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CATALYST STUDIES: CHROMATOGRAPHY

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Introduction

Catalysis is a branch of chemical kinetics of great industrial and commercial importance. Heterogeneous catalysts are certain particulate solids of high surface area (1–300 $m^2 g^{-1}$) that increase the rates of attaining equilibria. This is achieved by the temporary attachment of reactant molecules by moderate chemical bonds to active sites on their surfaces. Catalysts themselves are not consumed during the process, although their activity is eventually lost by surface degradation. Over 90% of the world's manufactured chemicals involve catalysis at one or more stages. The market is about £7×10^9 per annum, with £200 return on each pound spent on a catalyst.

Background to Heterogeneous Catalysis and Contributions from Gas Chromatography

The invention of gas chromatography (GC) in 1952 and its development since then have been widely reviewed. Before looking at the applications of GC to catalysis, it is necessary to summarize the major stages in the concepts of catalysis and the often independent technological achievements of industrial scientists and engineers. **Tables 1** and **2**, respectively, contain the important concepts and terms and the major technical advances in catalysis.

Catalysis has a much longer history than GC – indeed life itself may originate from the catalysed conversion of the primitive atmosphere into bioorganic molecules on the surfaces of clay minerals. The ancients used enzymatic catalysts unknowingly in fermentation to make wine and vinegar. It is salutary that these natural catalysts far outperform any of our synthetic catalysts at ambient pressures and temperatures. Silver, regarded for at least three millennia as having preservative and curative powers and long used for storing wines and wound treatments, has now re-emerged in the sterile surface coating, Amenitrop, whose active antibacterial and antiviral ingredients are silver thiosulfate complexes.

In catalysis empirical technology and industrial innovation have almost always outpaced scientific theory and understanding, but this is less so today; exceptions include the Haber process for ammonia production. Nevertheless, it has always been true that basic studies provide the intellectual framework and accelerate technical developments, i.e. they 'catalyse' progress!

The scientific study of catalysis started soon after the beginnings of chemistry and at the time when phlogiston theory still held some sway. In 1835 Berzelius coined the term 'catalysis' (which is Greek for *to loosen*) after realizing that research findings in the first decades of the nineteenth century demonstrated

Table 1 Terms and characteristics used in catalysis

Term	*Characteristics*
Heterogeneous catalysts	Large surface area solids that accelerate the rate of attaining equilibirum; they are themselves chemically unchanged by the reaction and therefore do not affect the final equilibrium yields
Active sites	Those unique sites on the surface where the catalytic event takes place. They are usually the steps, edges and kinks of the flat unreactive terraces, and often represent only a few percent of the total surface atoms. Interestingly, catalysis is chemistry at imperfections and discontinuities.
Specific activity	Rate of reaction per unit area of catalyst under standard reactant concentrations. Activity is sometimes defined empirically by the temperature needed for a reaction to reach an arbitrary rate of conversion.
Turnover frequency (TOF)	Number of product molecules formed per second per active site (10^{-2} to 10^{2} s^{-1} for synthetic catalysts, compared with 10^{3} to 10^{7} for enzymes).
Structure sensitive/insensitive reactions	Rate dependent on particle size and crystal face/rate invariant to size and face.
Selectivity	The fraction of reacted molecules converted to a desired product
Durability	How long the catalyst remains active

the accelerating effects of small amounts of materials that themselves were chemically unchanged by the reaction. He is sometimes erroneously quoted as suggesting an almost occult catalytic force, whereas in fact he clearly stated the new 'force' is 'a manifestation of the electrochemical affinities of matter' Michael Faraday had a clear concept of catalysis in 1834 even before Berzelius' presentation of the term to the Swedish Academy of Sciences. It is tempting to associate the discovery of catalysts with the alchemists vain search for the philosopher's stone to transmute base metals into gold; in some respects the traces of 'catalyst stone', which transform 'useless' raw materials into useful products, are more valuable than a stone for making ornamental gold. The appellation 'black art' still lingers, perhaps with some justification, since most industrial catalysts are still formulated by recipes that are incompletely understood and retain an aura of mystery.

