

Catalysts and the coming liquid fuel shortage



Fuel for cars of the future could come from many sources besides crude oil.

One of last year's petrol droughts in Sydney resulted from a combination of industrial strife and the closure of a refinery's 'catalytic cracker' for maintenance. As the city's population discovered, catalytic cracking, which involves the breaking of large hydrocarbon molecules to give the smaller ones needed in petrol, is an essential step in oil refining.

Another essential refinery operation is 'catalytic reforming'. In this process, hydrocarbon molecules are rearranged into similar-sized molecules with better anti-knock properties.

Both processes, and many more in the petroleum and petrochemical industries, depend on catalysis. In fact, some 90% of all chemical manufacturing processes require catalysts. A catalyst accelerates a chemical change and allows it to be accomplished more easily and selectively. Ideally, the catalyst is recovered unchanged from the reaction and can be used again and again.

The prospect of crude oil supplies falling seriously short of requirements poses a threat of future petrol droughts more severe than any experienced so far. Substitute liquid fuels will probably be needed — made from coal, natural gas, oil shale, wood, crop plants, and so on. Catalysts are certain to play vital roles in their production.

It would also be desirable to produce more petrol from every barrel of oil through improved catalysis in the refining process. A great deal of work is going on around the world on catalyst development for both oil refining and substitute-fuel production. Two CSIRO Divisions — those of Materials Science and Applied Organic Chemistry — and CSIRO's Fuel Geoscience Unit are among the Australian laboratories involved.

Zeolite catalysts

Many of the most important catalysts are constructed from refractory (heat-

resistant) oxides — for example alumina or silica. The oxides may be active in themselves, but often they serve as supports for highly active metals or their compounds — for example platinum or molybdenum sulphide. In catalytic processes, molecules of the reacting chemicals attach to the active sites of the catalyst, and as a result become more inclined to take part in the required reactions. Often, the details of what happens in the reactions are not at all well known.

The active catalytic material is mostly used in a finely dispersed form. This is because its activity is proportional to the exposed surface area. Small amounts of material can have remarkably large surfaces; just one gram of activated alumina, for example, can have a surface area of 400–600 sq m.

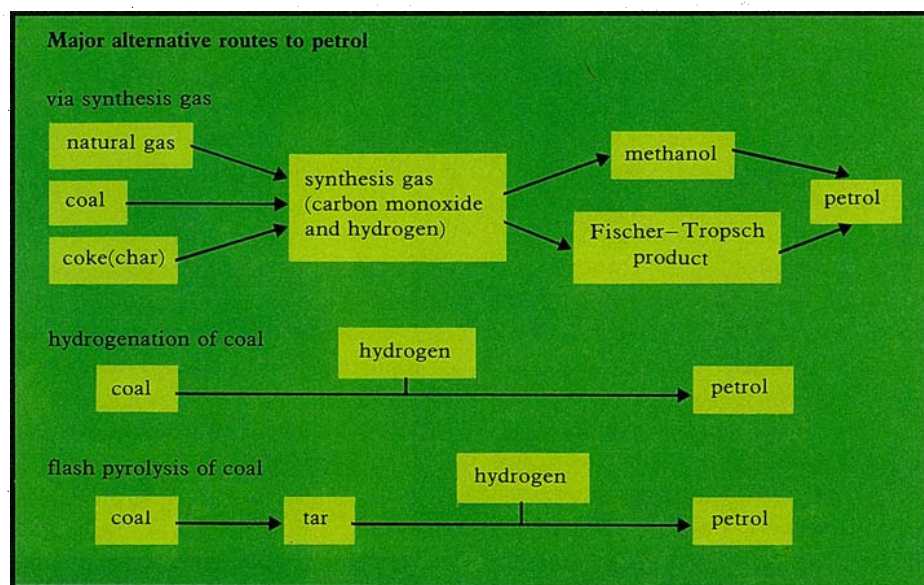
Scientists at the Division of Materials Science in Melbourne are excited at the prospects opened up by a new catalyst that shows promise of simplifying the production of petrol from a wide range of starting materials. Developed by Mobil Oil in the United States, the catalyst acts as a 'molecular sieve'. The minute channels running in a regular pattern through it are

wide enough to accommodate hydrocarbon molecules of the size range found in petrol, but not unwanted larger ones.

Code-named ZSM5, the catalyst is a 'zeolite', related to the crystalline zeolites long used in water treatment. The aluminosilicate skeletons of zeolites are negatively charged, and the molecular channels contain positively charged particles (cations). The type of cation present can be changed, altering the properties of the zeolite. The channels also initially contain water, but when this is removed they can accommodate other molecules, such as hydrocarbons and alcohols.

Zeolites are made by crystallizing alkaline solutions or suspensions of silica and aluminium hydroxide at high temperatures. The distinctive properties of ZSM5 result from the unusual alkali used in its production. This also makes the catalyst expensive. One aim of the CSIRO research is the development of alternative cheap methods of producing zeolites with similar or better properties.

