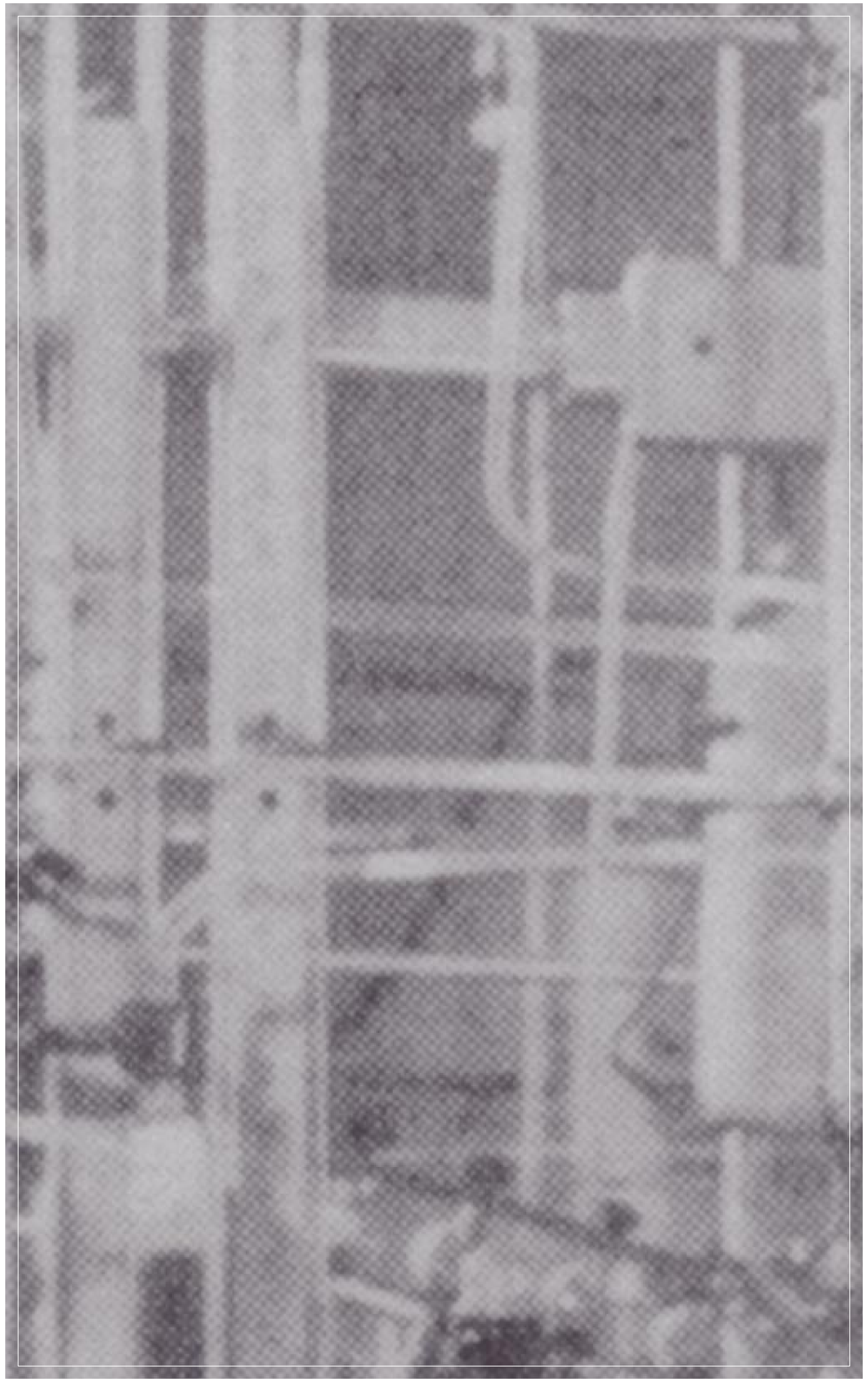


(1950 - 1999)