The burgeoning nineteenth century chemical industry quickly appreciated the utility and exploitability of catalysts and the lead chamber and contact processes developed rapidly, as did the hydrogenated hardening of vegetable oils and the synthesis of indigo. Perhaps the most important catalyst ever developed, because it averted world famine, was that for the high pressure synthesis of ammonia by Fritz Haber in 1909, and its commercialization by Badische Aniline and Sodafabrik. The technical development of the iron catalyst, which remains largely unchanged, exemplifies the rewards of painstaking research, a full appreciation of thermodynamics and the courage to build large scale industrial plants operating at the then unprecedented pressure of 300 atmospheres at 450°C. The process is a *tour de force* of chemical engineering linked with outstanding science.

The molecular understanding of catalysis really begins in the twentieth century, as have the majority of the catalysts and processes now in use. This is especially true of the petroleum and petrochemical industry, which in the 1960s and 1970s had annual growth rates of 15%. The outstanding development in the interwar years was the Houdry process for the catalytic cracking of heavy petroleum fractions into volatile gasoline components (C_2–C_{13}). The immediate postwar period saw developments such as: (1) platforming catalysts for upgrading gasoline research octane numbers (RONs) by isomerization of straight into branched alkanes and the dehydrogenation of cyclohexanes to aromatics; and (2) steam reforming of methane, naphtha and fuel oil feedstocks into synthesis gas, a carbon monoxide/hydrogen mixture important for ammonia and methane production. The recent development of vehicle exhaust catalytic converters based on rhodium-promoted platinum–alumina for converting carbon monoxide, nitrogen oxides and unburnt hydrocarbons into harmless products is a remarkable achievement for catalysis science, especially in view of the varying gas compositions and temperatures that have to be sustained.

The realization by Langmuir that catalysis involved short-range chemical bonds, which dictated that reactions occurred in surface monolayers, and Taylor's suggestion that catalysis occurred only at unique active sites, together with the discovery of the importance of atomic clusters with specific geometric arrangements by Balandin, were seminal to the growing

Table 2 Important stages and concepts in heterogeneous catalysis

Date	*Event*
The beginning!	Life originates on the surfaces of clay minerals
Prehistory	Enzymes for making wine and vinegar, sterile silver
1834/1835	Berzelius coins the term catalysis Faraday appreciates the occurrence of catalysis
1830–80	Industrial: H_2SO_4 by lead chamber, contact catalysts; synthetic dyes by mercury catalysis; hardening of oils
1900	Start of modern kinetics by Bodenstein and Ostwald
1900–14	Gasification of coal; syn-gas manufacture
1909	Haber's catalytic synthesis of ammonia
1918	Langmuir's monolayer and Rideal Ely mechanisms
1920s →	Petroleum industry: continuous processing; catalytic cracking; platforming catalysts
1923	Fischer–Tropsch hydrocarbons from syn-gas
1925	Taylor proposes catalysis occurs only at active sites
1925–36	Houdry catalytic cracking process to increase octane number of gasoline
1929	Balandin's proposal of catalysis on multiplet sites
1938	Brunauer–Emmet–Teller (BET) adsorption isotherm
1939–45	Synthetic substitutes for natural products like rubber
1941	Use of oriented metal films by Beeck and Schwab
1941	Fluidized-bed technology
1950–1970s	Explosive growth of the petrochemical industry
1952	**Gas chromatography introduced**
1955	Zeigler Natta stereoregular polymerization catalysts
1955	Sasol gasification of coal in South Africa
1956	Gas chromatographic reactors introduced
1960	Steam reforming of methane and naphtha to synthesize gas for ammonia and methanol manufacture
1964	Oxychlorination to make vinyl chloride monomer
1965	Microcatalytic chromatographic reactor introduced
1965	Sohio process for acrylonitrile and acrylic acid
1970 →	Surface science studies of surface–substrate intermediates and surface atom arrangements and restructuring
1976 →	Catalytic converters for exhausts emission control
1985 → 1990s	Control of and blending of refinery steams by GC Improvements in exhaust catalytic converters Development of catalytic power generators Hygiene catalysts: sterile coatings, oven cleaning ICI Hydcat process for hypochlorite removal from waste streams Immobilized enzymes – pharmaceutical production Zeolites and aluminium phosphate (ALPO) catalysts developed

detailed understanding, as were the applications of the absolute theory of reaction rates.

