from the respective monomers. This is achieved using a mixture of aluminium trialkyls and, as the key component of the Ziegler–Natta catalyst, titanium(III) chloride (TiC_3). Nowadays, $TiCl_3$ supported on solid magnesium chloride ($MgCl_2$) is the catalyst of choice.

1.3.2
Some Current Trends in Applied Catalysis

Since the mid-1980s, several other major themes have emerged in applied catalysis. Some of these reflect the growing commitment to protecting the natural environment, others represent the logical extension of pure research, whilst still others have arisen from a desire to produce foodstuffs and other useful products from precursors that are plentiful.

1.3.2.1 Auto-Exhaust Catalysts

In developing effective automobile catalytic converters, the fundamental question is how one may transform undesirable species such as carbon monoxide (CO), nitric oxide (NO) and small hydrocarbons (Figure 1.8) into harmless products such as carbon dioxide, nitrogen and water? Effective catalysts consist of fine platinum–rhodium bimetallic particles supported on high-area eerie oxide–alumina (CeO_2/Al_2O_3) mixed oxides which, in turn, are distributed on to a monolith of cordierite ($Mg_2Si_5Al_4O_{18}$), an aluminosilicate which, because of its structure (Figure 1.9), stands up well to thermal shock. Platinum alone is

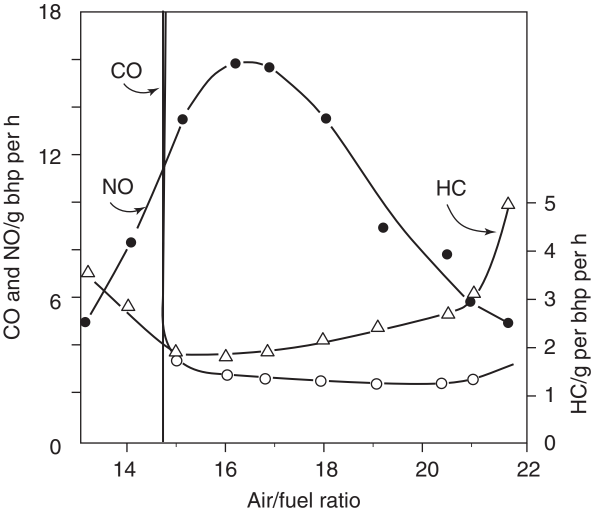


Figure 1.8 Effects of air/fuel ratio on the emission in auto-exhausts of hydrocarbon (HC), NO and CO (Hegedus and Gumbleton, 1980).

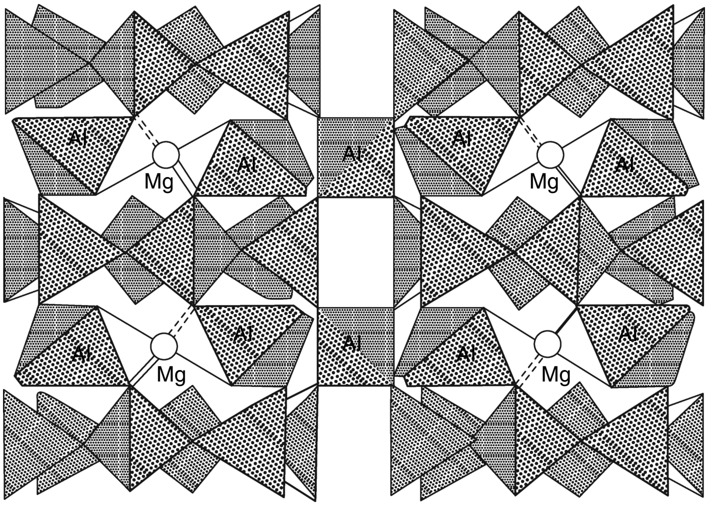


Figure 1.9 Thermal and mechanical stability are important properties required in a support material for the metals used (rhodium and platinum) in auto-exhaust catalysts. Synthetic cordierite ($Mg_2Al_4Si_5O_{18}$) has a structure closely akin to that of the very strong mineral and gemstone beryl. The interpenetrating rings and chains of corner-sharing tetrahedra (AlO_4 and SiO_4) confer these qualities upon the cordierite.

effective, since it coadsorbs CO and atomic oxygen; but rhodium as a 'promoter' improves the uptake of NO, thereby facilitating the conversion:

$$\text{CO (ad)} + \text{NO (ad)} \rightarrow N_2(g) + CO_2(g)$$

The γ-Al_2O_3 maintains the high area of the metal particles which it supports, but the added presence of CeO_2 is an extra advantage. It not only stabilizes the Al_2O_3 on to the cordierite, but, in view of its solid-state properties, it possesses the twin advantages of releasing and mopping up oxygen under reducing and oxidizing conditions respectively. (In $CeO_{x,}$ which has the fluorite structure, x may take the values $1.72 \leq x \leq 2$, while retaining its skeletal atomic structure.) Section 8.6 presents a full discussion of current auto-exhaust catalysts.

NO and NO_2, collectively termed NO_x, lie at the heart of smog, acid rain and the greenhouse effect. For as long as the internal combustion engine, employing high-temperature oxidation, is used the production of NO_x is inevitable. NO_x would not be produced if an effective catalyst for the low-temperature 'cool' (and clean) combustion of hydrocarbon fuel were developed. Alternatively, the development of an efficient electrocatalyst that would enable electricity to be produced directly from fuel combustion – in the modern version of a Grove fuel cell first described in 1839 – would have the extra bonus of a much higher overall efficiency in the use of the fuel for propulsion.

1.3.2.2 **Catalysts in Electrochemistry and Photoelectrochemistry**

The efficient production of fuels from inexpensive precursors by utilization of solar energy with cheap and stable chemical systems is nowadays the target of much pure and applied research. Desirable reactions are, typically, the reduction of water to hydrogen (H_2) and of carbon dioxide to methanol, each driven by the absorption of light. Since absorption of light creates electron–hole pairs – a 'hole' is simply that which is left behind in an orbital or band of orbitals when an electron is promoted to higher energy – the fuel-producing reaction must be accompanied by an oxidation reaction. Ideally, this oxidation reaction should consume a plentiful material, for example water, thereby generating oxygen (O_2) or, alternatively, produce a chemical of commercial value such as chlorine (Cl_2) from Cl^- ions. There is an analogy here with photosynthesis, which employs light absorption to produce vital organic materials and O_2 (Figure 1.10). Several photochemical schemes have been formulated with the aim to harness solar energy. To be effective, it is necessary to engineer solids with band gaps, that is energy separations of the highest filled and lowest unfilled orbitals, of around 2 eV, so as to take good advantage of the solar spectrum (Sections 8.7 and 9.3.8).

The engineering of semiconductor solids that absorb light leads us, in turn, to design 'dual-function catalysts' of a kind different from those discussed in Section 1.3.2.1, where we considered hydrocarbon reforming. What is meant here is that there should be (as in Figure 1.10) a semiconductor catalyst possessing

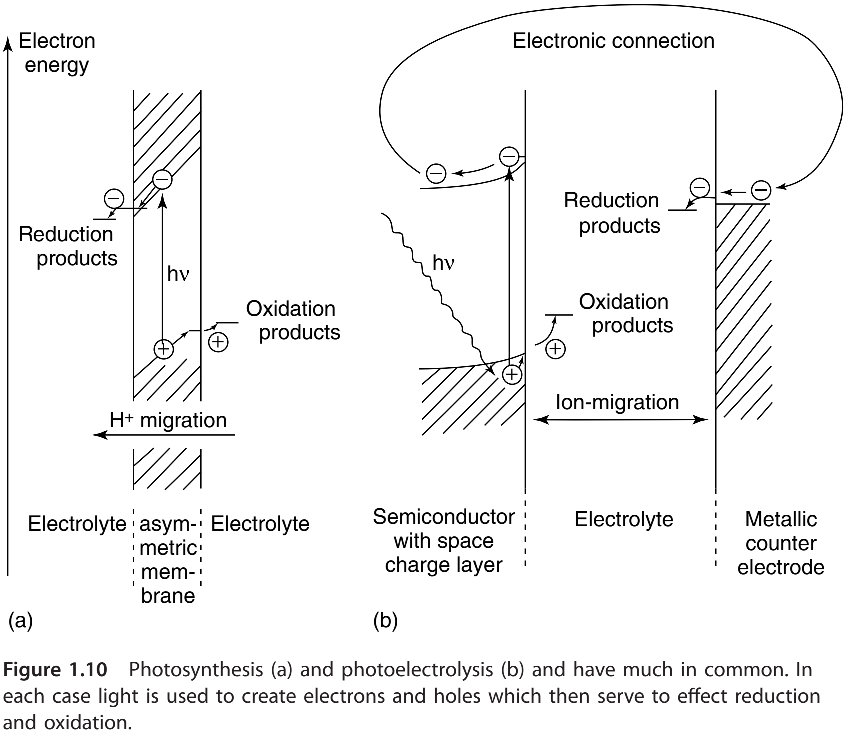


Figure 1.10 Photosynthesis (a) and photoelectrolysis (b) and have much in common. In each case light is used to create electrons and holes which then serve to effect reduction and oxidation.

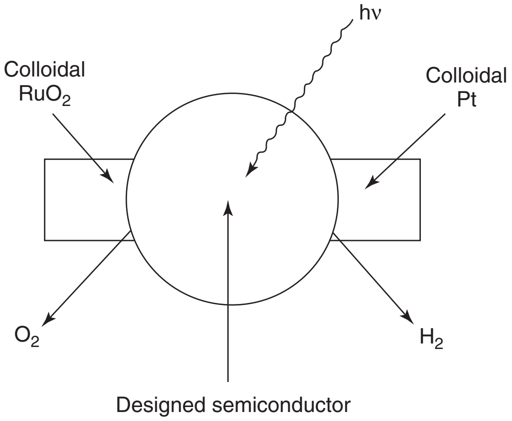


Figure 1.11 It should be feasible to design a semiconductor catalyst microcapsule for the photocleavage of water and other abundant materials (Section 9.3.8).

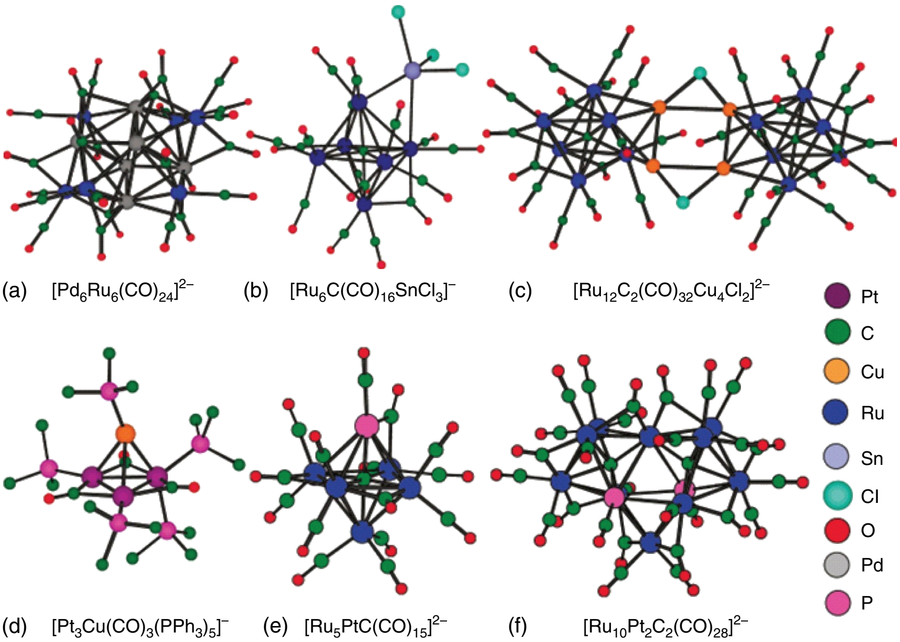
the appropriate electronic properties so that electrons and holes can be used to effect reduction at one electrode (say colloidal platinum) and oxidation at another (colloidal ruthenium dioxide, RuO$_2$) (Figure 1.11). Extending the ideas of the Swiss worker Grätzel, the entire catalyst 'capsule' or 'microcapsule', in which all three components cohere, would then be so arranged so as to effect continuous photocleavage of water.

The principles summarized in Figures 1.10 and 1.11 are also used in the solar-driven clean-up of environmentally harmful chemical by-products, especially chlorohydrocarbons, using titanium dioxide (TiO$_2$) as a photocatalyst (Section 9.3.11).

1.3.2.3 **Immobilized Metals**

A universally recognized way of combining the best features of homogeneous and enzyme catalysts on the one hand, and heterogeneous catalysts on the other, is to immobilize the former using an appropriate adsorbent, so that the resulting surface complex rivals or surpasses the performance of an analogous heterogeneous catalyst. Sometimes the adsorbent is inorganic such as silica or carbon; sometimes an organic polymer, sometimes an inorganic gel or crystalline solid. This expedient is designed to take advantage of the normally high selectivity of homogeneous catalysts, while at the same time ensuring that one of the key advantages of heterogeneous catalysts – relative ease of separation of products from reactants – is safeguarded. There are various ways available for derivatizing surfaces, and in particular for depositing highly dispersed metal atoms, metal clusters or ions, in an immobilized fashion on silica-rich surfaces.

One of the growth areas since the appearance of the first edition, is the preparation of high-performance nanostructured metal clusters, or bi-metallic clusters, distributed over the (enormous) internal areas of nanoporous supports, usually mesoporous silicas (such as MCM-41, MCM-48, SBA-15, etc). The rich profusion of silanol groups at the high-area silicas (typically $10^3\ m^2\ g^{-1}$) makes it readily possible to anchor at such surfaces precursor organometallic moieties (like those shown in Scheme 1.13 (Thomas *et al.*, 2003b)). Many other methods are described by the French worker Che in the *Handbook of Heterogeneous Catalysis* (eds G. Ertl *et al.*). He has concentrated on the use of metal complexes, whilst his compatriot Basset, and co-workers, have pioneered the use of immobilized organometallic compounds (Basset and Ugo, 2009). As described elsewhere by one of us (J.M.T.), a combination of high-resolution electron microscopy (HREM), especially in the so-called high-angle annular dark field (HAADF)-mode, is of particular importance in pinpointing both the size and spatial distribution of these nanocluster metals (or bimetals) on the silica support. In addition, scanning transmission electron tomography, also in the dark-field mode, is invaluable in characterizing these immobilized metal catalysts. In Chapter 3 these techniques, along with other relevant ones will be outlined.

