

Twenty-Five Years of Autocatalysts

By Martyn V. Twigg

Catalytic Systems Division, Johnson Matthey, Royston

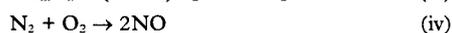
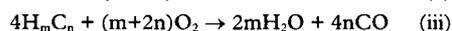
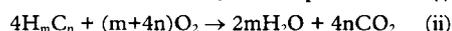
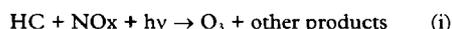
A quarter of a century ago the first autocatalysts were manufactured on a commercial scale by Johnson Matthey at Royston, near Cambridge, in England. This article looks at the background to this major contribution towards cleaning urban air and briefly traces the progress of car catalyst technology since the work of the early autocatalyst pioneers.

As early as the 1940s, some large cities had begun to experience problems of atmospheric pollution. The Los Angeles' basin in the U.S.A. was particularly affected, experiencing frequent natural ambient temperature inversions, which trap and recycle polluted air. Mass production of cars, powered by the internal combustion engine, was then giving tremendous personal mobility, but the very large numbers in cities were understood to be a major source of the man-made urban emissions (1).

Photochemical interactions between hydrocarbons and nitrogen oxides from car exhaust and oxygen occur in the lower atmosphere, forming ozone-containing "photochemical smog", Equation (i), identified as an important contributory factor to the pollution. The oxidation of fuel to carbon dioxide and water in engines, Equation (ii), was far from completely efficient. Unburned hydrocarbons and partially combusted products, particularly carbon monoxide (CO) and to a smaller extent oxygenates, such as aldehydes, were present in the exhaust gases*. Relatively high levels of CO were formed, Equation (iii), and, under the forcing conditions in the engine, nitrogen (N₂) and oxygen (O₂) reacted to establish a partial equilibrium with nitric oxide (NO), Equation (iv). Appreciable amounts of NO and its oxidised form, nitrogen dioxide (NO₂) (together referred to as NOx) can be present in exhaust gas.

The three major pollutants in exhaust gas are therefore HC, NOx and CO. Subsequent photoinduced reactions of the first two pollutants with oxygen forms ozone, which is a strong irritant, as well as low levels of other compounds,

notably peroxyacetyl nitrate, which is a very strong lachrymator irritant (3).



Johnson Matthey Targets Research

In the late 1960s, in the U.K., Johnson Matthey was developing catalyst technology to control the gaseous pollutants from industrial applications, such as the reduction of NOx in "tail gas" from nitric acid plants, and the destructive oxidation of odours from food processing facilities. These used catalysts based on platinum group metals (PGM); for instance, the reduction of NOx in tail-gas by methane (CH₄) was achieved particularly effectively over a rhodium (Rh) promoted platinum catalyst.

In the U.S.A. the 1970 Clean Air Amendments Act was the driving force to reduce emissions from cars. Political pressures from the environmental lobby had resulted in Senator Edmund Muskie announcing a plan to reduce emissions from cars by 90 per cent and highlighted the need to develop specific technology for automotive pollution control. The clean air legislation was also to apply to manufacturers exporting cars to the U.S.A. It was appreciated that engine modifications could provide improvements to emissions, but that additional measures would be needed after model year 1975 to comply with more stringent Federal and Californian limits. Catalytic converters became the chosen route after Johnson Matthey successfully demonstrated the positive benefits of

* Unburned hydrocarbons and oxygenated species are referred to as "hydrocarbons" and designated HC (2).

platinum-containing catalyst to clean up car exhaust (4). This resulted in demand by car manufacturers for samples of catalysts for test programmes, and by Johnson Matthey for their own projects.

The first work done by Johnson Matthey was in England at the Research Laboratories, at Wembley, in west London. But at the end of 1971 sample manufacture was transferred to the new Catalyst Development Laboratory at Royston and the Wembley research scientists concentrated on developing new catalyst technologies.

Catalyst Structures

Initially two catalyst structures were tested: pelleted catalysts, similar to those used in chemical industries, and "monoliths". In a monolith, the catalyst volume is a single structure with many small open channels running along its length, like a honeycomb. Johnson Matthey concentrated on "monolithic" catalysts, through which the hot exhaust gas from the engine would pass for conversion of pollutants to harmless species. This structure caused only a small drop in exhaust gas pressure, and its low heat capacity caused it to become hot quickly in use. Additional benefits of monoliths were that they did not suffer the attrition/erosion problems of pellets. Today, monoliths are the basis of all autocatalysts, and typically they have 400 cells inch^{-2} . Later Johnson Matthey developed some novel metal-based versions and experimented in making ceramic monoliths, but early monoliths were supplied mainly by Corning Glass and 3M-American Lava in the U.S.A.

Corning monoliths were prepared by an extrusion method which is now the standard route. In England, Imperial Chemical Industries (ICI) were also working in this area and invented some key processing methods which facilitated full-scale production (5).