Outline of Conventional GC in Catalysis Research

Since many of the developments in catalysis listed in **Table 2** predate the invention of GC in 1952, its contributions have inevitably been since then. However, all the important characteristics of catalysts defined in **Table 1** require analysis of complex gas mixtures. Thus inevitably the use of this powerful analytical technique in catalyst research is now endemic and pervasive; so much so that it is now used almost routinely in catalyst laboratories and on catalyst testing rigs. It is the technique *sine qua non* for multicomponent analysis, especially when allied to mass spectrometry and spectroscopic methods. It has revolutionized the analysis of complex volatiles in the same way that liquid and paper chromatography have caused a sea change in the analysis of complex involatile bioorganic molecules. It has replaced previous tedious and time-consuming methods such as fractional distillation, which have largely been abandoned since its advent (but see later for a discussion of the online infrared methods now in an advanced state of development). The complex nature of catalysis product streams is illustrated by the chromatograph of a gasoline in **Figure 1**.

The acceleration of reaction rates by catalysts arises because of the lowering of the energy barriers through the formation of surface compounds. The energy released by the making of surface bonds facilitates the scission or rearrangement of bonds in the substrate molecule, as depicted in **Figure 2**. The surface bonds must be of intermediate strength; if they are too strong permanent bonding to the surface occurs, and if they are too weak the perturbations are too small. This gives rise to an optimum value of the enthalpy of formation of the surface intermediate and the so-called 'volcano' plots when catalyst activity is plotted against bond enthalpy.

GC cannot give direct information about these crucial surface intermediates, although ingenious experiments using radiolabelling experiments and normal kinetic analysis and numerical modelling can lead to information about their nature. Major advances in surface spectroscopic techniques have occurred since the 1960s allow the observation and quantitation of minuscule amounts (10^{-3} monolayers) of stable and metastable surface species.

However, there has sometimes been a short-sighted overemphasis of the results of these powerful and expensive techniques and a neglect of those from cheaper methods of final product analysis such as GC.

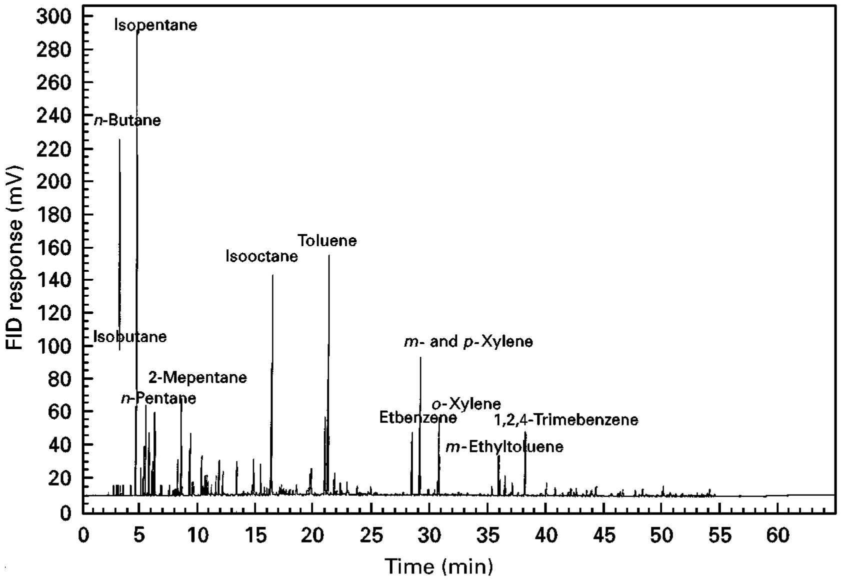

Figure 1 Chromatogram of a gasoline fraction (courtesy of Dr R. Malpas, Shell Research Ltd, Thornton Research and Technology, Centre).

There is the danger that the moieties seen by surface spectroscopies are mere spectators and not the active participants. Prudent researchers interlink surface science results with those from stable final product time profiles and conventional rate studies on the same catalyst. This problem has been highlighted in an elegant demonstration that the rates of ethene hydrogenation were invariant to the levels of the much studied surface ethylidenes. This underlines the essential importance of stable product analytical methods in catalyst research and evaluation. These are integral components for the study of catalysis in the multifarious reactor types in use, namely: batch, continuous stirred tank slurry, fixed and fluid bed, trickle bed, catalytic gauze and spinning basket.