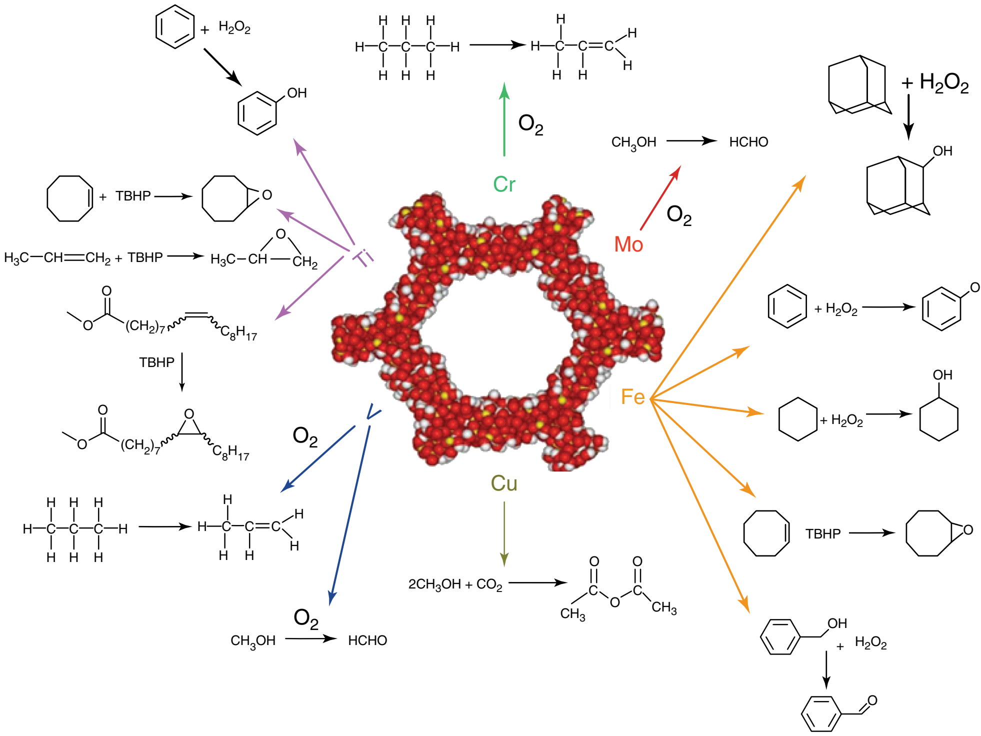


(a) $[Pd_6Ru_6(CO)_{24}]^{2-}$ (b) $[Ru_6C(CO)_{16}SnCl_3]^-$ (c) $[Ru_{12}C_2(CO)_{32}Cu_4Cl_2]^{2-}$

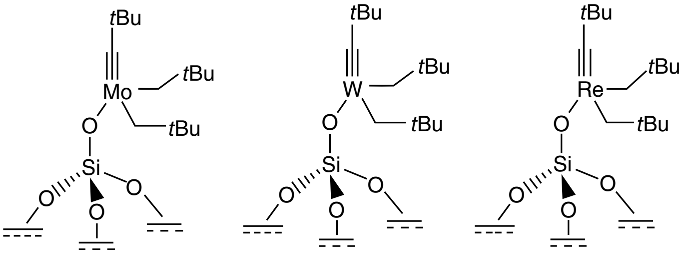
(d) $[Pt_3Cu(CO)_3(PPh_3)_5]^-$ (e) $[Ru_5PtC(CO)_{15}]^{2-}$ (f) $[Ru_{10}Pt_2C_2(CO)_{28}]^{2-}$

Scheme 1.13 (a–f) Mixed-metal carbonylates that serve as precursors for bimetallic nanocluster catalysts. (With permission from ACS (Thomas *et al.*, 2003b).)

Some of the recently reported selective oxidation reactions that are catalysed by the single-site metal clusters derived from the precursors shown in Scheme 1.13 are depicted in Scheme 1.14; and in Scheme 1.15 is shown a series of related single-site centres located at a high-area silica surface for conducting metathesis reactions.

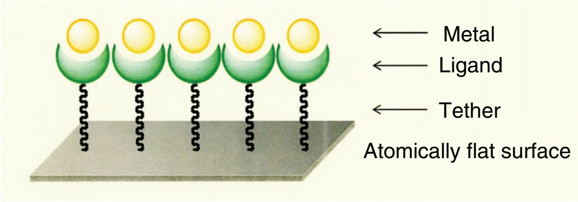


Scheme 1.14 Illustration of some of the selective oxidations that are catalysed by respective nanoclusters. (With permission from Springer (Thomas and Raja, 2006).)

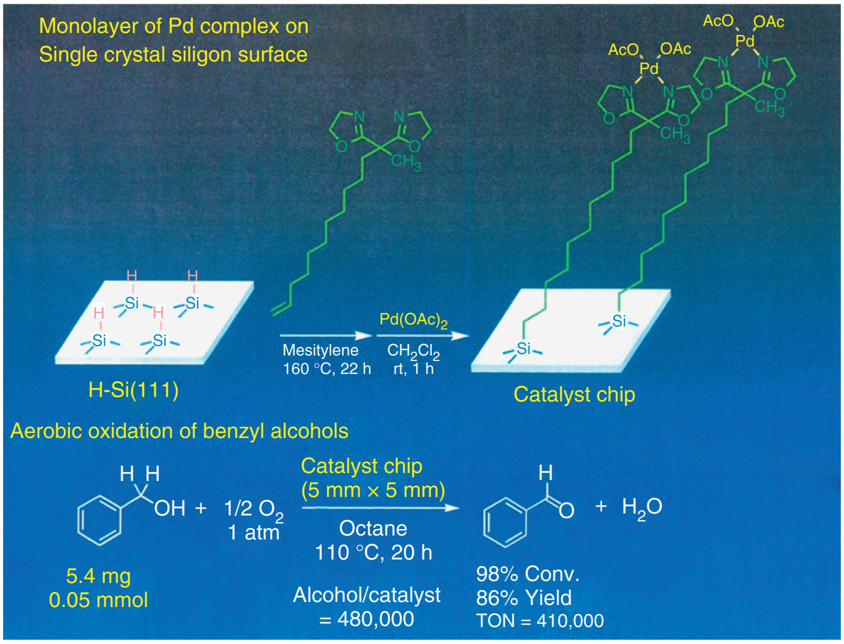


Scheme 1.15 Single active centres designed to catalyse metathesis reactions and deposited onto a silica surface. (With permission from Wiley-VCH (Copéret and Basset, 2007).)

There is another, fundamentally different and elegant way of also immobilizing metals and their complexes at atomically flat surfaces, such as single-crystal silicon or films of gold. This method, pioneered by the Japanese investigator Hara, is shown in Scheme 1.16, from which it is seen that a densely packed, yet spatially sufficiently separated, array of active centres is created. Here, in effect, is the very apotheosis of the 'laboratory on a chip'. Hara's work on such a 'monolayer' of



Scheme 1.16 Densely packed monolayer of tethered metal complex.



Scheme 1.17 Monolayer of Pd complex on single crystal silicon surface. With permission from RSC (Hara *et al.*, 2007).

active centres is symbolized in Scheme 1.17, where the selective aerial oxidation of benzyl alcohol to the aldehyde is seen to effected with exceptionally high turnover numbers (TONs) (See Section 1.4 below).

1.3.2.4 Immobilized Enzymes and Cells: Present and Future

Several tens of thousands enzymes are used for life on earth, but no more than about 6,000 enzymes have been identified. Several hundreds have been isolated, purified and characterized; but the structures of only some 500 are known in atomic detail. They effect, under the mildest of conditions, highly specific reactions at rates that far exceed those typical of ordinary catalysis (homogeneous or heterogeneous). The idea of intentionally immobilizing an enzyme on the accessible surface of a high-area carbon support was first demonstrated in the 1920s by

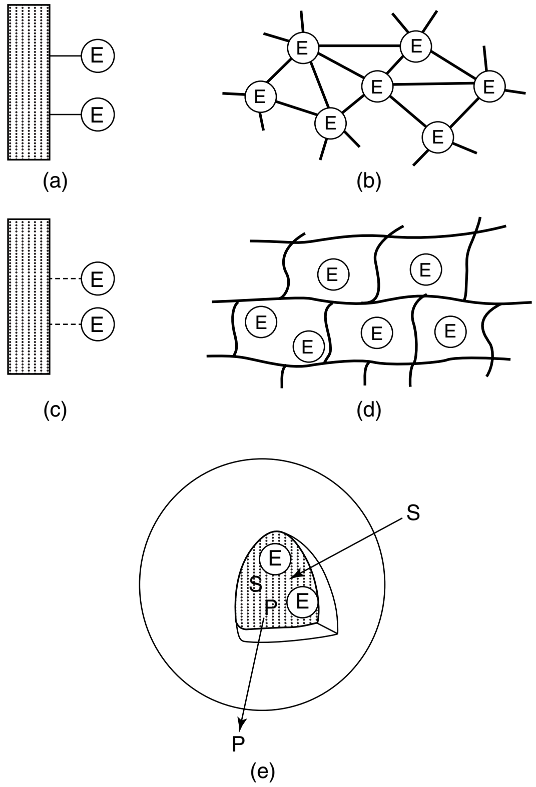


Figure 1.12 Schematic representations of immobilized enzyme systems. E, S and P stand for enzyme, substrate (i.e. reactant) and product molecules, respectively. (a) Covalently bonded enzyme–polymer conjugate; (b) covalently bonded intermolecularly crosslinked enzyme conjugate; (c) adsorbed enzyme–polymer conjugate; (d) polymer lattice-entrapped enzyme conjugate and (e) microencapsulated enzyme (Zaborsky, 1976).

Nelson and Griffin. Their strategy was later imaginatively exploited by Katchalski and his colleagues at the Weizmann Institute in Israel. Nowadays polymeric supports (Figure 1.12) are favoured: but solids such as pillared clays might prove even more effective, since they are more rugged.

The activity of an enzyme covalently bonded to its polymeric conjugate (the support) can vary from zero to a value even greater than that of the native enzyme. One cannot, in general, predict the activity of the bound enzyme but it is usually lower than that of the dispersed parent. The first commercial process utilizing an immobilized enzyme catalyst was the resolution of amino acids with an aminoacylase adsorbed on an anion-exchange resin. Resolution of racemic mixtures was effected by the hydrolysis of *N*-acetyl-DL-amino acids by the immobilized enzyme in a packed-bed reactor; this was accomplished in Japan by the Tanabe Seiyaku Company. The enzyme amidase, which cleaves penicillin G or V to the penicillin nucleus, has also been successfully immobilized using techniques evolved by the

Table 1.1 Some current industrial-scale applications of immobilized biocatalysts.

Application	Enzyme	Microorganism
Optical resolution of α-amino acids	Amino acylase	*Aspergillus oryzae*
Glucose isomerization	Xylose (glucose) isomerase	*Actinoplanes sp.*
Starch saccharification	Glucoamylase	*Aspergillus niger*
Steroid conversions	11-β-Hydroxylase	*Curvilarice lunata*
6-Aminopenicillanic acid from benzylpenicillin	Penicillin acylase	*Escherichia coli*

pharmaceutical companies Beecham (in the UK) and Bayer (in Germany), in association with Lilly and Dunnill at University College, London. Another important process is the isomerization of glucose to fructose with the immobilized enzyme, glucose isomerase. The scale of this process is reflected by the fact that in the mid-1980s over a billion (10^9) kilograms of fructose were produced (for the soft drink market) from corn syrup in the USA alone (Table 1.1).

Immobilized enzymes also play a central role in modern-day sensor technology. This again is an example of heterogeneous catalysis in which biological processes and electrochemical principles merge. Several automated systems for assaying enzymes in blood or other fluids rely on immobilized enzymes. The Enzymax Analyser (Leeds and Northrup Co.) uses an immobilized glucose oxidase to convert the glucose into δ-gluconolactone and hydrogen peroxide (H_2O_2), the latter being quantitatively monitored by an electrochemical probe.

1.3.2.5 **Ribozymes**

One of the surprises to emerge from the work of biological chemists during the mid-1980s was the discovery made by Cech and Altman that RNA could function as a catalyst. Catalytic RNAs, or ribozymes (which is a term applied to both metal-free and metal-containing RNAs), are of profound significance so far as the fundamental principles of biocatalysis in general are concerned, since they are ideal molecules for ‘evolution’ experiments *in vitro.* A large, heterogeneous pool of RNAs can be subjected to multiple rounds of selection, amplification and mutation, leading to the development of variations that have some desired phenotype (genetic characteristics acquired as a result of interaction of the inherited characteristics with its environment). Such experiments allow the investigator to correlate specific genetic changes with quantifiable alterations of the catalytic properties of the RNA.

The work of Lehman *et al.*, at the Scripps Institute in California, began with a pool of 10^{13} variants of the *Tetrahymena* ribozyme: they carried out *in vitro* evolution experiments that led to the generation of ribozymes with the ability to cleave an RNA substrate in the presence of Ca^{2+} ions, an activity that does not exist for the wild-type molecule. Over the course of 12 generations, a seven-error variant emerged that has substantial Ca^{2+}-dependent RNA-cleavage activity.

Bartel and Szostak, at Massachusetts General Hospital, used an interactive *in vitro* selection procedure to isolate a new class of catalytic RNAs (ribozymes) from a large pool (some 10^{15}) of different random-sequence RNA molecules. These ribozymes ligate two RNA molecules that are aligned on a template by catalysing the attack of a 3′-hydroxyl on an adjacent 5′-triphosphate – a reaction similar to that employed by the familiar protein enzymes that synthesize RNA. The corresponding uncatalysed reaction also yielded a 3′,5′-phosphodiester bond. *In vitro* evolution of the population of new ribozymes led to improvement of the average ligation activity and the emergence of ribozymes with reaction rates that were 7 million times as fast as the uncatalysed one.

Whereas the full biotechnological significance of ribozymes is not yet apparent, it is clear that the *in vitro* evolution experiments that they allow make it possible to elucidate important aspects of both evolutionary biology and structural biochemistry on modest and accessible timescales. Ribozymes, like catalytic antibodies, constitute the other side of the coin so far as creating biological macromolecules that catalyse chemical reactions are concerned. On the one side there is the rational design of enzymes – either by assembling miniature, artificial, 'mimicking' enzymes or by use of site-selective mutagenesis – whilst on the other there is the selection from a large pool of randomly generated biomolecules a few that present an effective array of catalytic functional groups to a reactant (substrate).