Industrial developments

“Science clears the fields on which technology can build” Werner Heisenberg

Some 80% of chemical processes use catalysts whose sales are approximately $\$10^{10}$ but which is less than 1% of the revenue from the products they create! It is little wonder that there have been worldwide investments by both Governments and Industry in research in the field of catalysis and that the catalyst market is increasing at an annual rate of nearly 10%. The United Kingdom through its Foresight Challenge Initiative highlighted catalysis as a priority area for funding and from which emerged the Institute of Applied Catalysis (IAC) a partnership between Government, Industry and Universities and analogous to that which led almost simultaneously was created in the Netherlands, the National Institute for Catalysis Research (NIOC). In the USA a report was published as a result of a Workshop held in 1997 at the A.C.S. Headquarters in Washington outlining the future needs of the Chemical Industry in the area of Catalysis. Two major goals were delineated: (a) an acceleration of the catalyst development process and (b) the development of catalysts with selectivity approaching 100%. Catalysis was seen worldwide as a key to the future of the chemical industry and mankind with a recent Department of Energy (U.S.A.) initiative, the Catalysis Research Symposium held in New Mexico (Cat. Tech., 3, 42, 1999), drawing together the projects underway in the National Laboratories directed towards “supporting potential commercialization and/or eco-friendly chemistry”. It was recognised that catalysis needed to be promoted more aggressively in the USA if it was to improve its funding position.

It was the world-wide demand for energy after the Second World War and the emergence of large oil fields in Saudi Arabia in the mid 1940s, resulting in the availability of relatively cheap petroleum, that provided the impetus for the expansion of catalytic processing. Prior to the Second World War (1900-1940) the chemical industry was coal-based with emphasis on ammonia synthesis, production of nitric acid, fat hardening and methanol synthesis. The development of the petrochemical industry was rapid in the early 1950s which resulted in new fuels becoming available, the growth of the polymer industry, the significance of selective oxidation, hydroformylation and other homogeneous reactions. The discovery of large supplies of natural gas (for example in the North Sea) stimulated interest in hydrocarbon chemistry and with the “oil crisis” in the mid-1970s there was pressure on the efficient use of energy and raw materials. In addition legislation regarding environmental aspects including both the problems of pollution by automobile exhaust gases and industrial emissions were factors which required attention and where heterogeneous catalysis emerged as playing a crucial role.

The milestones reached in industrial catalysis in the 20th century, and which testify to its significance in wealth creation, were highlighted by Thomas and Thomas in 1997 (see below).

Heinz Heinemann at the 11th International Congress on Catalysis - the 40th Anniversary Meeting - focused on a number of major developments in catalytic technology between 1956 and 1996. They were Ziegler-Natta catalysis; steam reforming using $NiK_2Al_2O_3$; catalytic cracking with faujasite zeolites; bimetallic catalysis; low pressure methanol synthesis; autoemission control; gasoline from methane; selective oxidation using $TiSiO_2$ and metallocene catalysis. The low pressure methanol process developed by ICI at Billingham, led to some 80% of the world production of methanol being produced using the copper-zinc oxide catalyst

Milestones in the introduction of industrial heterogeneous catalysis during the 20th 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 (sulphuric acid production)	V_2O_5
1930	Catalytic cracking of oil (fixed-bed, Houdry process)	Montmorillonite clays
	Expoxidation 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 decolorization 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
	Hydrodesulphurization	(Co, Mo) sulphides
	Hydrotreatment of naphtha	$C0-Mo/Al_2O_3$
	Oxidation of naphthalene to phthalic anhydride	(V, Mo) oxides
1960	Oxidation of butene to maleic anhydride	(V, P) oxides
	Oxidation of propylene to acrolein	(Bi, Mo) oxides
	Ammoxidation of propylene to acrylonitrile	(Bi, Mo) oxides
	Improved means of reforming hydrocarbons	Pt-Ir on Al_2O_3
	Pt-Re on Al_2O_3	
	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
	Oxychlorination of ethylene to vinyl chloride	Cu chloride
	Triolefin process (propylene to butene and ethylene)	$Mo(CO)_6$ or $W(CO)_6$ on Al_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)	$CuO/ZnO/Al_2O_3$
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 to 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-methylopropylene	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 to ethylbenzene	H-ZSM-5
	Methanol to gasoline (petrol) (MTG)	H-ZSM-5
	Conversion of ethylene and acetic acid to vinyl acetate	Pd
	Oxidation of t-butanol to methyl methacrylate	Mo oxides
	Improved means of liquefying coal	(Co, Ni) sulphides
	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 Conversion of light alkanes to arompatics	Ga-ZSM5
	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-1-ene to 2-methylpropylene	H^+-Ferrierite H^+-Theta-1 (acidic zeolites)
	Isomerization of oxime of cyclohexanone to -caprolactam	Silicoalumino-phosphate molecular sieve (SAPO-11)
	Ammonoxidation of cyclohexanone to its oxime using H_2O_2	Ti-silicalite