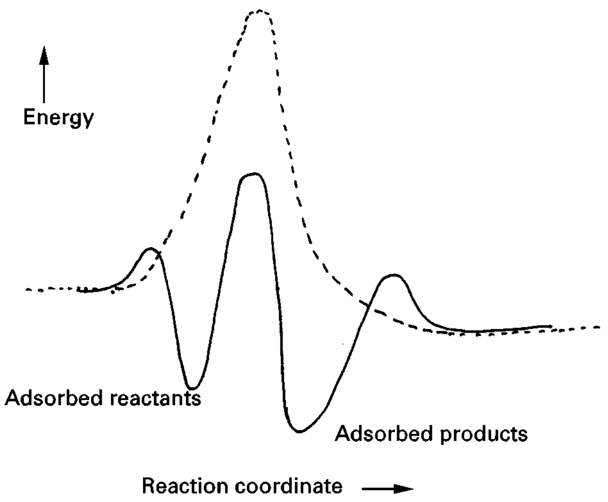

Figure 2 Energy diagram for a reaction occurring homogeneously and heterogeneously.

The high sensitivity of GC (detection limits of 0.1 to 1 ppm) enables very low conversions to be studied. This reduces the problems of poisoning by products of secondary reactions. GC is used routinely and extensively in laboratory research to find new catalysts and processes for existing and new products. It is also used in all the scale-up stages to full plant operation. The output of the plant is constantly monitored by GC and other methods of analysis and the results used to trim operating conditions to meet product specifications when there are changes in feedstock composition, flow rates, and reactor temperatures and pressures.

Conventional reactor studies can be readily automated by using multiple sample loop valves activated by signals from minicomputers, which also acquire and process the compositional data and GC conditions in digital modes. A semiautomatic pulsed small reactor system with a simple timing device for sampling at prescribed times and early data acquisition and processing methods was described as early as 1960.

A commercial laboratory rig incorporating GC is now marketed for catalytic studies at pressures of several hundred atmospheres and temperatures up to 350°C (Chemical Data Systems, Pittsburgh, USA). The pulse of products from the high pressure microreactor is depressurized in a multiple loop valve so that its pressure is compatible with that of the carrier gas stream into which it is injected. The unit is semiautomatic and data acquisition, processing and control is by a personal computer (PC).

The very ease of using GC routinely often means that the technique is not mentioned in the title of research papers in the open literature, in much the same way that the use of NMR is often assumed and not noted in papers on synthetic organic chemistry. Perusal of recent issues of journals such as the *Journal of Catalysis* and the *Journal of Applied Catalysis* indicate that about 40% have used GC for product analysis, while a BIDS search of the years 1991–97 shows the linking of GC with catalysis in about 90 papers each year.

It is worth emphasizing that process improvement is more common than purposeful or serendipitous invention and discovery. This is because large companies prefer to expand and advance by steady or even marginal changes associated with low risk rather than to initiate new high risk processes requiring large capital investment and many years of negative cash flows and long payback periods. An example is hydrocracking, which was not considered worthwhile by most of the oil companies until Chevron (California, USA) brought the first hydrocracking plant on stream in the mid-1960s – competition is as much the mother of invention as necessity! The scale of operations provides the motivation for marginal improvements; a catalyst that increases the yields of a product by 1% can earn £1 million per annum if product turnover is £100 million p.a. It is in such marginal improvements that GC can prove so valuable because of the ease of measuring such small changes in product yields.

GC has played a role in the development of devices to protect the environment from the complex chemical wastes from the chemical semiconductor and electroplating industries. It was used in the development of the remarkable 'three-way' catalytic converter fitted into motor vehicle exhausts. The simultaneous oxidation of carbon monoxide and unburnt hydrocarbons alongside the reduction of nitric oxide in the same catalyst bed exposed to widely different exhaust compositions and temperatures from ambient to 1000°C) is a major chemical and engineering achievement. Even the humble kitchen stove has been rendered self-cleaning by incorporating manganese dioxide/zeolites/ferrites into its glass enamel coatings. The application of catalysis and GC in environmental protection is increasing in importance.