1.4
Definition of Catalytic Activity

It was essential at the outset to define catalytic selectivity in order to appreciate the subtleties involved in the phenomenon of catalysis (Section 1.2.1). Having referred frequently to 'catalytic activity', we must now specify precisely what is meant by this term.

In general, the rate of any gas – solid- or liquid – solid-catalysed reaction can, as we shall discuss in detail in Chapter 2, be expressed as the product of the apparent rate coefficient k and a pressure- (or concentration-) dependent term:

$$\text{rate} = kf(p_i) \tag{1.3}$$

where p_i is the partial pressure of the reactant i. The rate coefficient for the overall catalytic reaction may incorporate the rate coefficients of many of the elementary reaction steps that precede the rate-determining step. For several reasons this rate coefficient will change as the prevailing conditions of the reaction (temperature, pressure, surface concentrations, etc.) vary, and it is operationally convenient to use the Arrhenius equation:

$$k = A' \exp(-E' / RT) \tag{1.4}$$

where A' is a temperature-independent pre-exponential factor and E' is the *apparent* activation energy of the catalytic reaction; E' cannot be expected to be the true activation energy, even if the catalyst structure remains unchanged with varying temperature, because the concentration of reactant at the catalyst surface will, in general, be temperature-dependent. For this and other reasons it is best not, as seems first logical, to define catalytic activity in terms of activation energy. Far more convenient is the use of the concept of *turnover frequency* (TOF) or TON.

The TOF is simply the number of times n that the overall catalytic reaction in question takes place per catalytic site per unit time for a fixed set of reaction conditions (temperature, pressure or concentration, reactant ratio, extent of reaction). In words:

$$\text{TOF} = \frac{\text{number of molecules of a given product}}{(\text{number of active sites}) \times (\text{time})}$$

or:

$$\text{TOF} = \frac{1}{S}\frac{\mathrm{d}n}{\mathrm{d}t} \tag{1.5}$$

where S is the number of active sites. When the number of active sites S is known, as is generally the case with enzymatic processes and almost invariably with homogeneously catalysed reactions, the TOF can be specified quantitatively. In heterogeneous catalysis , however, it is sometimes difficult to determine the number of active sites. For such situations, S is often replaced by the total, readily measurable, area A of the exposed catalyst. Clearly, $(\mathrm{d}n/\mathrm{d}t)/A$ sets a lower limit to the TOF.

As well as in terms of the unit total area, the TOF can also be expressed per mass or per volume of the catalyst, or, in chemical engineering contexts, per volume of packed reactor. The IUPAC recommendation is that TOF, expressed per unit total area, be termed the '*areal rate of reaction*' but this usage is not yet in vogue. Note that TOF is a rate, not a rate coefficient, so that it is necessary to specify all the prevailing conditions of the catalytic reaction.

Notwithstanding what was said earlier about the difficulties of determining the number of active sites in a heterogeneous catalyst, the use of TOF as a measure of catalytic activity is sensible, partly because with some such catalysts (e.g. zeolites and enzymes) it is possible accurately to specify the number of active sites; and even with finely dispersed supported-metal catalysts it is increasingly possible, using the techniques described in Chapter 3, to count the number of surface atoms. Comparisons can therefore profitably be drawn between catalytic activities of single-crystal model catalysts studied in the laboratory and of real-life catalysts used in industrial plants.

1.4.1
Magnitude of Turnover Frequencies and Active Site Concentrations

For most heterogeneous reactions involving the catalytic transformation of small molecules in the temperature range 100 – 500 °C and pressures of up to a few bars, turnover frequencies fall between 10^{-2} and $10^{2}\,\mathrm{s}^{-1}$. These values are to be compared with those associated with well-known enzymatic reactions: 10^3 for chymotrypsin, 10^4 for urease and acetylcholinesterase, and 10^7 for catalase. It is striking how much larger the frequencies are for enzymes than for their inorganic analogues. The differences can be much less between enzymes and the immobilized catalysts discussed above and also between enzymes and zeolitic catalysts. Indeed, since it is possible to determine the precise number of active sites in zeolites such as ZSM-5 (Figure 1.6), TOF can be quantitatively specified. It transpires that the activity of this catalyst at about 450 °C, for certain reactions, rivals that of an enzyme under ambient conditions: for the cracking of 1-hexene, the TOF is 5×10^2; for the isomerization of this alkene it is about 10^7.

To link turnover frequencies with reaction rate coefficients and other kinetic parameters used to describe catalytic activity, it is instructive to cite the work of Haag *et al.* on ZSM-5 catalysts in further detail (Figure 1.13). We note that the first-order rate coefficient for the cracking of the 1-hexene is 800 times as large as that of the *n*-hexane. Many commercial processes occur with first-order rate coefficients in the range $0.1-1.0\,\mathrm{s}^{-1}$. Thus the active site concentration needed to achieve such technically relevant reaction rates – a magnitude cross-hatched in Figure 1.13 – would be about 1500 ppm for the cracking of *n*-hexane and about 10 ppm for that of 1-hexene. It is noteworthy that kinetic principles require some 10^{18} active sites per cm^3 of catalyst volume to obtain technically useful catalytic conversion rates in a process operating at 500 °C and requiring an activation energy of $125\,\mathrm{kJ\,mol}^{-1}$.

It is often advantageous to quote reaction probabilities, R_p, instead of turnover frequencies. R_p reveals the overall efficiency of the catalyst and is defined thus:

$$R_\mathrm{p} = \frac{\text{rate of formation of product}}{\text{rate of incidence of reactant}} \tag{1.6}$$

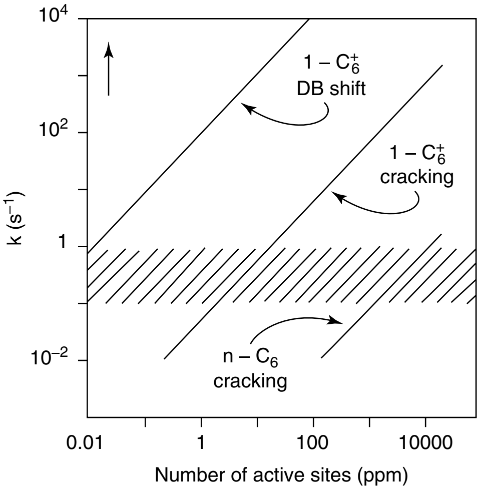


Figure 1.13 Plot of first-order rate coefficients versus concentration of active sites in ZSM-5 catalysts for the cracking of *n*-hexane (n-C_6), for the cracking of 1-hexene (1-C_6'') and for the shift of double bond in 1-hexene (DB shift of 1-C_6'') (Haag, Lago and Weisz, 1984).

It is simply the TOF divided by the flux of reactant incident upon the catalyst (see Eq. (2.1)).

1.4.2
Volcano Plots

Another quite widely used index of catalytic activity is the temperature required for the reaction under consideration to attain an arbitrary degree (or rate) of conversion. This approach can be misleading. Relative activities of a series of catalysts will vary with the degree of conversion chosen unless all the catalysts exhibit the same activation energy, a situation not likely always to prevail. There is something to be said, therefore, for using as an index of catalytic activity the relative efficiencies of different catalysts at the same temperature, although, ideally, one ought to relate activity to energies of activation and pre-exponential factors. But fixing a certain temperature may turn out to be just as arbitrary as fixing a certain degree of conversion quite different orders of catalytic efficiency may be obtained if a different standard temperature is fixed. On balance, the criterion of temperature at fixed conversion is preferred over conversion at fixed temperature, chiefly on the practical consideration that temperatures of equal conversions are measured quantities, whereas conversions at equal temperatures are partly extrapolations.

The type of curve that results when this particular index of catalytic activity (temperature at fixed conversion for a series of related metals) is plotted against some enthalpic function of those metals is illustrated in Figure 1.14. This is known as a *Balandin volcano plot*. It is the enthalpy of formation of the metal formate

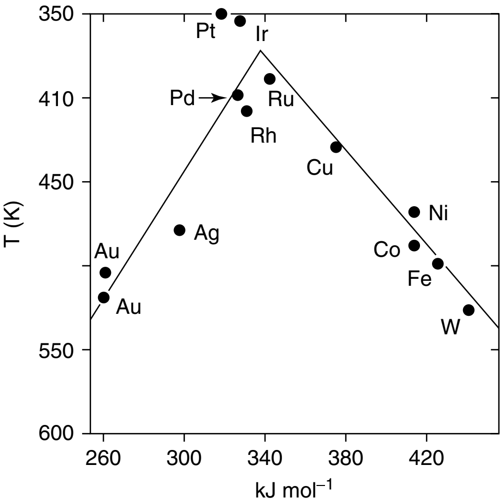


Figure 1.14 A typical volcano plot of the kind discussed by Balandin. The ordinate gives the temperature for a specified conversion of the reactant (formic acid) on a metal catalyst, and the abscissa gives the enthalpy of formation of the metal formate (Fahrenfort, van Reijen and Sachtler, 1960).

that is plotted on the abscissa in this case, where we focus on metal-catalysed decomposition of formic acid. If the data on the ordinate of Figure 1.14 are plotted against the enthalpy of formation per metal atom of the highest oxide, the resulting curve is known as a *Tanaka–Tamaru plot*, and when the enthalpy of formation per mole of oxygenation of the most stable oxide is plotted along the abscissa, the curve is known as a *Sachtler–Fahrenfort plot*. All three curves are volcano-shaped; as we shall see later, the significance of this fact is that it offers broad support to Sabatier's idea that an intermediate compound is formed at the surface of a catalyst. Too high an enthalpy of formation would not facilitate catalysis, and neither would too low a value as, in this case, there would be little propensity for the intermediate compound to form. An optimum value of the enthalpy would balance out these two conflicting tendencies, and this is why the peak of the 'volcano' corresponds to the highest catalytic activity.

1.4.3
Evolution of Important Concepts and Techniques in Heterogeneous Catalysis

In catalysis, as in most other subjects, concepts and techniques are inextricably mingled. Theoretical insight naturally prompts experiment; correspondingly, technical virtuosity engenders fresh perception, which, in turn, stimulates ever more ambitious experiment. Nowadays, thanks to the repertoire of delicate techniques at our disposal (see Chapter 3), less than a 1000th of a monolayer of adsorbed material – on a solid surface of area less than 1 cm^2 – can be identified. Moreover, the nature of its bonding before and after attachment to the catalyst can be probed both by direct experiment and by theoretical computation. Oxidation states of surface atoms – their steady-state concentration as well as their spatial distribution – can likewise be determined, at least for model catalysts though not usually for their real-life analogues. However, we cannot probe the transition states directly, in view of their exceptionally short lifetimes unlike the situation that now prevails in certain gas-phase reactions. Experience teaches us, as we shall see, that the lifetime of species implicated in heterogeneous catalysis exceeds 10 μs; the crucial acts of electronic and atomic rearrangement generally involve a much more rapid timescale, of the order of pico-or femto-seconds.

It is prudent to trace the emergence of some of the key concepts and experimental advances in catalysis since the early twentieth century. By 1920, thanks largely to the work of Sabatier, it had been appreciated that a metal, such as nickel, which catalysed hydrogenations possessed its activity because it could readily form an intermediate hydride which, in turn, decomposed to regenerate the free metal. Langmuir, probably influenced by W. H. Bragg, had almost completed his landmark demonstration of the inadequacy of the Nernst theory – which had satisfactorily explained the kinetic features of the dissolution of solids in liquids – to account for gas uptake and reactions at surfaces. In due course, after Langmuir, Rideal, Hinshelwood and their associates had studied the kinetics of many heterogeneously catalysed reactions, it became possible to formulate some generalized principles to account for the various rate–pressure relationships that had been observed experimentally. Thus, the Langmuir – Hinshelwood mechanism (Chapter 2) for catalysed processes postulated that the rate of a heterogeneous reaction is controlled by the reaction of the adsorbed molecules, and that all adsorption and desorption processes are in equilibrium. The Rideal – Eley mechanism (Chapter 2), on the other hand, envisaged that a heterogeneous reaction could take place between strongly adsorbed atoms (that is, those chemisorbed) and molecules held to the surface only by weak, van der Waals, forces (that is, those physically adsorbed).

In the next decade, H. S. Taylor advanced cogent reasons for believing that preferential adsorption on a catalyst surface would take place at those atoms situated at peaks, fissures and other topographical discontinuities. Moreover, it was implied that such atoms would have greater catalytic activity than those on flat surfaces. This was the genesis of the idea of 'active sites' and 'active centres', terms which, along with 'catalyst poisoning' or 'deactivation' to which they are related, are still widely used, but with rather wider meanings. Most present-day authors use the term '*active site*' to describe the locus of catalytic conversion; but often, especially in discussions on chemisorption *per se,* this same term is used to specify that site at which adsorption is strongest. It will emerge in Chapter 2 that strong adsorption is inimical to catalysis, so that the most 'active' site for chemisorption is by no means the most favourable site for facile chemical conversion. In his classic paper, Taylor said, with remarkable perspicacity, that 'the amount of surface which is catalytically active is determined by the reaction catalysed', and also wrote about mechanisms 'whereby both the constituents of a (catalysed) hydrogenation process may be attached to one and the same (surface) atom'. The first of these quotations is most relevant to modern interpretations of kinetic oscillations in catalytic oxidations such as the burning of carbon monoxide (CO) on platinum studied by Ertl and others. The second foreshadows some of the views expressed four decades later in formulating modes of interconversion of various surface intermediates that are σ- or π-bonded as transient ligands on the same metal atom or ion. This second notion also contains the germ of the ideas overtly expressed by Nyholm, Burwell, Rooney and others in the early 1960s about the kinship between homogeneous and heterogeneous catalysis.

Taylor also suggested that the process of chemisorption frequently involves an activation energy, an idea that was soon to receive theoretical support when Lennard-Jones introduced potential-energy diagrams as an interpretive framework for discussing adsorptive and catalytic phenomena. Another important contribution by Taylor and his school in Princeton and by Farkas in Cambridge was to employ D_2 and deuterated reactants for studies of hydrogenation. This strategy, and others based on it, was to prove exceptionally fruitful in ensuing years in mechanistic studies in the hands of numerous workers with access to mass spectrometric analysis.