The 3M company used a paper layering technique, with alternate layers of flat and corrugated sheets, which were impregnated with a suspension of ceramic oxide powders before firing to remove the paper and give a rigid monolith. These two processes gave products with different properties, but neither type of mono-

lith had catalytic activity itself. Cordierite ($2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$) which has a low coefficient of expansion, made it the material of choice for ceramic monoliths, and is still used today.

Catalyst Formulation Developments

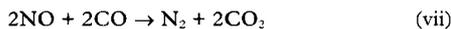
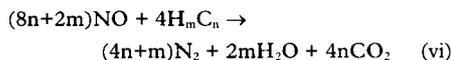
Initially, catalysts containing nickel, copper, cobalt or iron, similar to those used in the production of methanol and ammonia (6) had been assessed as autocatalysts, but had insufficient activity, especially at low temperatures. Moreover, they were very susceptible to poisons derived from the fuel. The catalysts eventually chosen were based on the highly active PGMs (7).

Although PGMs are more poison resistant than base metal catalysts, sulfur and lead did affect their performance, lead being the worst, as it forms an inactive alloy with the active catalyst metallic phases (8). These had already been recognised in the U.S.A. as harmful, and "cleaner" gasoline was being introduced. Unleaded gasoline is needed for catalysts to control automotive emissions, and this was introduced first in the U.S.A. and later, increasingly, around the world. The environmental benefits from this in itself are very significant.

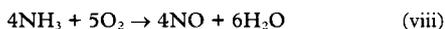
Depositing PGM directly on the monolith channels gave poor catalyst performance: because there was little to prevent small metal crystallites from migrating and coalescing to large crystallites with low surface area. Therefore, the Wembley research group developed technology to increase the surface area available to the PGM by providing the monolith with a higher surface area material. This was based on alumina (Al_2O_3) with stabilising additives and a process was developed to coat monoliths with a high surface area "washcoat". The washcoat had to be even, and not block the channels, while adhering strongly to the substrate. The washcoat rheology was critical during coating. Expertise was soon developed, and high performance catalysts were manufactured and employed on cars (9).

For a few years, the emissions limits could be met by oxidation of HC and CO and exhaust gas recycle (EGR), as in Equations (ii) and (v).

However, legislation tightened and it became necessary to control NO_x emissions. The only way to do this was to reduce it catalytically to nitrogen (N₂), as in Equations (vi) and (vii):



Early concepts used two catalysts: the engine was run slightly rich to enable reduction of NO_x over a Pt/Rh catalyst, then air was introduced between the catalysts to enable the second one to oxidise remaining CO and HC. It was important that the first catalyst reduced NO_x to N₂ with high selectivity, because if ammonia (NH₃) was formed, it would be oxidised over the second catalyst to NO_x according to Equation (viii).



Development of Three-Way Catalysts

From earlier experience with catalytic NO_x reduction with CH₄, Johnson Matthey had developed low light-off Pt/Rh oxidation catalysts which were used by some European car manufacturers (10). With them, if the engine was operated close to the stoichiometric point (the air:fuel ratio corresponding to complete combustion), some NO_x control was obtained via reduction, even though oxidation reactions were taking place. Suitable catalyst formulations were important in optimising this behaviour (11).

By 1979, oxygen sensors had been developed and placed in the gas close to the exhaust manifold to provide feedback control to the fuelling, so conditions could be maintained around the stoichiometric point using electronic control. This enabled good consistent catalytic performance, and the use of Pt/Rh catalysts to simultaneously control HC, CO and NO_x became the preferred system. Because all three pollutants were controlled with one catalyst, the concept was named the "Three-Way Catalyst", TWC.

Early TWCs had a narrow operating air:fuel range over which all three pollutants were removed, and from about 1980 they were almost universally fitted to cars sold in the U.S.A. Since

then effort has been directed towards improving catalyst performance: enhancing activity, thermal durability, selectivity and widening the air:fuel ratio operating window. Catalyst improvement went with increasingly sophisticated fuel management systems; carburettors gave way to single point fuel injection and then multi-point injection into the inlet manifold, and latterly direct injection into the cylinder.

Expansion at Royston

During the early 1970s washcoating processes were intensively investigated and developed, later to be transferred to Johnson Matthey plants around the world. At first, development activities and plant design phases ran in parallel. The rate of the initial process development and implementation was frantic and complicated by the Royston manufacturing area being too small for the anticipated increasing demand. An adjacent building, previously used for developing equipment for army tanks, had to be purchased.

In late 1973, construction of the first catalyst production line at Royston was completed. Contracts had been signed to produce catalysts for Volkswagen cars exported to the U.S.A., and negotiations were well advanced with Rolls Royce and British Leyland in the U.K. and with the Ford Motor Company in the U.S.A. The large number of catalysts needed in the U.S.A. required a big plant to be constructed there. Before this was done, a proving run was undertaken at Royston to demonstrate process viability. This was achieved in spite of the "three-day working week" resulting from the national miners' strike in December 1973. Electricity allocated to the Royston site was limited, so catalyst production was given all the available power: no other heating and lighting was permitted, and the run was very successful.