Microcatalytic Chromatographic Technique

The microreactor is probably the most direct link between GC and catalysis and has been widely used for catalyst research since it was first described in 1955. A schematic of the system is shown in **Figure 3**. The principle of this 'one shot' technique is simple. A small catalytic reactor is placed as near as possible to the entrance of a GC column. Small pulses of reactant are injected into an inert or reactive carrier gas stream just before the reactor. Reaction takes place in the catalyst bed and the unconverted reactant pulse together with volatile products are swept into the GC column where the components are separated in the usual way and then detected by a rapid response microthermal conductivity detector. A useful adjunct, employed even in the earliest studies, is to place a Geiger detector in the exit stream from the thermal conductivity detector so that the radioactivity of each peak can be determined. This extends the method to include tracer experiments using ^{14}C- and tritium-labelled compounds. The advantages and disadvantages of the microreactor are listed below.

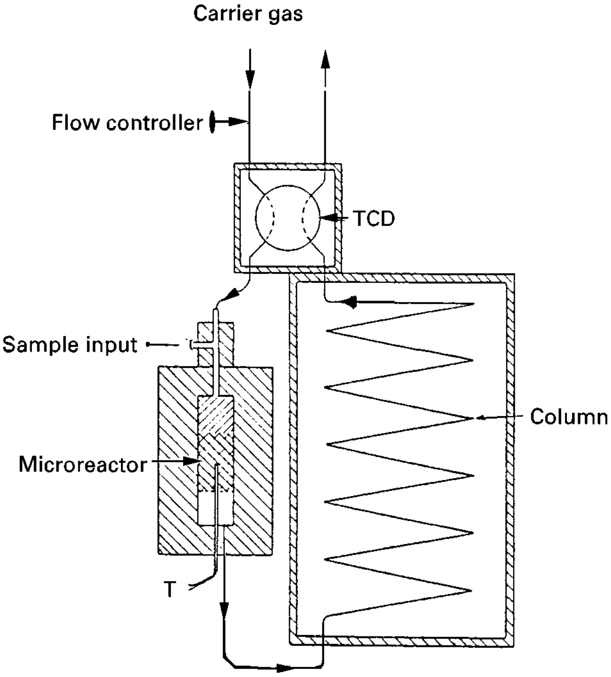

Figure 3 Schematic of a microcatalytic chromatographic reactor. TCD, thermal conductivity detector.

Advantages

1. Rapid surveys of new or modified catalyst are possible, enabling rapid assessment of whether the changes in catalyst formulations have been beneficial or detrimental (but see item 6 below). The rate of acquisition of results ultimately depends on the speed of analysis; because of its relatively slow speed, the interval between successive pulses can be tens of minutes in packed columns but less

in the high speed wall coated open-tubular columns (WOTC) now available.

2. The high sensitivity of GC enables very small reactant pulses to be used with a consequent reduction in the risk of poisoning active sites by trace impurities.
3. Radioactive tracer experiments are straightforward, enabling the path of individual reaction sites in reactant molecules to be tracked into the product molecules.
4. By careful analysis of the changes in product yields with changes in flow rate (contact time) and sample size, the rate expression of the reaction can be established and rate constants and Arrhenius parameters estimated (but see Disadvantage 2).
5. The technique is particularly well suited for kinetic isotope experiments. Alternate pulses of a deuterated and protonated reactant can be injected into the microreactor so that their reactions are compared on exactly the same catalyst sample under identical conditions. Very accurate measures of primary and secondary kinetic isotope effects (the ratio k_D/k_H) can obtained and subtle mechanistic detail unravelled.
6. Poisoning effects can sometimes be monitored if the activity of the catalyst is found to diminish with successive pulses, an aspect that can be enhanced by using longer contact times or larger pulses.
7. The developments in data acquisition, storage and processing, coupled together with the use of highly reproducible and readily automated loop sampling valves, benefit and facilitate the use of the microcatalytic reactor for mechanistic and kinetic studies and for catalyst screening.

Disadvantages

1. Steady-state conditions are often not achieved in the short contact times used in microreactors. This can be useful for kinetic studies, but is a disadvantage for screening tests of a new catalyst or a new formulation since the catalyst will usually operate commercially in a continuous flow configuration, where steady-state or pseudo steady-state conditions prevail.
2. Accurate measures of the residence time of the reactant pulse in the catalyst bed are essential for reliable kinetic measurements. The time cannot be calculated simply from the outlet gas volumetric flow rate and the bed volume because of the considerable pressure drop between the reactor and the end of the GC column, which varies with flow rate. The corrected residence tine t_r is determined from the following equation derived by application of the gas laws to the exiting carrier gas flow rate:

$$t_r = \frac{2aL}{3V_0}\frac{P_r T_0}{P_0 T_r}\frac{(P_i/P_r)^{3/2} - 1}{(P_i/P_r)^2 - 1}$$

where L is the reactor length and a its cross-section; V_0, P_0 and T_0 are the volume flow rate, pressure and temperature at the end of the GC column; P_i and P_r are the pressures at the inlet and outlet of the reactor.