In the late 1930s significant advances came in the wake of Brunauer, Emmett and Teller's theory of physical adsorption (Chapter 2), which offered, for the first time, a moderately reliable method of measuring surface areas of catalysts. This meant that comparisons of activity in a family of related catalysts could thereafter be put on a quantitative basis. It was soon demonstrated that the pore-size distribution, another important characterizing property of a catalyst, could be retrieved from adsorption isotherms.

Significant contributions also emerged in the mid-1940s from the (then) USSR. Balandin formulated his multiplet theory, the prime feature of which hinged on the postulate that the activity of a catalyst depends to a large degree on the presence on the surface of correctly spaced groups (or multiplets) of atoms to accommodate the various reactant molecules; Kobozev proposed the idea that 'ensembles' – the smallest group of catalytically active atoms – might be a helpful concept in surface phenomena. The computations of Twigg and Rideal at Cambridge in 1940, in addition to earlier ones by Eyring in the USA and the later experiments of Beeck, also in the USA, lent support to the view that a 'geometric factor' could be important in catalysis. Balandin, Krylov and their co-workers used their multiplet theory to predict that metals with interatomic distances ranging from 2.48 to 2.77 Å should exhibit catalytic activity for the hydrogenation of benzene and the dehydrogenation of cyclohexane, since, for these reactions, the metal spacings match the interatomic distances in the cyclic molecules. This prediction has been verified experimentally. Interestingly, Balandin's schematic picture of his so-called 'sextet complex' (Figure 1.15) is strikingly confirmed by recent studies of benzene on nickel, where the aromatic molecule is found to lie flat on the metal surface; by the beautiful X-ray crystallographic studies of Gallop *et al.* (Figure 1.16), who find evidence of π-bonded and σ-bonded modes of attachment of benzene in the cluster compounds $[Os_3(CO)_9(C_6H_6)]$ and $[Os_3H_2(CO)_9(C_6H_4)]$ respectively; and in the elegant low-energy-election diffraction (LEED) studies by Somorjai and van Hove of benzene adsorbed on single-crystal faces of rhodium (Figure 1.17). Notably, both from LEED and X-ray studies, there is some evidence (from C–C bond distances) of a triene structure in which the benzene sits flat on top of an array of metals as substratum.

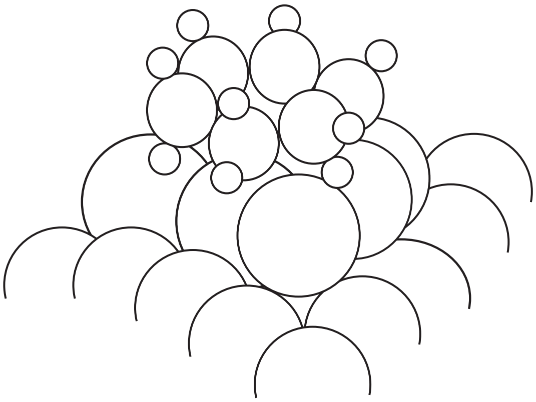


Figure 1.15 Schematic illustration of the Balandin concept of multiplets involved in the bonding to certain metals that are good catalysts for cyclohexane–benzene interconversions. This particular multiplet is a sextet (see text).

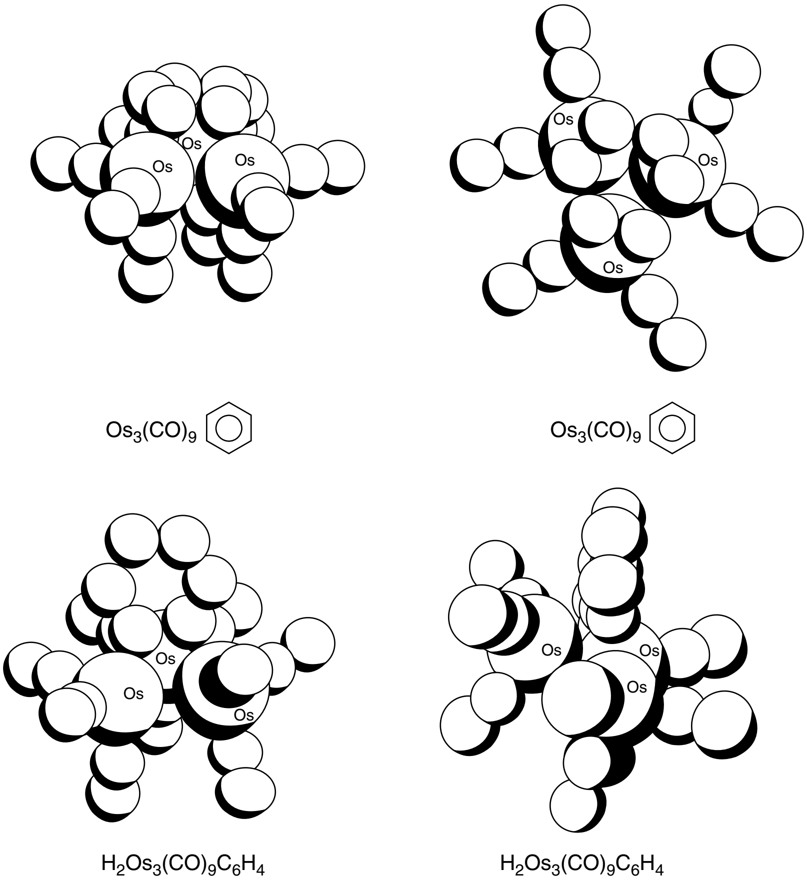


Figure 1.16 (a–d) Experimental evidence from metal carbonyl cluster chemistry of σ- and π-bonded benzenoid groups to the tri-osmium skeleton. (With permission from ACS (Gallop *et al.*, 1992).)

By the mid-1940s, arguments based on the electronic band structure of the bulk catalyst became fashionable; and in 1950 Dowden published his famous classification of catalytic solids into metals, semiconductors and insulators. The idea that catalytic activity could be directly related to bulk electronic properties, although at first promising in interpreting the behavioural trends within the compositional variations in a fixed alloy system, turned out to be oversimplified, especially when it was later realized that surface compositions could be very different from bulk ones. With solid oxides and chalcogenides, however, some progress was made by Hauffe, Weisz, Wolkenstein, Stone and others in predicting degrees of uptake of reactants in terms of the fundamental properties of the semiconductor. (Band theory and band structure are still of great relevance in numerous contexts in heterogeneous catalysis, as we shall discuss later.)

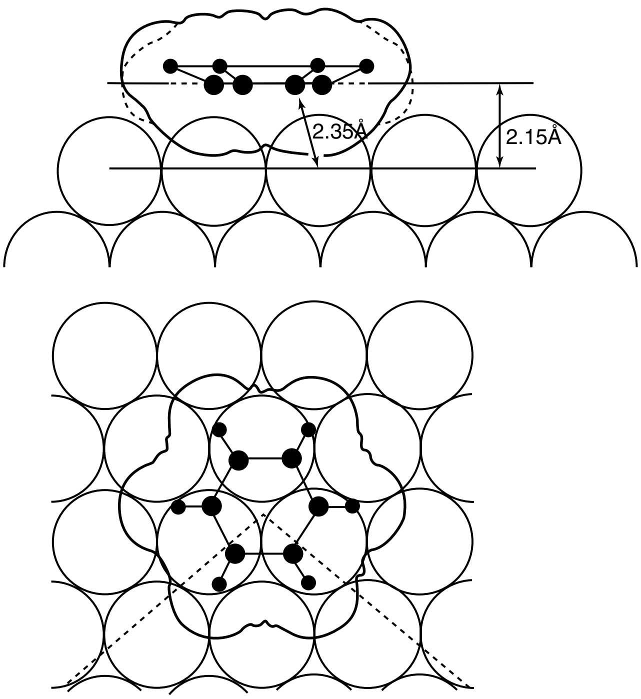


Figure 1.17 Elevation and plan view of the benzene molecule bound to a close-packed surface of rhodium. From the bond distances it is thought that the adsorbed benzene has a triene structure. (With permission from RSC (Somorjai, 1984).)

Two significant landmarks in the mid-1950s were the discovery by Ziegler and Natta of stereoregular polymerization, and the full-blooded introduction, first by Eischens, Terenin and Sheppard and their co-workers, of spectroscopic methods for probing adsorbed species attached to supported catalysts. Other spectroscopic techniques, along with diffraction methods, began to be widely used to their fullest advantage in the early to mid-1960s. Turkevich, Kazansky and Lunsford separately pursued the use of electron spin resonance to probe the status of transition metal ions (in zeolites) and of unusual valences of oxygen in oxides. Germer and his school were prominent in the application to surface studies of LEED discovered much earlier. Photoelectron spectroscopy, pioneered by Siegbahn, Price and Turner, was demonstrated by Thomas *et al.* to be sensitive enough to detect adsorbed monolayers and, in particular, by Roberts and Joyner, to establish beyond doubt that CO on certain metals is dissociatively adsorbed. Auger electron spectroscopy (AES) was found to be a very sensitive technique for detecting light elements at surfaces; and electron-energy-loss spectroscopy (EELS) was resurrected and shown to be a powerful means of probing the vibrational modes of chemisorbed entities. By the early 1970s it was realized that combined experimental approaches, incorporating dynamic mass spectrometry for monitoring temperature-programmed desorption, LEED, AES, X-ray and

UV-induced photoelectron spectroscopy, as well as other probes for monitoring the electronic and atomic states of surfaces, were feasible for the study of model catalysts.

So far as recent experimental advances are concerned, the current preoccupation is with the development of techniques suited to the *in situ* studies of real-life catalysts – see, for example Section 3.10.4.

Several key concepts invoked nowadays in discussions of heterogeneous catalytic phenomena have emerged since the early 1970s. We shall elaborate these later, but it is helpful to adumbrate at this stage points of general interest relating to these concepts. First we recognize that numerous surface entities may be present on reacting catalysts. Some of these, however, are no more than 'spectator species' which are not implicated in the critical steps of catalysis, Ethylidyne (CH_3C), for example contrary to earlier suggestions, plays no significant role in the hydrogenation of ethylene on supported palladium catalysts. Unusual states of oxide ions (O^-, O_2^-, O_3^- and O_4^-) on oxide catalysts have been identified, and the first of these (O^-) when bound to a Li^+ ion as a substitutional dopant in MgO, is directly implicated in the catalytic oxidative dimerization of CH_4.

Second, Boudart's subdivision of catalysts into 'structure-sensitive' and 'structure-insensitive' categories has proved to be a profitable concept. A catalytic reaction is said to be structure-sensitive if its rate changes markedly as the particle size of the (supported) catalyst is changed, or as the crystallographic face of a (single-crystal) catalyst is altered. Conversely, the rate of a structure-insensitive reaction is not significantly modified by such changes. The hydrogenolysis of ethane ($C_2H_6 + H_2 \rightarrow 2CH_4$) and the synthesis of ammonia are good examples of structure-sensitive reactions: the metal catalysts used for these reactions are particularly susceptible to poisoning. The hydrogenation of ethylene or benzene and the oxidation of CO, on the other hand, are examples of structure-insensitive reactions, in which the effect of poisons on the metal catalyst is relatively minor.

Third, there is the notion of a functional or multifunctional catalysis. The recognition that supported metal catalysts (e.g. palladium or platinum on AI_2O_3 or zeolites) behave in a clearly identified dual fashion has helped enormously in the design of catalytic reactors. In the hydroprocessing of petrochemicals, for example the metal serves to dissociate H_2 as well as to facilitate the equilibration of alkanes, alkenes and alkynes, whereas the acid support serves to catalyse the build-up of vital carbonium ion (alkylcarbenium ion) intermediates (Figure 1.7). We note that the support functions not only to stabilize the highly dispersed catalyst (thereby retaining high surface area), and to activate the metal by electron transfer between it and metal, but that it can also be directly involved in crucial elementary steps in overall reactions.

Implicit in the sketch in Figure 1.18 is the 'spillover' of hydrogen atoms that are generated by dissociation of H_2 at the metal particle. Hydrogen atoms which spill over in this fashion, and are mobile on the support, play an important role in many heterogeneously catalysed hydrogenations.

We note also that the Brønsted acidity of an oxide or mixed-oxide catalyst is of major importance in many catalytic processes. It was long ago recognized by

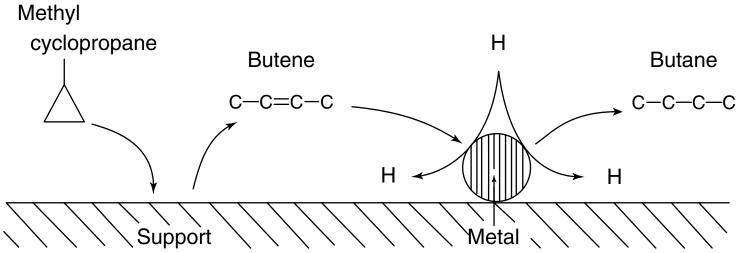


Figure 1.18 A bifunctional catalyst such as platinum on $A1_2O_3$ facilitates the isomerization of methylcyclopropane to 2-butene as well as the hydrogenation of 2-butene to butane. (After Boudart.)

Bernadskii in Russia and Pauling in the USA that aluminosilicates possess pronounced (Brønsted) acidic properties. This fact was skilfully harnessed by Rabo and others in developing the zeolitic catalysts mentioned earlier and discussed further in Chapter 8. A good acidic oxide or mixed oxide is one in which the surface OH groups at the solid A dissociate such as to yield $A-O^- + H^+$ rather than $A^+ + OH^-$. It is advantageous, therefore, to incorporate a second oxide BO (a basic one) to provide a coordination shell in which the oxide ion attached to A can be accommodated, thus increasing the acid dissociation constant. On this score, we expect, and do indeed find, that the following oxide 'solid solutions' are good Brønsted acids: $SiO_2-Al_2O_3$, $P_2O_5-AI_2O_3$, SiO_2-ZrO_2, $B_2O_3-AI_2O_3$ and Ipatieff's 'SPA' (solid phosphonic acid).