introduced in 1972. A spin-off for the academic community was the generous sponsoring of fundamental research of catalysis at copper surfaces. In a similar way Johnson-Matthey encouraged academic interest in motor-car exhaust catalysis with, in both, cases E.P.S.R.C. - one of the United Kingdom's Research Councils - playing an important role.

The significance of methanol synthesis via 'syn-gas' as a route to diverse chemical products is illustrated below (taken from "Principles and Practice of Heterogeneous Catalysis" Thomas and Thomas, 1997).

Selective oxidation including both dehydrogenation and oxydehydrogenation, particularly for the conversion of butane and butenes for MTBE production, has also been of major interest with reactor design and process engineering making significant improvements to the technology.

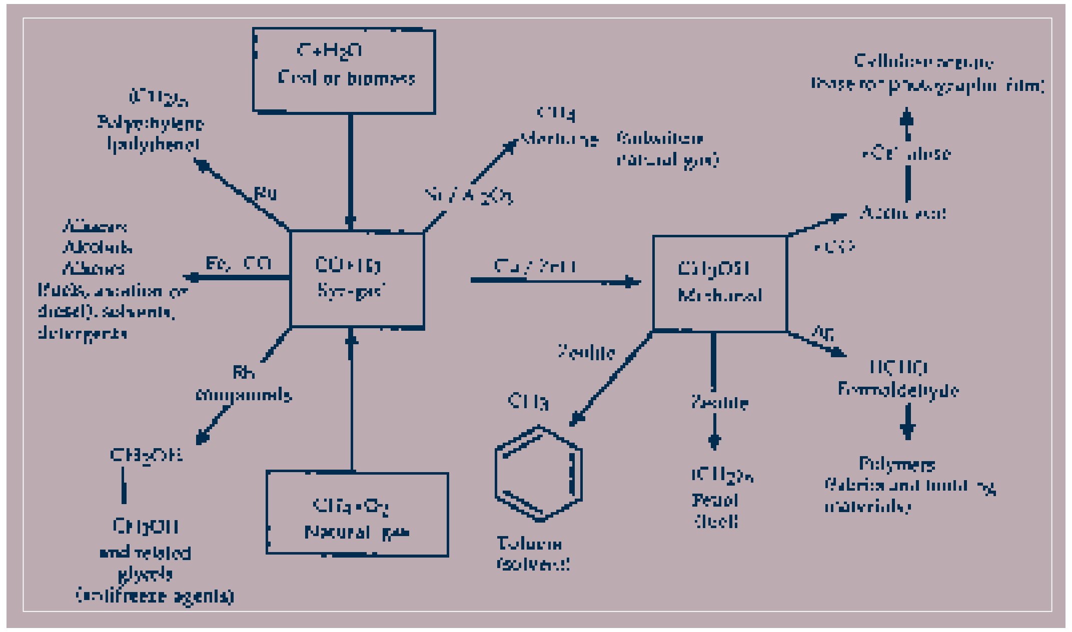
It was Johnson Matthey in the late 1960s that initiated developments in catalyst technology for controlling gaseous pollutants such as NO_x in "tail gas" from nitric acid plants and the destruction of odours from food processing facilities. The catalysts were based on the platinum group metals with a rhodium promoted platinum catalyst being effective for the reduction of NO_x by methane. The 1970 USA Clean Air Act was the driving force for reducing emissions by cars and by 1975 catalytic converters were seen as the chosen route after Johnson Matthey successfully demonstrated the benefits of platinum containing catalysts to clean up car exhausts. The first work was done at their research laboratories at Wembley (England) but by 1971 sample manufacture had been transferred to the new Catalyst Development Laboratory at Royston. Monoliths for the catalysts were supplied by Corning Glass and 3M-American Lava in the U.S.A. with ICI in England inventing some key processing methods which facilitated full scale production.