Nonlinear first-order plots result if the uncorrected residence time is used, whereas excellent linearity is obtained by using corrected residence times.

3. If the carrier gas is itself a reactant, its depletion in the gas pulse leaving the reactor can result in artefacts because of changes in detector sensitivity when the pulse components pass through the detector. This can be avoided by split stream techniques. In microreactor studies of the dehydrochlorination of 1,2-dichloroethane, air was used as the carrier gas to eliminate the builid-up of carbonaceous poisons when inert carrier gases were used. The problem of different amounts of oxygen feeding into the flame ionization detector (FID) flame at different flow rates was overcome by splitting the stream leaving the GC column, so that the air supply to the flame could be held constant by venting different amounts of excess air through a control valve in the column exit stream. Peak broadening and overlapping occurs in the catalyst bed and in the dead volume between the end of the reactor and the beginning of the GC column, leading inevitably to some loss of resolution.
4. The data obtained are inherently integral despite the small contact times used, so that the technique is not readily adapted to give differential reaction kinetics.
5. Most catalyst laboratories will probably use microcatalytic chromatographic reactors in the near to medium-term future, especially since high speed numerical computer methods are now available to model the differential equations of flow and reaction in these reactors. These results place rigorous and stringent tests on the reaction mechanisms proposed and reliable estimates of rate parameters for some of the rate-determining steps can result. These numerical modelling techniques are much better than the use of the approximate though complicated rate expressions, which contain functions of many rate parameters often conjoined and requiring much ingenuity and chemical intuition to untwine. However, the necessity for intricate valving, pressure and temperature corrections, and computer control and data acquisition

and processing, leads to a loss of the essential simplicity of the microreactor technique. These elaborations may lead researchers into using conventional catalytic reactors with proscribed switching of the reacted gas streams into multi-loop sampling valves linked to GC and GC-MS analysers.

Chromatographic Catalytic Reactors (CCR): the Use of Fluid Logic Modules

A GC catalytic reactor deliberately combines the chromatographic separation of components with a catalytic function in the same reactor bed. The technique, first described in 1956, is a variant of the microcatalytic reactor just discussed. The reactor, in conjunction with pulse techniques, can be used for yield enhancement by displacing equilibria and for preserving primary products from secondary reactions with one of the reactants. The yields of primary products from a conventional catalytic reactor are ultimately limited, either thermodynamically through the value of the equilibrium constant, or kinetically by consumption of primary products, which often react more rapidly with one of the reactants, such as oxygen, than does the other reactant, such as an alkene or alkane. Both these limitations can be avoided in a chromatographic catalytic reactor (CCR). The equilibrium limitation arises because the catalyst accelerates the second-order back-reactions as much as it does the forward reaction. The back-reactions may be minimized by chromatographically separating the products from each other. **Figure 4** illustrate the case for the simple equilibrium, $A = B + C$. The back-reaction can only occur in the initial regions of the column where there is overlap between the B and C peaks. If the bed is long enough, then complete conversion of A into B and C is possible. The laws of thermodynamics are not broken because the equilibrium limitation is circumvented by an energy input to maintain the gas flow and peak separation. By CCR it has been possible to achieve virtually complete dehydrogenation of cylcohexane to benzene at temperatures where the equilibrium constant was $10^{-3}\,\mathrm{mol\,L^{-1}}$. The yields of useful primary products such as alcohols and epoxides are often low because of their rapid secondary reactions. The secondary reactions can be reduced chromatographically by holding back the primary product on the catalyst surface while the reactant pulse rapidly sweeps down the column because of its lower retention. **Figure 5** illustrates the simplified situation for the reaction sequence given below:

$$\mathrm{RH} + \mathrm{O_2} \rightarrow \mathrm{ROH} \qquad [\mathrm{I}]$$

$$\mathrm{ROH} + \text{“O”} \rightarrow \mathrm{CO_2} + \mathrm{H_2O} \qquad [\mathrm{II}]$$

The occurrence of reaction [II] can be reduced by rapid separation of the reactant pulse containing oxygen from the ROH formed and retained in the catalytic chromatographic column. By using a silica-supported silver oxide CCR, large quantities of crotonaldehyde have been preserved in the catalytic oxidation of but-1-ene. The lifting of both the thermodynamic and kinetic limitations is enhanced by using narrow injected pulses. Injectors based on fluid logic modules, which have no moving parts and none of the intrinsic delays of actuating the opening and closing of solenoid valves, are ideal for this task and have previously been used for fast GC analysis. Pulses down to 10 ms have been generated and further reductions are possible.