It cannot be overemphasized how important a role Brønsted acidity plays in such processes as the catalytic cracking, alkylations and isomerizations of hydrocarbons. The gradual progression from acid-washed clays and silica–aluminas of the 1950s to the crystalline, well-defined zeolite catalysts of the present for effecting these processes underlines this fact. In simple mechanistic terms, we see (Figure 1.19) the role of Brønsted catalysts in generating the carbonium (i.e. alkylcarbenium) ions which, as demonstrated in different contexts by Koptyug in Siberia and by Olah in the USA, are the versatile intermediates that serve to propagate the desired chemical changes. The development by Weisz *et al.* of shape-selective inorganic catalysts took advantage of the convenient fact that the active sites (which are here synonymous with the loci of the detachable protons) are situated largely inside the pores and cavities of the solid, and are accessible only to those species possessing the requisite shape and diffusive characteristics. By taking advantage of the ability of neutron-scattering procedures to solve the structure of powdered catalysts, we now have a picture, in atomic detail, of the active and hence the acid site in La^{3+}-exchanged zeolite-Y, where the 'active' proton is initially generated as a result of intra-crystallite cation hydrolysis: $La^{3+} + H_2O \rightarrow (LaOH)^{2+} + H^+$.

The period from the mid-1960s to the late 1970s witnessed much conceptual activity and turmoil, prompted chiefly by the increasing pace with which new types of experimental information were uncovered. Quite apart from the discoveries that surfaces often had atomic structures different from equivalent sheets in the

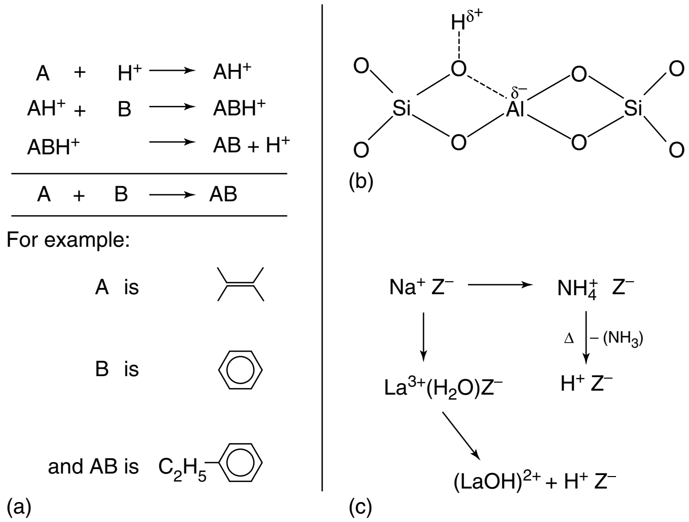


Figure 1.19 A Brønsted acid catalyst, such as a zeolite or an exchanged clay, functions through its ability to release and accept protons (a). There is one acid hydrogen for every tetrahedrally bonded aluminium in the zeolite (b). Zeolitic catalysts are often rendered acidic (H^+Z^-) by exchange with NH_4^+ ions followed by heating; or by simple exchange with polyvalent ions (e.g. La^{3+}) which then hydrolyse the bound water (c).

bulk solids, that substantial amounts of ordered impurities were present at exterior surfaces of solids, and that electronic reorganization was associated with these impurities, several other important bodies of facts and concepts became apparent or took on a new significance. The concepts of ensembles as well as geometric factors were resuscitated; intermediate compound formation and electronic factors received further attention; there was widespread use of isotopic labelling to elucidate reaction mechanisms and the nature of surface intermediates; the ideas of organometallic chemistry and of solid-state physics and the greater appreciation of the nature of orbital interactions and bonding were assimilated into surface chemistry; major advances were registered in our understanding of enzyme catalysis, largely as a result of the seminal work of D. C. Phillips and C. A. Vernon, who interpreted the crystal structure of lysozyme with and without the polysaccharides it catalytically attacks.

The concept of ensembles has gained considerable prominence because, without it, it seems impossible to interpret the catalytic behaviour of alloys or the poisoning of single-component surfaces. At the root of this concept is the notion that, for many metal-catalysed reactions, a family or 'ensemble' of several contiguous surface atoms can form bonds with a molecule, or be in some loose sense implicated in the formation of a transition state. Ponec and Sachtler and Sinfelt, working with alloys such as Pt–Au, Ru–Cu and Ni–Cu, came independently to the conclusion that hydrogenolysis requires the largest ensemble of surface nickel atoms. The ensemble requirement for a given reaction can be studied by diluting the metal in an alloy with a chemically inert metal, thus reducing the concentration of large ensembles of the active metal on the surface. It seems that as many as 12 contiguous nickel atoms are required for the splitting of C_2H_6 to CH_4. For CO dissociation on metal, large ensembles seem to be required: for the dehydrogenation of propane on Pt–Au alloys, one exposed metal atom suffices. The role of ensembles in the poisoning of catalysts was discussed elegantly by Rideal. He showed, as have others in greater detail subsequently, that the deposition of species of poison (e.g. sulfur or phosphorus atoms) on uniform transition-metal catalysts will selectively inhibit the reactions that demand the larger ensemble sizes. For adspecies (poisons) which are distributed randomly, the surface concentration of ensembles of size n (i.e. θ_n) will vary as $(1-\theta_\mathrm{P})^n$, where θ_P is the fraction of the surface covered by the poisonous species. The situation at the catalyst surface can be much more complicated if there are interactions between the species of poison.

The geometric factor re-emerged as a useful concept in catalysis when analogies were drawn between the functioning of certain homogeneous catalysts on the one hand and hydrodesulfurization catalysts (MoS_2) on the other. On the grounds that MoS_2 catalysts function best when the metal centre is coordinatively unsaturated, so as then to be in a position to accommodate bound hydrogen atoms and the organic reactant as ligands, it is evident that the non-basal faces of the layered sulfide will (and indeed do) exhibit greater catalytic activity than the basal surfaces, in which the metal atoms are submerged below the sulfur atoms (Figure 1.20).

Important as geometric effects undoubtedly are, they seldom dominate all other factors. We are reminded of this in contemplating the sharp contrast in

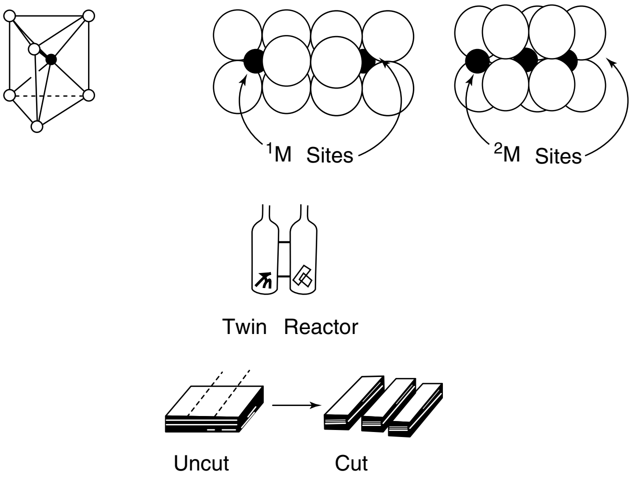


Figure 1.20 At the edges of crystals of transition-metal chalcogenides (e.g. MoS_2) there are some singly (^{1}M) and doubly (^{2}M) coordinatively unsaturated sites. For a given mass of crystalline catalysts, their surface concentration can be increased by cutting perpendicular to the basal planes. Tanaka probed the catalytic performance of such sites using a twin reactor, one limb of which contained uncut crystals, the other cut crystals of MoS_2.

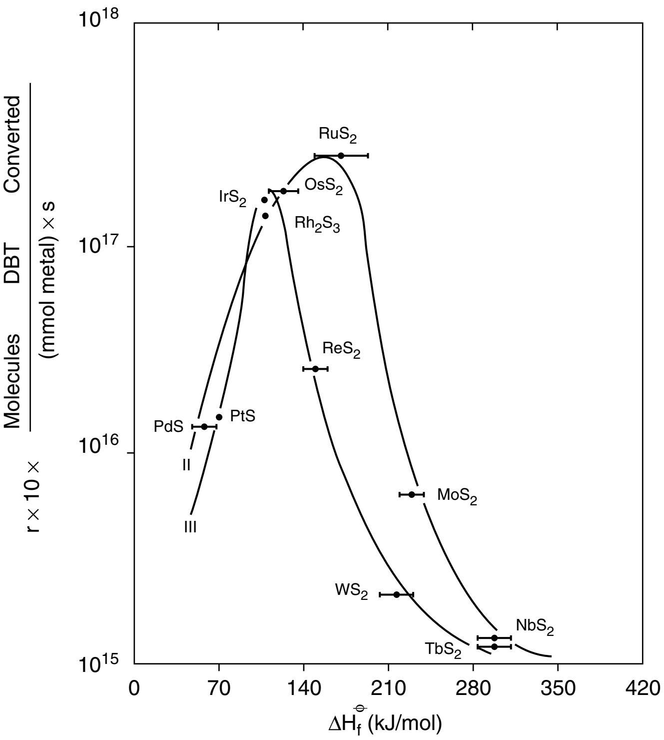


Figure 1.21 Catalytic activity in the hydrodesulfurization of dibenzothiophene varies in a 'volcano' fashion (see text) as a function of the enthalpy of formation of the bulk metal sulfide. (With permission from Elsevier (Chianelli and Pecoraro, 1984).)

behaviour between metallic platinum (generally a good catalyst) and metallic gold (generally a poor catalyst except when it is extremely finely divided). These metals have exactly the same structure (face-centred cubic) and their interatomic spacings differ by only a small percentage. The same can be said of silver and gold. Even in the case of hydrodesulfurization, electronic factors can be very important, as demonstrated in the volcano plot of Chianelli and Topsoe, who showed that catalytic activity can vary by several powers of 10 in proceeding along the sulfides of a series of transition metals (Figure 1.21). From this volcano plot we deduce that the enthalpy of formation for maximal activity takes an intermediate value: the most effective catalysts are those metal sulfides which have the ability to form and regenerate sulfur vacancies, required to create coordinative unsaturation at the metal centre.

The re-emergence of the intermediate compound theory of catalysis first propounded by Sabatier occurred amongst Dutch workers. As early as 1954, Mars and van Krevelen concluded that the catalytic oxidation of hydrocarbons took place in two steps: a reaction between the oxide and the hydrocarbon, in which the latter is oxidized and the former reduced, followed by the reaction of the reduced oxide with O_2 to restore the initial state. Obviously the tendency of an oxide (or a mixed oxide) to donate its structural oxygen is of key importance in governing its efficacy as a selective oxidation catalyst. This is of crucial importance in the oxygen-storage capacity of CeO_{2-x} in the auto-exhaust catalyst. If reduction of the oxide catalyst is too facile, it may be active, but it ceases to be selective; however, if it is not facile it may be active, but it ceases to be selective; if it is not facile enough the catalyst inevitably is of low activity. These generalizations echo our earlier remarks about volcano plots (Figures 1.14 and 1.21). Again, it is a balance between ease of loss of oxygen from the solid and the ability to convert gaseous oxygen into the bulk oxide, as well as the mobility of the entities (electrons and ions) that hold sway in the solid (Figure 1.22).

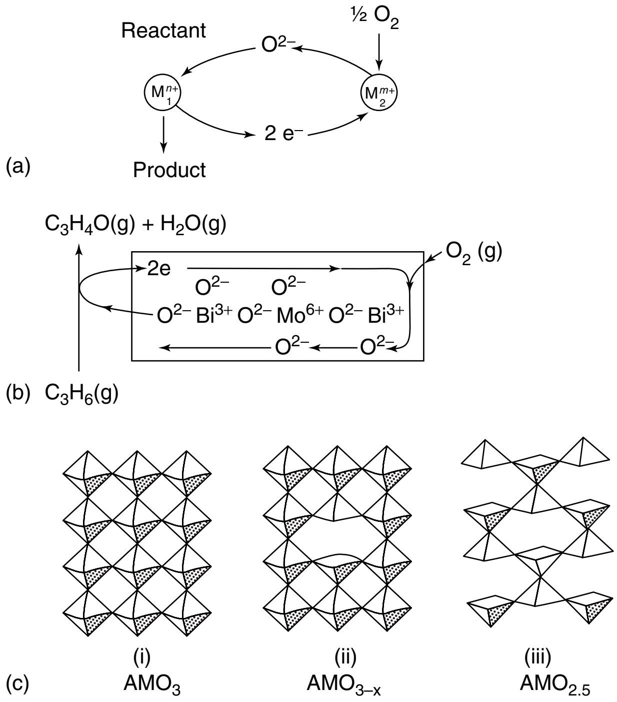
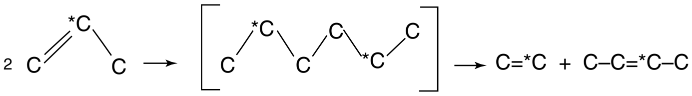


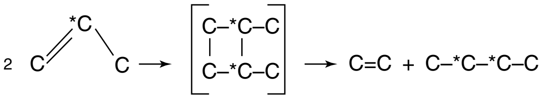
Figure 1.22 (a) In certain catalytic oxidations the so-called Mars–van Krevelen mechanism (an extension of Sabatier's original view) operates in which the hydrocarbon uproots oxygen from the oxide and the loss from the solid is subsequently made good by incorporation of gaseous oxygen. (b) Bismuth molybdate catalysts function in this way in the conversion of propylene into acrolein. (With permission from Elsevier (Grasselli and Burrington, 1981).) (c) Some perovskite catalysts (general formula ABO_3; see Chapter 5), simplified in this schematic representation, are good selective oxidation catalysts. On releasing structural oxygen, octahedra become square pyramids, but the skeletal structure remains intact.