Shortly afterwards construction of a very large plant began at Wayne, Pennsylvania, to supply the U.S. market. The Royston plant was officially opened in February 1974, and by the end of April the world's first autocatalyst production pieces were being made for Volkswagen. Subsequently, other companies were supplied, and as production numbers increased, a second

line was installed at Royston. Development and introduction of new catalyst formulations then followed rapidly.

Global Growth

At an early stage Johnson Matthey invested extensively in test facilities in the U.K. and U.S.A. for evaluating autocatalysts on engines and cars. Initially work was done at Ricardo Consulting Engineers in Sussex, although a small test facility had been installed at Wembley. As demand for testing increased, an enlarged facility was built at Royston: four static engine cells, and a "rolling road" for making measurements on cars, all then state-of-the-art. Over the years, these underwent numerous improvements, until a major expansion to provide a modern "European Technology Centre" was opened in February 1995. This ongoing investment in R & D reflects the importance placed by Johnson Matthey on technical developments in this area. Indeed, Johnson Matthey now has Autocatalyst Technology Centres at Royston, in Pennsylvania (U.S.A.), Kitsuregawa (Japan), Gothenburg (Sweden) and at Curitiba (Brazil). In addition fundamental scientific aspects are worked on at the Corporate Technology Centre, near Reading, England, to where the original Wembley Research Laboratories moved in 1975.

The importance of Royston as Johnson Matthey's main European production unit diminished in the early 1990s after a much larger facility was built in Brussels and opened in 1991, to serve the growing European market. This followed a plant in Sydney, Australia, opened in 1985, and the world's largest plant, in Wayne (Pennsylvania, U.S.A.) which began production in 1974. Since the Belgium plant was built, further plants have been established in South Africa, Mexico, Malaysia, Argentina and India.

Recognition of the Pioneering Work

The importance of the technology developed by Johnson Matthey was recognised in 1976 by a "Queen's Award" for Technological Achievement. In 1980, five of the original autocatalyst team received the Fellowship of Engineering's MacRobert Award (12) and in

1992 two "Queen's Awards" were granted: for Environmental Achievement and for Export Achievement.

Conclusions

The development of autocatalysts has enabled major reductions in emissions from automobiles. Over a quarter of a century, many millions of tons of pollutants have not been released into the atmosphere. This has improved urban air quality, with many associated environmental benefits. Research and development continues to be pursued at the highest levels: new aftertreatment systems are being developed for lean-burn gasoline, diesel engines, and engines burning a range of alternative fuels, being some examples. It can be said that pioneering work still continues today on many environmental fronts, with the intention of bringing about yet further social benefits.

References

- 1 A. J. Haagen-Smit and M. M. Fox, *Ind. Eng. Chem.*, 1956, **48**, 1484
- 2 In Europe total hydrocarbons (THC), including the most difficult to oxidise methane, are measured, partially oxidised oxygenates are not. In the U.S.A. methane is excluded, but oxygenates are included in "non-methane organic gases" (NMOG)
- 3 R. P. Wayne, "Chemistry of Atmospheres", 2nd Edn., Oxford University Press, New York, 1996
- 4 G. J. K. Acres and B. J. Cooper, *Platinum Metals Rev.*, 1972, **16**, (3), 74
- 5 J. J. Benbow, L. W. Lord and D. J. Heath, *British Patent* 1,385,907; 1972; J. J. Benbow and J. Bridgwater, "Paste Flow and Extrusion", Oxford University Press, New York, 1993
- 6 M. V. Twigg, "Catalyst Handbook", 2nd Edn., Manson Publishing, London, 1996
- 7 J. C. Summers *et al.*, *Ind. Eng. Chem. Res. Dev.*, 1972, **11**, 2; G. J. Barnes, in: "Catalysis for the Control of Automotive Pollutants", *Advances in Chemistry Series* 143, ACS, Washington, 1975
- 8 M. Shelef, K. Otto and N. C. Otto, *Adv. Catal.*, 1978, **27**, 311
- 9 M. L. Church, B. J. Cooper and P. J. Wilson, SAE Tech. Paper, 1989, 890815; M. Shelef and H. S. Gandhi, *Platinum Metals Rev.*, 1974, **18**, (1), 2; E. J. Sercombe, *op. cit.*, 1975, **19**, (1), 2
- 10 G. J. K. Acres, *British Patent* 1,390,182; 1971
- 11 G. J. K. Acres, B. J. Cooper, A. F. Diwell and W. D. J. Evans, *U.S. Patent* 3,951,860; 1976; B. J. Cooper, W. D. J. Evans and B. Harrison, "Catalysis and Automotive Pollution Control", eds. A. Crucq and A. Frennet, Elsevier, Amsterdam, 1987, p. 117
- 12 The recipients were Gary Acres, Brian Cooper, Barry Cooper, David Evans and Dennis Webster