Process Monitoring and Control

The wealth of detail given by GC about the composition of streams leaving reactors and purification units such as distillation columns can, in principle, be used for manual, semiautomatic or fully automatic process

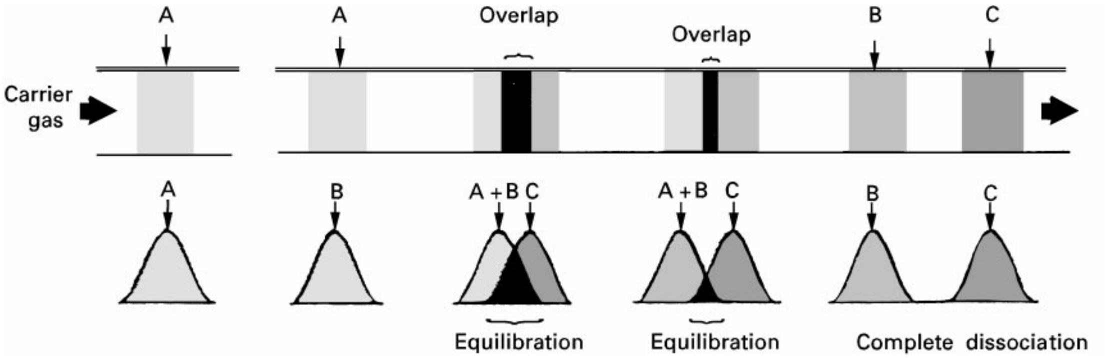

Figure 4 Illustration of how the equilibrium, $A \rightarrow B + C$, is displaced in a GCC reactor.

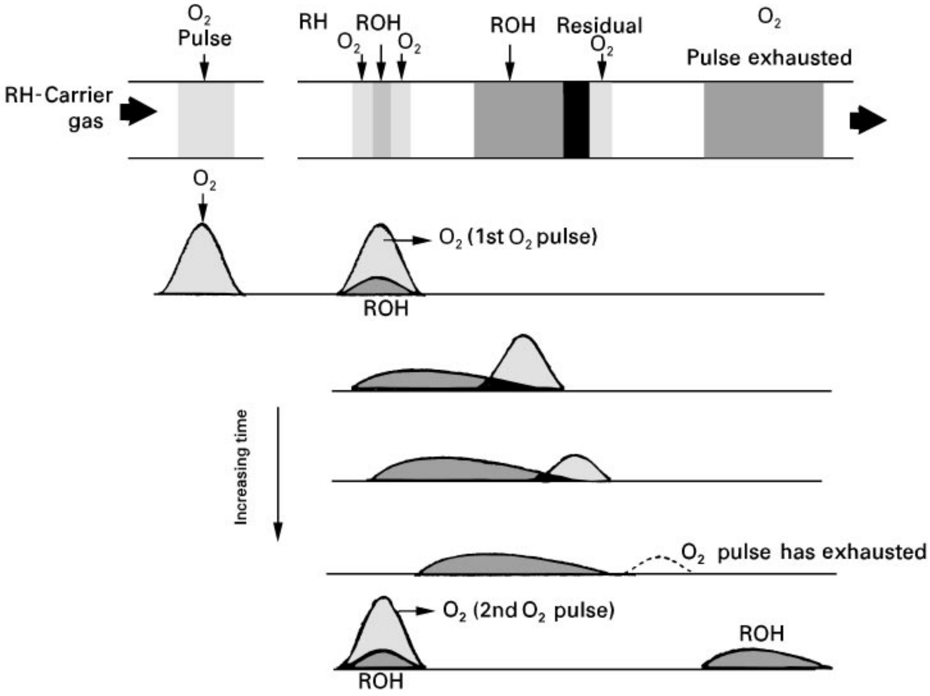

Figure 5 Illustration of how a primary product, ROH, is preserved from secondary reactions with oxygen in a GCR.