1.4.3.1 Mechanistic Insights from Isotopic Labelling

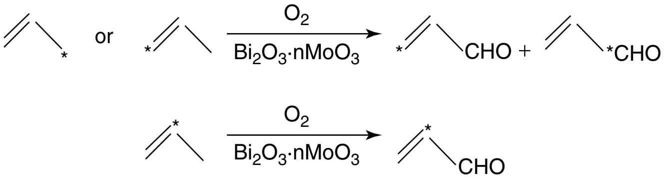
Experiments employing isotopically labelled reactants have greatly clarified our understanding of the mechanisms of catalysed reactions. As stated earlier, H. S. Taylor foresaw the value of using deuterium as a probe shortly after its discovery. Decades later, with the greater availability and ease of detection of radio-isotopes, many ingenious investigations were made of 'live' catalyst surfaces, especially by Thomson and his school at Glasgow. In the early 1960s, they showed that, in general, only a fraction of chemisorbed species participate in catalysis, and that the surfaces themselves are energetically heterogeneous. They also pinpointed how much carbonaceous material is present at the surfaces during the conversion of hydrocarbons on metal catalysts. A good example of how ^{14}C-labelling elucidates reaction mechanism concerns the disproportionation of propylene: $2C_3H_6 \rightarrow C_2H_4 + CH_3CH{=}CHCH_3$. Does this reaction, catalysed by ReO_3/Al_2O_3, proceed via a linear or a cyclic intermediate? The two alternatives are represented by Schemes 1.18 and 1.19. By labelling the propylene in the 2-position, the Dutch workers Mol and Moulijn found that the ethylene showed no radioactivity, whereas the butene had twice that of the starting gas. The first mechanism is, therefore, not valid, and a four-membered intermediate, as shown in Scheme 1.19, must be implicated. Using both 1-*C- and 3-*C-labelled propylene it was also established that the identity of the terminal CH_3 group is retained during the disproportionation. Over bismuth molybdate catalysts Sachtler, working with 1-, 2- and 3-labelled propylene, showed that the terminal CH_3 does lose its identity in the course of its conversion into acrolein (Scheme 1.20).



Scheme 1.18

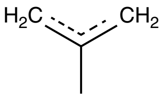
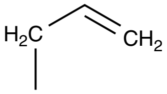
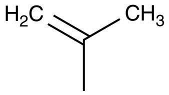
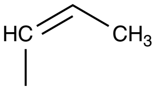
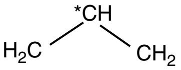


Scheme 1.19



Scheme 1.20

Table 1.2 Intermediates identified when propylene reacts with oxide catalysts.

Catalyst	**Intermediate**	**Name and hapticity**
$Bi_2O_3 \cdot nMoO_3$		π-Allyl (tri)
Ga_2O_3; $A1_2O_3$		σ-Allyl (mono)
$A1_2O_3$	 and	Propen-2-yl (mono)
		Propen-l-yl (mono)
Zeolites, ZrO_2		Carbenium ion (zero)

(After Kemball (1984).)

This suggests that a π-allyl intermediate is formed. Approaches such as these have established the identity of numerous intermediates at oxide and other catalyst surfaces. Propylene alone gives rise to five distinct intermediates, depending upon the nature of the oxide catalyst used (Table 1.2). We see that the hapticity of the ligand (the number of carbon atoms in the ligand directly bonded to the surface) can range from one to three.

Isotopic labelling has proved invaluable in numerous other catalytic contexts, for example Ponec's proof of the dissociation of CO as a primary step in Fischer–Tropsch synthesis; the demonstration by Lambert of the comparative unimportance of adsorbed dioxygen in the silver-catalysed synthesis of ethylene oxide; and the separate experiments of Keulks, of Adams and of Ashmore, which demonstrated that structural oxygen from solid catalysts was incorporated into the products of selective oxidation. These days, stable isotopes are more convenient to monitor (by mass spectrometry and NMR) than radioactive ones. They are almost invariably used in the transient response method of probing the surfaces of fine catalysts, described in Chapter 3.

1.4.3.2 **Concepts from Organometallic Chemistry**

So far as the incorporation of the ideas of organometallic chemistry into the concepts of catalysis is concerned, an important factor has been the realization that metal atoms attached to organic ligands can be bound in a multiplicity of ways (involving *a* and/or π bonds) with more or less donation to, or back-donation from, the metal centre. Combining the results derived from difference sources, we see in Figure 1.23 how the bonding and energetic situation for an isolated metal atom attached to CO differs from that pertaining to a metal surface.

In 1966 Bond drew attention to the usefulness of conceptually isolating the d-orbitals of individual atoms at the surface of a transition-metal catalyst. By so doing, it follows logically why both terminal and bridge-bonded CO should exist at catalyst surfaces. With a fuller appreciation of band theory and the language of solid-state physics (Chapter 5), we can more fully appreciate that interactions between the orbitals of an isolated CO molecule can be favoured with 'localized' orbitals in the metal.

In addition, the demonstrated mobility of ligands on the surfaces of small organometallic clusters vindicated the interpretations of others who saw evidence for similar phenomena at the surfaces of bulk catalysts. Another important set of insights that organometallic chemistry has given to the student of catalysts is into the manner in which atoms of carbon can attach themselves to metals. Carbon is now reckoned to be ubiquitous on the surfaces of many transition metal and alloy catalysts, but comparatively little is known about the way in which it is bonded. So far, several non-reactive cluster carbides have been discovered since Dahl's remarkable discovery in 1962 of the compound $Fe_5C(CO)_{15}$. Examples of non-reactive 'cage' and peripheral carbide clusters are shown in skeletal outline in Figure 1.24.

The recognition of the so-called 'agostic' interaction (in the terminology of Brookhard and Green), $C-H\cdots M$, is also an important step forward in organometallic chemistry, and likely to be of future value in catalysis. The agostic interaction results because, in effect, transition metals can form stable complexes in which the electronic requirements of the metal are satisfied by interaction with the electrons of the C–H bond. Such interactions might be considered to resemble those present in transitory species in the processes of β-elimination/olefin insertion (Scheme 1.21).

So far, agostic interactions have been identified with some 15 or so different metals, and they encompass a range of C− environments, with the carbon ring being α-, β-, γ-, δ- or ϵ- to the metal involved in the three-centre interaction (Figure 1.25). $N-H\cdots M$ interactions have also been identified.

Yet a further advantage of incorporating the concepts of organometallic chemistry into catalysis is seen in the formulation of reaction mechanisms. In this regard Clarke and Rooney have made valuable contributions, especially in invoking the role of metallocyclobutanes in metal-catalysed homologation reactions (the formation of the next-higher *n*-alkane). The mechanism they proposed consists of addition of surface methylene (for the existence of which there is good evidence) to the unsubstituted vinylic carbon of an *α*-olefin, which is formed initially by dehydrogenation. The resulting metallocyclobutane may then hydrogenate to yield the next-higher homologue or isomerize to the corresponding *α*-olefin which, in turn, may repeat the same reaction (Scheme 1.22).

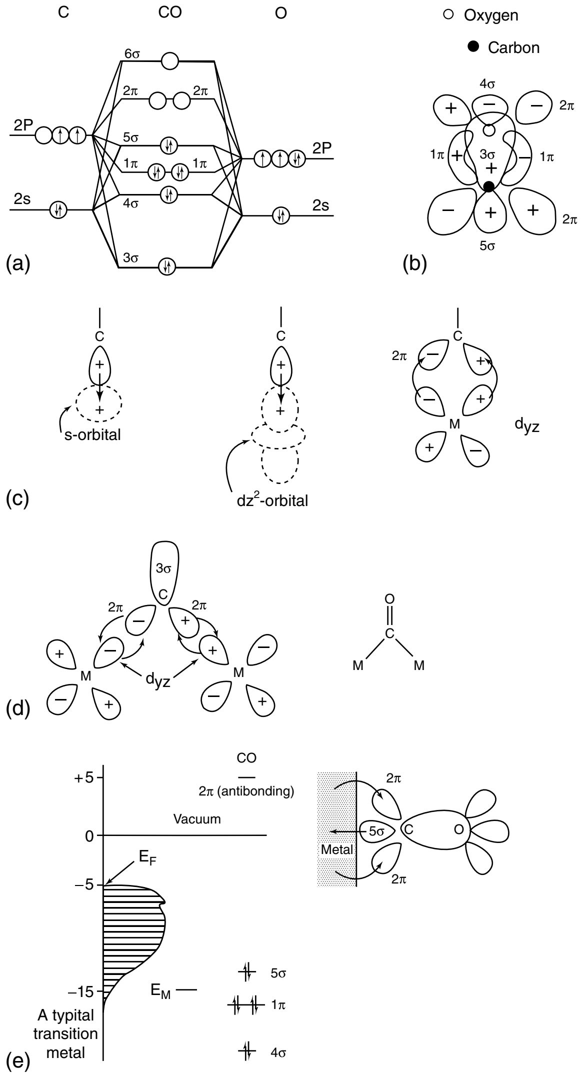


Figure 1.23 (a) The molecular orbitals formed when oxygen and carbon combine to yield CO (the antibonding 2π-orbital is sometimes referred to as 2π*). (b) The orbital limits of the various σ- and π-orbitals in CO. In (c) the arrows denote the direction of electron transfer when CO is attached to a metal centre. As well as donation of σ-electrons from the CO to the metal, there is back-donation of electrons from the d-orbitals of the metal to the antibonding orbitals of the CO. (d) The orbital interactions involved in bridge-bonding of CO. (e) The relative energies of the various energy levels of the bonding and antibonding orbitals of CO, as well as the highest occupied molecular orbitals (HOMOs) of the isolated metal (E_M) and the bulk metal (E_F) (Shustorovich and Baetrold, 1985).

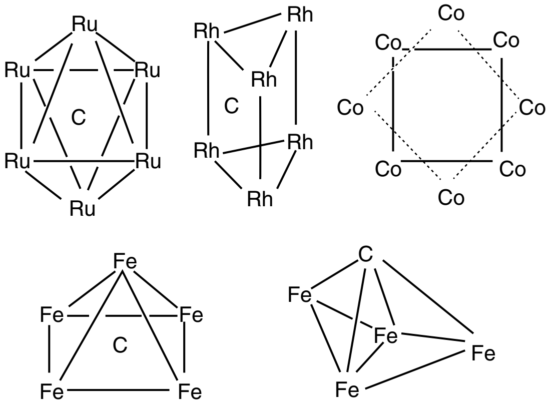
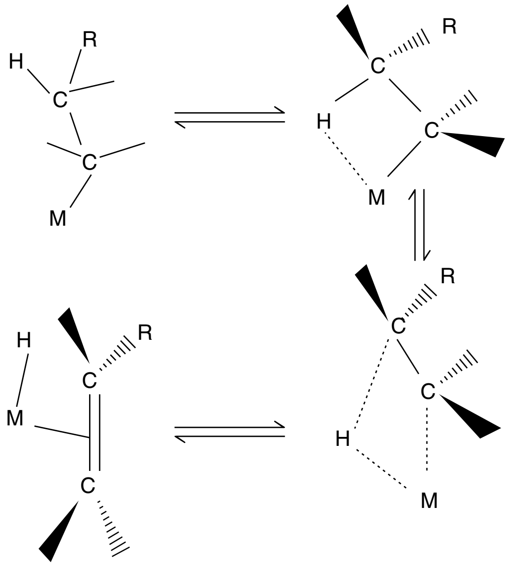


Figure 1.24 Nonreactive 'cage' and peripheral carbide clusters.



Scheme 1.21

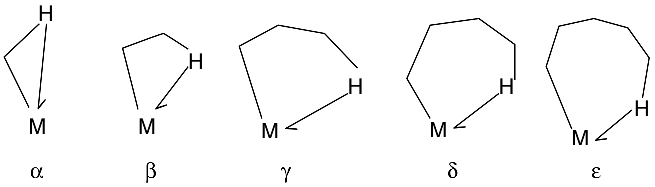
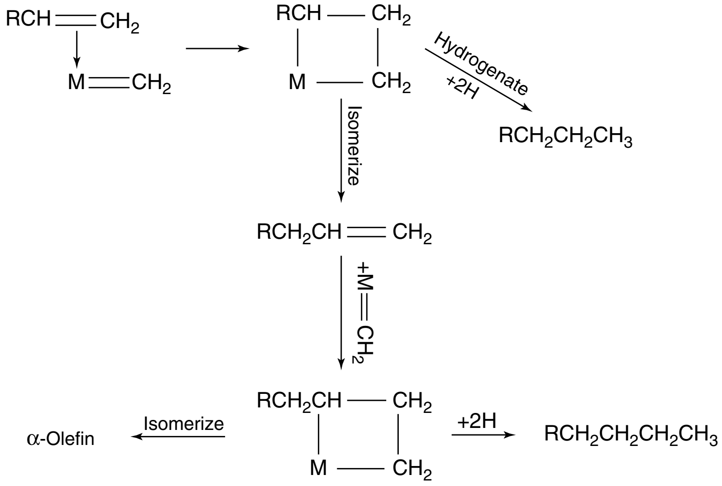


Figure 1.25 C–H environments for agostic interactions in organometallic complexes.



Scheme 1.22

1.5
Key Advances in Recent Theoretical Treatments: Universability in Heterogeneous Catalysis

In their conceptual and computational approach to *Molecular Heterogeneous Catalysis,* van Santen and Neurock (2006) have dealt with the essential ingredients to appreciate the complexity and status of catalysis from the viewpoints of the theoretical chemist and physicist – see also Norskov *et al.* (2002). It will be seen that the Brønsted–Evans-Polanyi (BEP) relation, which is rapidly gaining prominence in interpretations of catalytic phenomena, is of major importance. Based on an extensive set of DFT calculations (see Sections 5.7 and 5.8), Norskov *et al.* showed that, for a certain class of catalytic reaction, there is a universal reactant independent relation between the reaction activation energy and the stability of reaction intermediates. This leads directly to a universal relationship between absorption energies and catalytic activity, which can be used to pinpoint what it is that determines the best catalyst for a given reaction. In Chapter 2 we shall elaborate this approach further. Suffice it to say that, thanks to DFT in the hands of Nørskov and his school, we can explain why the following facts hold good:

- Ru and Fe are the best catalysts for ammonia synthesis,
- Co, Ru and Fe are the best catalysts for the Fischer–Tropsch synthesis,
- Pt, Pd and Ag are the best oxidation catalysts,
- Pd, Pt and Rh are the best auto-exhaust catalysts for removal of nitric oxide.

Elucidating the crystal structure of a heterogeneous catalyst is of prime importance on the road to understanding the mechanism of its action and also in suggesting related new structures worthy of synthesis. When it is difficult or impossible to obtain single crystals, or well-ordered, phase pure-powdered specimens of a given catalyst, much progress can be made via *atomistic simulations.* Considerable progress has been made in the development of interatomic potential that can be utilized to carry out *energy minimizations* in order to find the most stable structures for different oxide metal and zeolite systems. The reader is again referred to the monograph by van Santen and Neurock (2006) and also to one edited by Catlow (1997). Lattice energy minimization techniques have been quite successful in simulating the lowest energy structures of various metal oxides, zeolites and microporous aluminophosphates (ALPOS).