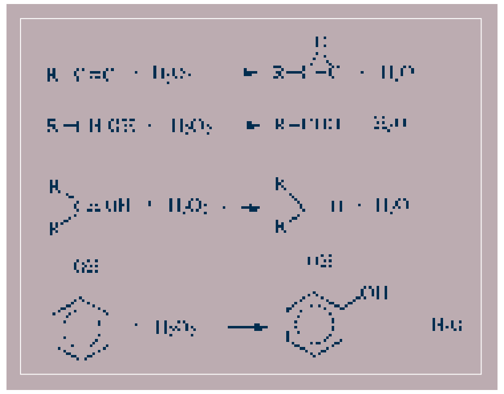
Early concepts used two catalysts: the engine was run slightly rich to enable reduction of NO_x over Pt/Rh then air was introduced so that the second catalyst oxidized the residual CO and hydrocarbons. The first catalyst had to be highly effective in reducing NO_x to N_z because if NH_3 was generated it would be oxidized over the second catalyst to NO_x.

$$2CO + O_2 \rightarrow 2CO_2$$

$$(8n+2m)NO + 4H_mC_n \rightarrow (4n+m)N_2 + 2mH_2O + 4nCO_2$$

$$2NO + 2CO \rightarrow N_2 + 2CO_2$$





The first autocatalyst production pieces were supplied for Volkswagen by the Royston plant in 1974 and by the early 1990s other larger facilities had been built in Brussels and Sydney with the world's largest plant in Wayne (Pennsylvania). A recent article by Twigg has reviewed progress over the last 25 years in autocatalyst technology. The Johnson-Matthey Team under Gary Acres was awarded the Queen's Award for Industry for its innovative contributions to the development of autocatalysts in 1976. It was the development of the automotive catalysts that made Pt-Rh the largest volume of catalysts produced replacing catalyst cracking catalysts.

In 1991 the use of metallocene-catalysed polymerization reactions became commercial technology for the manufacture of polyethylene and polypropylene - these accounting for nearly 40% of all thermoplastics and elastomers. Metallocenes are also now finding use in the formation of novel polymers which may well be competitive with the more traditional polymers, nylon, polycarbonates and polyesters. From an academic point the metallocenes are of particular interest in that they are single site catalysts comprising a metal atom sandwiched between parallel planar cyclopentadenyl groups. Equally significant are the development of titanium silicates as oxidation catalysts of which TS-1 is an example enabling highly selective oxidations to take place using hydrogen peroxide in the presence of oxygen as an oxidant to give epoxides (see below).

As mentioned earlier interest in the synthesis of pharmaceuticals and fine chemicals has increased with organic synthesis acquiring more significance in catalytic chemistry. Zeolites have, for example, found to be useful in synthesis reactions leading to greater selectivity and therefor able to achieve the demands that environmental legislation now puts on the chemical industry.

In discussing future priorities, the Catalyst Technology Roadmap Report, involving both industrialists and academics in the U.S.A., identified the following as being most crucial:

- Make design of catalysts possible through a combination of experiment, mechanistic understanding and computational chemistry.
- Develop methods for high throughput testing and synthesis of catalysts.
- Improve in situ techniques for catalyst characterization.
- Develop methods for the synthesis of catalysts with specific site architecture.

Regarding the areas where improvements in catalyst technology could have the greatest impact the Report highlighted Selective Oxidation; Alkane activation and Byproduct and Waste minimisation.

We should also not lose sight of the role of heterogeneous catalysis in the troposphere - the significant that solid aerosols, natural liquids and photoinduced reactions play in the chemistry of the earth's atmosphere. Although reactions may be slow, the enormous volume of the earth's atmosphere can result in huge amounts of reaction products. Studies of such reactions are only just beginning although the role of water vapour in heterogeneously catalysed reactions, such as the hydrogenation of nitric oxide at low temperature, was studied by photoelectron spectroscopy some years ago. Both bond cleavage and hydrogenation to generate immide species were facile.

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"Chemistry without catalysis would be like a sword without a handle, a light without brilliance, a bell without sound."

Alwin Mittasch