control. Automatic GC has been applied to determine gasoline components and a linear algorithm has been developed relating Reid vapour pressures, boiling points and ASTM distillation curves to component indices with good correlations and repeatability. The method has been developed further to enable the RON of a gasoline to be determined automatically by GC analysis with a standard deviation of only 0.09 for RON values in the range 90 to 100. The method has not yet been taken to the point of closing a control loop so that a reactor or a distillation column is controlled by GC, although this closure is feasible.

GC suffers as the control element because of the time needed for analysis. The response time of the plant must be longer than the time for analysis, which is usually tens of minutes, and there is a clear need to develop faster GC based on short narrow-bore open-tubular columns and variants. It is relevant that a method called the 'optical octane dipstick' is now being used in many refineries. This uses a nondispersive near-infrared analyser (NIR) to determine the absorbence at five wavelengths. Apparently a very good measure of RON is obtained from an algorithm linking these absorbencies to ASTM/RONs determined in a standard Petter engine. Clearly this spectroscopic method is faster than GC but can only be used for a narrow range of RONs and composition. The more detailed compositional description by GC analysis could outweigh its present relative slowness. The NIR control units already in use pave the way forward by posing a challenge to the analyst to speed up chromatographic methods. If the challenge can be met, then the closing of control loops for catalytic reactors based on GC will follow.

Current Trends and Future Prospects

Table 3 lists some of the recent developments that are close to commercial realization together with more speculative, but possible, advances in the new millennium. GC will play an important part in the catalyst

Table 3 Current trends and future prospects

Gas turbines for electricity generation powered by catalytic combustion of natural gas and biomass
Better electrochemical catalysts with high durability for fuel cells based on methaonl and eventually hydrocarbons
Production of propene oxide by the catalytic partial oxidation of propene
Home and hospital hygiene based on catalyst-containing surface coatings
Treatment of commercial and domestic waste
Search for power generation from renewable resources and sunlight-activated catalytic dissociation of water into hydrogen and oxygen
Enzymes immobilized on rugged supports may provide ways of fixing nitrogen at ambient temperatures and also of achieving commercial chiral synthesis
Closing of control loops for catalytic reactors, distillation columns, etc., based on GC analysis of product streams and neural control networks

theories and technologies that will be needed to bring these ideas to fruition. The tasks are challenging, even formidable, and require the commitment of scientists and engineers as well as the provision of vast funds for research, development and capital investment by governments and industry.

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CATALYST STUDIES: CHROMATOGRAPHY

Isolation: Magnetic Techniques

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The first experiments with magnetic separation of cells date from the 1950s when lymphocytes were magnetically separated after *in vitro* phagocytosis of iron granules. The real boom in the application of magnetic labels for cell isolation came in the 1980s and since then an enormous amount of work has been done in both the development and application of this technique.

Magnetic separation of cells has several advantages in comparison with other techniques. In general, the magnetic separation procedure is gentle, facilitating the rapid handling of delicate cells in an unfriendly environment. It permits the cells of interest to be isolated directly from crude samples such as blood, bone marrow, tissue homogenates, stools, food, cultivation media, soil and water. The cells isolated by magnetic separation are usually pure, viable and unaltered. Magnetic separation is a simple, fast and efficient procedure and the whole separation process can be performed in the same tube. Large differences between magnetic permeabilities of the magnetic and nonmagnetic materials can be exploited in developing highly selective separation methods. The separation procedure can easily be scaled up if large quantities of living cells are required.

Principles of Magnetic Separation of Cells

Two types of magnetic separation can be distinguished when working with cells. In the first type, cells to be separated demonstrate sufficient intrinsic magnetic moment so that magnetic separations can be performed without any modification. There are only two types of such cells in nature: magnetotactic bacteria containing small magnetic particles within their cells and red blood cells (erythrocytes) containing high concentrations of paramagnetic haemoglobin. In the second type, cells of interest have to be tagged by a magnetic label to achieve the required contrast in magnetic susceptibility between the labelled and unlabelled cells. The attachment of magnetic labels is usually attained by the use of affinity ligands of various types, which can interact with target structures on the cell surface. Usually antibodies