The programme known as GULP (General Utility Lattice Programme) developed by Gale is a general method towards simulating the structure and energetic for 3D ionic and molecular solids as 'defect' structures. It allows the calculation of a range of structural, mechanical and thermodynamic properties including relative energies, the preferred sitings of sorbates, bulk modulus, Young's modulus, dielectric constant refractive index, phonon and other vibrational frequencies, entropy, heat capacity and Helmholtz free energy.

1.5.1
Some Major Current Developments in Heterogeneous Catalysis

Particle-size effects constitute one of the major topics of investigation at present, especially in regard to the remarkable catalytic performance of gold nanoparticles. Bimetallic nanoparticles, which are already extensively used in catalytic reforming in the petroleum industry ever since pioneering work of Sinfelt, have undergone a renaissance, largely because smaller (and frequently mono disperse) nanoparticles exhibiting high activity and selectivity may now be routinely prepared from molecular precursors. Also because of improvements in preparative techniques, the complex phenomena of fluctuations and bistabilities on catalyst nanoparticles has become highly prominent. This, in turn, has demanded a re-examination of the role of catalyst support as a determinant of activity and selectivity.

A significant and growing area in heterogeneous catalysis is the design and exceptional performance of single-site catalysts, which exhibit many of the advantages of molecular (homogeneous) catalysts and metalloenzymes, but few of their disadvantages in that separation of products from reactants is readily effected. Apart from initiating a new era – in asymmetric heterogeneous catalysis and a return to the prospects of exploiting chiral surfaces in electrocatalytic and related fields – single-site catalysts offer one of the very few widely applicable strategies for the design of new catalysts (see Section 9.8).

Other major topics of great interest are:

- the design and preparation of solid-acid catalysts, a topic of continuing interest to one of us (see Thomas (1992));
- the catalytic breakdown of biomass;
- the functionalization of abundant naturally occurring hydrocarbons;

- (as outlined earlier in this chapter) the conversion of highly functionalized organic species in the plant world into feedstocks and fuels of the kind summarized in Figure 1.4.

All these topics will be considered in greater detail in later chapters, especially Sections 9.6 and 9.7.

1.6
Milestones Reached in Industrial Catalysis in the Twentieth Century, and Some Consequential Challenges

The milestones reached (Table 1.3) in catalysis in industrial challenges in the twentieth century signifies the central importance of the subject in the creation of wealth. But the general public is rightly becoming more concerned with environmental issues, and decisions are now being made that are not primarily based on science and technology. Public concern is a potent influence; and for many industries where catalysis already looms large it is becoming increasingly difficult to obtain permits, eliminate waste, construct incinerators and receive and transport toxic or otherwise hazardous materials.

In the twenty-first century it will become increasingly necessary to devise processes with close to 100% yields, to effect catalyst recovery, to regenerate and to recycle on a routine basis, and in all this catalysis will play an increasingly dominant role. Elimination of by-products and process waste is becoming a major issue and will demonstrably determine the viability of future chemical processes. It is a sign of the times that the State of California decreed that, in AD 2000, 2% of the motor vehicles on its roads must have zero deleterious emission, even though ways of securing this end at the time of the edict were by no means clear.

Hazardous and toxic materials such as HF, HCN, HCl, H_2SO_4, H_3PO_4, CI_2, acrylonitrile, formaldehyde, ethylene oxide and phosgene, for example are more-or-less essential building reagents in the chemical industry since they often possess reactivity or functionality required for further chemical reactions. Future business practices which entail the inventory and transportation of these materials will almost certainly have to be avoided or drastically diminished.

Methyl isocyanate (MIC) is familiar as it was at the centre of the tragic incident that occurred in Bhopal, India, some years ago. At that time and in that place MIC was produced by the phosgenation of methylamine:

$$CH_3NH_2 + COCI_2 \rightarrow CH_3NCO + 2\ HC1$$

It is no longer acceptable to store MIC as was done in Bhopal, and the use of reagents such as phosgene is greatly discouraged. The consequence of this is that industrial companies have sought, and succeeded in producing, safer alternatives. The DuPont Company, for example now use the catalytic dehydrogenation process (although by 1993 they had not yet disclosed the nature of the catalysts that they

Table 1.3 Milestones in the introduction of industrial heterogeneous catalysis during the twentieth century.

Decade	Process	Catalyst (prime constituent)
1900	Methane from $CO + H_2$ (syn-gas)	Ni
	Hydrogenation of fat	Ni
1910	Liquefaction of coal	Fe
	Synthesis of ammonia from $N_2 + H_2$	Fe/K
	Oxidation of ammonia to nitric acid	Pt
1920	High-pressure synthesis of methanol from $CO + H_2$	(Zn, Cr) oxide
	Fischer–Tropsch synthesis of alkanes, alkenes and alkanols from $CO + H_2$	Co, Fe
	Oxidation of SO_2 to SO_3 (sulfuric acid production)	V_2O_5
1930	Catalytic cracking of oil (fixed-bed, Houdry process)	Montmorillonite clays
	Epoxidation of ethylene	Ag
	Oxidation of benzene to maleic anhydride	V
1940	Catalytic reforming of hydrocarbons (gasoline)	Pt/Al_2O_3
	Hydrogenation of benzene to cyclohexane	Ni, Pt
	Inversion of sucrose (and decolourization of golden syrup)	Immobilized enzyme (invertase) on charcoal
1950	Polymerization of ethylene to polyethylene:	
	Ziegler–Natta	Ti
	Phillips process	Cr
	Production of polypropylene and polybutadiene (Ziegler–Natta)	Ti
	Hydrodesulfurization	(Co, Mo) sulfides
	Hydrotreatment of naphtha	$Co{-}Mo/Al_2O_3$
	Oxidation of naphthalene to phthalic anhydride	(V, Mo) oxides
1960	Oxidation of butane to maleic anhydride in O_2	$(VO)_2P_2O_7$
	Oxidation of propylene to acrolein	(Bi, Mo) oxides
	Ammoxidation of propylene to acrylonitrile	(Bi, Mo) oxides
	Improved means of reforming hydrocarbons	Pt–Ir on $A1_2O_3$ Pt–Re on $A1_2O_{3vz}$
	Metathesis of alkenes	(W, Mo or Re) oxides
	Improved means of cracking of hydrocarbons	Zeolites (Faujasite-based)
	Production of vinyl acetate from ethylene	Pd/Cu
		Cu chloride
	Oxychlorination of ethylene to vinyl chloride	
	Triolefin process (propylene to butene and ethylene)	$Mo(CO)_6$ or $W(CO)_6$ on $A1_2O_3$
	Production of *ortho-xylene* from phthalic anhydride	V_2O_5 on TiO_2
	Hydrocracking	$Ni{-}W/Al_2O_3$
	Water-gas shift (at high temperatures)	$Fe_2O_3/Cr_2O_3/MgO$
	Water-gas shift (at low temperatures)	$CuO/ZnO/Al_2O_3$

(*continued overleaf*)

Table 1.3 (*Continued*)

Decade	Process	Catalyst (prime constituent)
1970	Xylene isomerization (shape-selective formation of *para*-xylene)	H-ZSM-5 (zeolite)
	Methanol from CO + H_2	Cu–Zn/Al_2O_3
	Disproportionation of toluene to benzene and *para*-xylene	H-ZSM-5
	Catalytic dewaxing	H-ZSM-5
	Auto-exhaust catalyst	Pt, Rh, Pd on oxide
	Conversion of benzylpenicillin into 6-aminopenicillanic acid (production of semisynthetic penicillins)	Immobilized enzyme (penicillin amidase)
	Isomerization of glucose to fructose	Immobilized glucose isomerase
	Hydroisomerization	Pt/zeolite
	Selective reduction of NO with NH_3	V_2O_5 on TiO_2
	Production of MTBE (methyl *t*-butyl ether) from methanol and 2-methylpropylene	Acidic ion-exchange resins
	Fructose-enriched from glucose (from glucose syrup)	Immobilized cells (*Arthrobacter*)
	Hydrolysis of raffinose	Immobilized cells (*Mortierella vinacea*)
1980	Conversion of ethylene and benzene into ethylbenzene	H-ZSM-5
	Methanol to gasoline (petrol) (MTG)	H-ZSM-5
	Conversion of ethylene and acetic acid into vinyl acetate	Pd
	Oxidation of *t*-butanol to methyl methacrylate	Mo oxides
	Improved means of liquefying coal	(Co, Ni) sulfides
	Production of diesel fuel from CO + H_2 (syn-gas)	Co
	Hydrotreatment of hydrocarbons	Pt/zeolite Ni/zeolite H^+-Ferrierite
	Catalytic distillation (in MTBE production)	Acidic ion-exchange resins
	Vitamin K_4 production	Pd membrane
	Dehydrocyclization ('Cyclar') of alkanes	Ga–ZSM5
	Conversion of light alkanes to aromatics	
	Oxidation of methacrolein	Mo–V–P (hetero-polyacid)
	Hydration of isobutene	
	Polymerization of tetrahydrofuran	Phase-transfer catalysis
1990	Production of dimethyl carbonate from acetone	Cu chloride
	Conversion of phenol to hydroquinone and catechol	Ti–silicalite
	Isomerization of but-l-ene to 2-methylpropylene	H^+-Ferrierite acidic H^+-Theta-1 zeolites

Table 1.3 (*Continued*)

Decade	Process	Catalyst (prime constituent)
	Isomerization of oxime of cyclohexanone to ϵ-caprolactam	Silicoalumino-phosphate molecular sieve (SAPO-11)
	Ammoxidation of cyclohexanone to its oxime using H_2O_2	Ti–silicalite
1990	Production of acrylamide from vinyl cyanide	Immobilized nitrile hydratase
	Complete combustion of natural gas (at about 1300 °C)	Noble metals and/or mixed oxides
	'Sweetening' of natural gas by selective oxidation of H_2S to S	Mixed oxides
	Oxidation of benzene to phenol via cyclohexene	Zeolite
	Methanol to light alkenes	Silicoalumino-phosphate molecular sieve (SAPO-34)
	Olefin oligomerization (Shell polygasoline and kerosene process)	Zeolite
	Production of L-aspartic acid and L-alanine from ammonium fumarate	Immobilized micro-organisms
	Conversion of toluene into toluene *cis*-glycol	*Pseudomonas putida*
	Production of 2,6-diisopropylnaphthalene using propylene as alkylating agent	Acidic zeolite (mordenite)
	Decomposition of hypochlorite	NiO
	Dehydration of alkanols	Heteropolyacid salts

developed for these reactions):

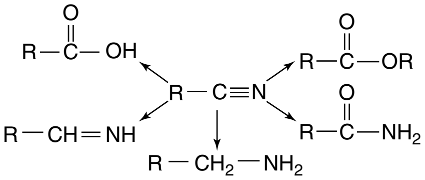
$$CH_3NH_2 \xrightarrow{CO} CH_3NHCHO \xrightarrow{O_2} CH_3NCO$$

The DuPont strategy enables them to make MIC and to convert it *in situ* into an important agrichemical product. *In situ* manufacture will become progressively more prominent in the twenty-first century, since it greatly reduces the risk of unwanted exposure.

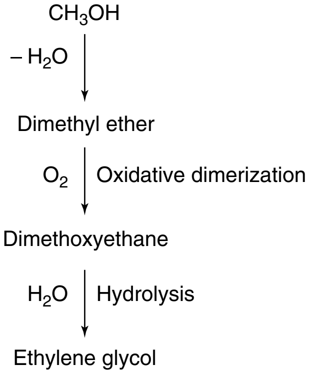
This example, entailing a re-analysis of the entire mode of manufacture, could be replaced many times over. The EniChem Company in Italy, in its novel catalytic method of manufacturing the useful monomer dimethyl carbonate, which formerly used massive quantities of phosgene, now follows the following 'safe' process:

$$CH_3COCH_3 + O_2 \rightarrow (CH_3)_2CO_3$$

Yet another example concerns hydrogen cyanide (prussic acid), HCN, which is the starting point for introducing the versatile nitrile functionality in a wide range of organic commodities. Amides, acids, amines, esters, and so on, are all readily generated from the corresponding nitrile (Scheme 1.23).



Scheme 1.23

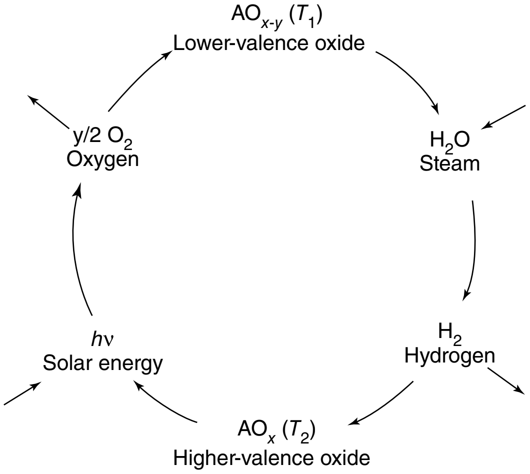


Scheme 1.24 Production of ethylene glycol from methanol.

All this underlies the recognition that catalysis is of central importance, and is likely to remain so into the foreseeable future, in securing environmentally benign products. Catalysis likewise holds the key to the safer and cheaper manufacture of desirable products. Typical processes are shown in Schemes 1.24 and 1.25.

An attractive method for the utilization of solar energy is its direct conversion into chemical fuels (e.g. syn-gas), thereby making it available as a source either of chemical feedstock, or of heat (by catalytically effecting a reverse reaction – see Figure 1.26), or both. The Russian ADAM–EVA cycle depicted in Figure 1.26 is already functioning smoothly. Recent advances in capturing solar energy are given in Chapter 8 and 9.

Conceptually it is convenient to divide the future challenges into broad categories such as environmental (Figure 1.27), technological (including biotechnological) (Figure 1.28) and fundamental. And although it is possible to draw up a list of targets as is done in these tables, it must never be forgotten that these three categories are quite arbitrary; the distinctions between them are blurred. Purists rightly argue that, in most circumstances, the solutions to practical problems almost invariably demand a deeper understanding of fundamentals. Moreover, distinctions between the technological and biotechnological can themselves be fuzzy. Recall that hitherto, for example the source of C_{10}–C_{14}-hydrocarbons for use in, say, detergency was petrochemical. Nowadays, thanks to major advances in the production of transgenic plants and other consequences of the molecular biological revolution, it is possible to develop oilseed rape hybrids rich in C_{12}-oils. Other routes are described in Sections 9.6 and 9.7. And when it



Scheme 1.25 Thermochemical cycles with metal oxide for the production of hydrogen from water. Ideally the higher' oxide needs to decompose (catalytically) very rapidly at a high temperature T_2 and the steam to react with the 'lower' oxide at a low temperature T_1.

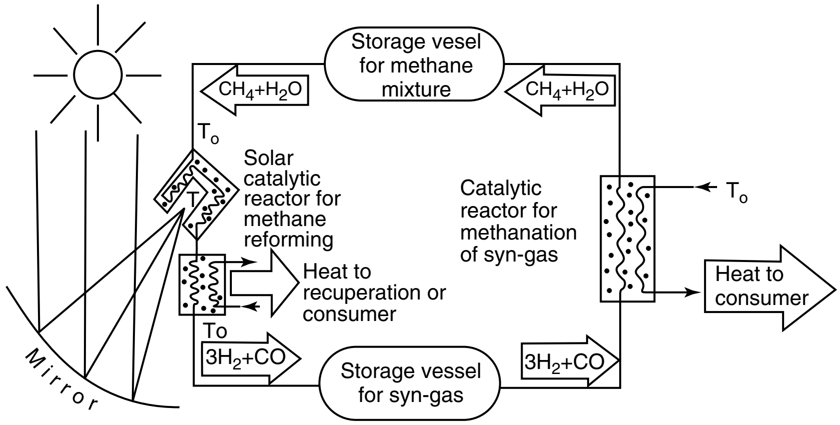


Figure 1.26 Scheme of thermocatalytic conversion of solar energy based on the closed thermochemical 'ADAM–EVA' cycle; T is the temperature inside the cavity of the solar catalytic reactor; T_o is the temperature of environment. With permission from Zamaraev (1996).

comes to biocatalysts, and the use of immobilized cells, modified organisms or cloned genes (to generate spectacularly stereoselective and active catalysts), the distinction between heterogeneous and homogeneous systems also becomes less well defined.

Returning to fundamentals, it is almost a truism that the perennial quest has to be understanding the factors that enhance specificity, increase activity and improve lifetime. A better catalyst must, by definition, do one or all of these things. To understand better how we may achieve these ends is the pervasive theme of this book.

- Development of ‘zero-waste’ processes
- Minimization of hazardous products and ‘greenhouse’ gases
- Replacement of corrosive liquid acid catalysts by benign solid acid catalysts
- Evolution of sustainable systems
- Reduction in volume of by-products (avoidance of processes that generate salts)
- Development of processes requiring less ‘consumption’ of catalysts
- Elimination of voluminous by-products

Figure 1.27 Selection of environmental challenges.

Challenge

- Reformulated transport fuels (containing lower amounts of aromatics and volatile components, and larger amounts of more completely combustible additives)
- Development of (catalytic) automobiles operating on methanol dissociation[i]
- Better catalysts for hydrodesulfurization, hydrodenitrification of light oils and coals and hydro-treatment of heavy oils and tars
- Single-step synthesis of desirable products:
    - — acetaldehyde from ethane
    - — aromatics from ethane
    - — phenol from benzene
    - — acrolein from propane
    - — acrylonitrile from propane by ammoxidation[ii]
    - — acetic acid from methanol
    - — 2-methylpropylene from syn-gas
- Better methods for isomerizing linear alkanes into branched-chain ones
- Functionalization of light alkanes, especially methane (e.g. by use of heterogenized metalloporphyrins, P450s or cytochromes)
- Efficient routes to cheaper feedstocks for the chemical and pharmaceutical industries[iii]
- Development of robust, re-usable, chiral catalysts
- New shape-selective catalysts, for example, for non-thermodynamic ratios of mono- and di-methylamines from methanol and ammonia
- Development of processes using CO_2 as reactant[iv]
- Cheaper and safer methods of generating hydrogen[v]
- New catalytic membranes[vi]
- Better electrocatalysts for fuel-cell consumption of plentiful hydrocarbons
- Development of modified enzymes, organisms or transgenic plants for ‘natural’ production of polymers[vii]
- Families of solid catalysts for ‘tunable’ conversion of methanol into either ethylene or propylene
- Fischer–Tropsch catalysts for sharply defined reaction products
- Efficient, safe methods of generating hydrogen peroxide (from H_2 and O_2)[viii]
- Designed solids capable of controlled release of structural elements such as oxygen or hydrogen
- Uniform, molecular-sieve catalysts (of redox or Brønsted type) possessing well-defined larger pores (40–100 Å diameter)
- Engineered proteins for pharmaceutical use[ix]

Figure 1.28 Selection of technological challenges.

i A vehicle running on a fuel in which methanol dissociates to CO and H_2 on board has many attractions. First, such a fuel is more efficient than undissociated methanol. Second, the heat required for endothermic dissociation of the alcohol can be supplied by the engine exhaust gas. This recovers waste heat and increases the heating value of the fuel. Third, an engine functioning in this manner can be operated with excess air (*i.e.*, under lean burning conditions), which facilitates the complete combustion of CO and hydrocarbons. Lastly, problems associated with formaldehyde emission are appreciably reduced, and emissions of the oxides of nitrogen are likewise greatly diminished.

ii Section 9.5.2

iii Sections 9.6 and 9.7

iv Section 9.5.4.1

v Section 9.4

vi Section 8.5.2

vii Section 9.6

Zeneca plc (formerly ICI) produced 100 tons of the natural polymer Biopol in 1993. Biopol is a bacterial storage polymer, produced by fermentation of an alkaligenous strain. It consists of polyhydroxybutyrate or a copolymer with polyhydroxyvalerate. It is both biocompatible and biodegradable

viii In 1992, several companies including Mitsubishi, DuPont and Interox announced palladium-or platinum-based catalysts for this synthesis.

ix Section 9.6

Figure 1.28 (*Continued*)

Problems

These problems focus largely on thermodynamic and a little on strategic aspects of catalysis. They are intended to consolidate the readers assumed acquaintance with thermodynamic and related considerations. In each subsequent chapter the problems set are linked directly to the topics discussed in that chapter, and serve to illustrate or extend the relevant principles.

1.1 Using only thermodynamic principles, show that for any given temperature and total pressure the maximum conversion of hydrogen into ammonia occurs when the ratio of hydrogen to nitrogen in the feed gas to an ammonia synthesis reactor is 3 : 1.

1.2 Natural gas consists chiefly of methane. It has been suggested that one way of avoiding dependence on oil for the production of important chemicals is for benzene to be produced according to the following reaction:

$$6\ CH_4(g) \rightarrow C_6H_6(g) + 9\ H_2(g)$$

Before embarking on a search for a suitable catalyst to effect this conversion, we must first determine whether this reaction is feasible. Pursue this question quantitatively given that ΔC_p for the above reaction is:

$$\begin{aligned} &42.0 - 32.1 \times 10^{-3}T + 3.83 \times 10^{-6}T^2 \text{cal K}^{-1}\text{mol}^{-1} \\ &\quad = 176 - 134 \times 10^{-3}T + 16.0 \times 10^{-6}T^2 \ \text{J K}^{-1}\text{mol}^{-1} \end{aligned}$$

(Hint: You should begin by consulting thermodynamic tables in other text books, or in National Bureau of Standards compilations, and work out $\Delta H^{\ominus}_{298}$ and $\Delta S^{\ominus}_{298}$ for the proposed reaction.)

1.3 Investigate the effect of temperature on the disproportionation of toluene, given the accompanying data.

T (°C)	50	100	150	200	250
K_o	0.059	0.065	0.070	0.074	0.078
K_m	0.206	0.208	0.209	0.210	0.211
K_p	0.0837	0.0875	0.0904	0.0928	0.0949

K_o, K_m, K_p are thermodynamic equilibrium constants for the disproportionation reaction yielding benzene and *ortho-*, *meta-* or *para-*xylene respectively.

What temperature would you choose to effect (a) the best conversion into *m*-xylene and (b) the best conversion to benzene? What effect would total pressure have on the product distribution?

1.4 Choose an approximate operating pressure for the industrial preparation at 500 °C of methanol from synthesis gas (a mixture of carbon monoxide and hydrogen), given the following data on free energies ($\Delta G^\ominus$) and enthalpies ($\Delta H^\ominus$) of formation:

	CO(g)	CH_3OH(g)
$\Delta G^\ominus_{298}$ (kJ mol^{-1})	−7 836	−9 241
$\Delta H^\ominus_{298}$ (kJ mol^{-1})	−6 310	−11 483

1.5 The composition of a gas emerging from the secondary reformer of a modern ammonia plant has the following composition:

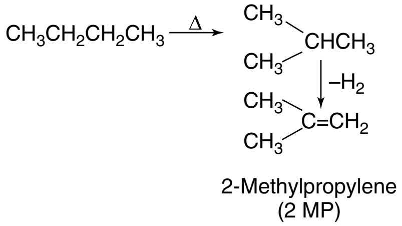
39.5% H_2, 16.3% N_2, 28.3% H_2O, 4.5% CO_2, 10.7% CO, 0.2% A and 0.5% CH_4

Assuming that equilibrium is established, what would the CO content of this gas be if it were fed directly to the first stage of a shift converter employing an iron oxide/chromium oxide catalyst and operating at 450 °C? The equilibrium constant for the reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

is 7.337 at 450 °C. Why is it normal practice to have a low-temperature (about 250 °C) shift converter as a second stage? Would the same catalyst as used for the high-temperature (first) stage be an appropriate choice for the second stage?

1.6 With the phase-down in the use of lead additives in petrol (gasoline), there is a growing need to obtain blending agents which have high octane numbers. One such material is methyl *tert-butyl* ether, MTBE (2-methyl-2-methoxypropane). It can be synthesized, using clay catalysts (see Ballantine *et al.* (1985)) from isobutene (2-methylpropylene (2MP)). An attractive route for the production of isobutene, which is comparatively scarce in contrast to methanol, of which there is a glut, is to take *n*-butane (from natural gas), isomerize it to isobutane (iB) and then to dehydrogenate the latter to 2-methylpropylene (2MP), as shown in Scheme 1.26. Shape-selective zeolitic catalysts are good for the first and platinum on



Scheme 1.26 Production of 2-methylpropene from *n*-butane.

alumina for the second of these two steps. Of considerable importance in designing a feasible operating system are the equilibrium fractions of the various possible isomers. These equilibrium fractions are shown in Figure 1.29 for a total pressure of 1 bar.

Explain how such quantitative information is derived; and discuss which temperature ranges are the most appropriate for overall conversion. Consult the literature (e.g. Natarajan, Wright and Thomas (1993)) for an alternative catalytic route to 2MP.

1.7 A popular method of producing formaldehyde on an industrial scale is to pass a mixture of methanol vapour and air at a total pressure of 1 bar over a metallic silver catalyst at 550 °C. During the course of this process, the silver slowly loses its lustre and gradually disintegrates. Using the following data, examine whether this might be due to the formation of silver oxide:

$$\Delta G^{\ominus}_{298}(\mathrm{Ag_2O}) = -10.826\ \ \mathrm{kJ\ \ mol^{-1}}$$
$$\Delta H^{\ominus}_{298}(\mathrm{Ag_2O}) = -30.556\ \ \mathrm{kJ\ \ mol^{-1}}$$

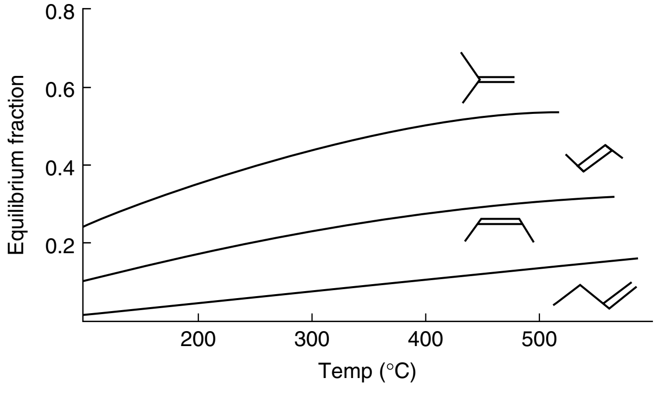
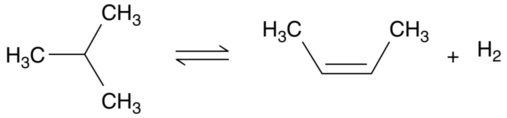


Figure 1.29 Equilibrium fraction of various alkenes in the thermal dehydrogenation of isobutane:



The relevant heat capacities (J K^{-1} mol^{-1}) are: Ag, 26.75; Ag_2O, 65.63 and O_2, 31.35.

1.8 Benzaldehyde can be generated from carbon monoxide and benzene over an appropriate catalyst at 50 °C and 500 bar total pressure. Given the information below, describe the calculations by which you would estimate an upper limit to the fraction of the benzene converted into benzaldehyde:

a) heat capacities and standard free energies and enthalpies of the compounds in question at 298 K;
b) the densities of benzene and benzaldehyde at 298 K;
c) $p-V$ data for carbon monoxide at 20 and 30 °C in the pressure range up to 500 bar.

1.9 Nitric oxide leads to the depletion of the ozone layer ($NO + O_3 \rightarrow NO_2 + O_2$). Since NO is liberated in vast quantities from power stations currently in use, efforts are now underway to reduce its concentration by catalytic ammoxidation using $V_2O_5-TiO_2$. One such reaction is: $4\ NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$. Write down other feasible reactions leading to N_2 or N_2O and H_2O as sole products. From thermodynamic data, estimate the equilibrium constants of these reactions.

1.10 Several strategies are available for the use of catalysts in harnessing solar energy. One of these, illustrated in Figure 1.26, is the so-called ADAM–EVA cycle operated by the Boreskov Institute; another, by the Weizmann Institute in Israel, has been described (Dostrovsky, 1991). Both these thermocatalytic converters entail the cycle of ‘syn-gas’ production (from the endothermic reaction $CH_4 + H_2O$) followed by methanation ($CO + 3H_2 \rightarrow CH_4 + H_2O$) with liberation of heat. But several other strategies are available, for example production of syn-gas and production of hydrogen.

a) Indicating which catalyst and the reactor conditions you would use, draw up a minimum of eight specific syntheses of products (such as alkanes, alkenes, alkanols and gasoline) that could be produced from a solar furnace.
b) Starting from either Fe_2O_3 or Fe_3O_4 and water, describe a feasible set of reactions and conditions (including appropriate catalysts) for the solar production of hydrogen and oxygen.

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