Each route has its own advantages and drawbacks. Approaches combining elements of more than one route are also possible.





Lining up for the precious fluid.

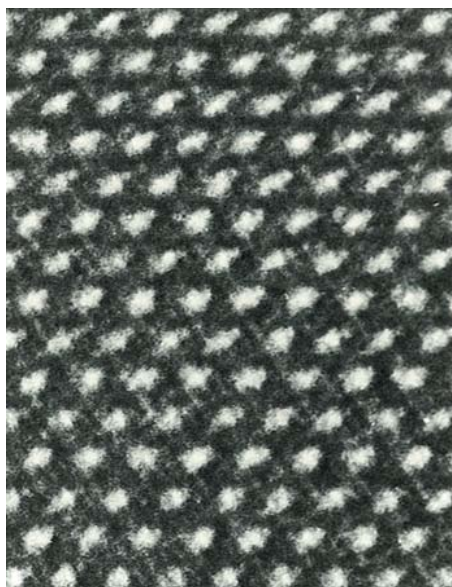
Methanol to petrol

Mobil has shown that its catalyst can be used to make petrol from methanol. This conversion, which was impossible before, is important because well-established technology exists for making methanol from coal, natural gas, and even wood and crop residues.

The methanol can be used directly as a liquid fuel. But it provides less energy per litre than petrol, and can be used satisfactorily in current car engines only in petrol blends containing less than 20% methanol. If the new catalyst provides an economic process for converting methanol to petrol, the benefits will be substantial.

Dr John Anderson, Dr Tom Mole, and Mr Victor Christoverson, of the Division of Materials Science, have examined the workings of the ZSM5 catalyst at the molecular scale and have produced a detailed description of what happens as methanol is converted to the hydrocarbons of high-octane petrol. They found that the catalyst stimulates a building process in which the single carbon atoms from methanol molecules attach themselves one by one to the carbon chains of hydrocarbon molecules. The process can go no further when these molecules reach the size limit imposed by the diameter of the catalyst channels. However, cracking of this large molecule to two smaller molecules allows further methanol to react.

The scientists are looking at other possible applications of the catalyst; their early results indicate that it, or similar zeolite catalysts, could be used in many



This 5-million-times magnification shows the regular array of channels passing through a ZSM catalyst crystal.

fuel-conversion operations. One possibility is making petrol from ethanol, the product of the various energy crops that are being suggested as partial answers to the coming liquid fuel shortage. The possibility of using the catalyst to reform liquefied petroleum gas (LPG) to petrol is also being looked at.

Experiments suggest that the zeolite catalyst could play an important role in boosting the production of high-octane petrol in conventional refineries. It can simultaneously 'crack' large hydrocarbon molecules and 'reform' smaller ones to give a product rich in the molecules of high-octane petrol.

Synthesis gas to petrol

One way to produce petrol from source materials other than crude oil is to make

synthesis gas (a mixture of hydrogen and carbon monoxide), convert this to methanol in a catalysed high-pressure reaction, and then employ the zeolite catalyst to convert the methanol to petrol. Synthesis gas is most easily made by the nickel-catalysed reaction of natural gas (methane) with steam. In the longer term, it will need to be made by the high-temperature action of oxygen and steam on coal (or coke).

The synthesis gas does not have to be converted first to methanol. One of the existing coal-to-oil processes — the Fischer–Tropsch method used by Germany in World War II and by South Africa today — produces liquid fuel directly from synthesis gas. But the Fischer–Tropsch product is not a particularly good source of petrol. The petrol fraction is of low octane-number, and much of the product is long-chain (waxy). The process has poor specificity for the hydrocarbons of petrol, and extensive further processing is needed to yield satisfactory motor spirit.

By combining ZSM5 with conventional Fischer–Tropsch iron catalyst, Dr Linda Bruce and her colleagues in the Division of Materials Science have obtained from synthesis gas a liquid product much closer to a satisfactory petrol. The Division intends to continue research on zeolite-containing catalysts with the aim of developing Fischer–Tropsch catalysts having greater specificity than the conventional iron ones.

Hydrogenation catalysts

Fischer–Tropsch plants run at a pressure of about 3 MPa (about 30 times atmospheric pressure) and a temperature of 200–250°C. These conditions are mild compared with those required for petrol-from-coal processes that involve direct hydrogenation of coal.

However, hydrogenation has the advantage of producing more liquid fuel per tonne of coal. The Germans used it, as well as the Fischer–Tropsch process, to make petrol during the forties, and it has been widely regarded as a more promising means of relieving the coming petrol shortage. Its big disadvantage lies in the extreme operating conditions required (temperatures above 450°C and pressures greater than 30 MPa), making a hydrogenation plant expensive, complex, and prone to problems. Another disadvantage is the dependence of the process on the type of coal used.

At the Fuel Geoscience Unit, a team led by Dr Michio Shibaoka is studying the reactions of catalysts with the various

A new catalyst shows promise of simplifying the production of petrol from a wide range of starting materials.

microscopic constituents of coal, known as 'macerals', during hydrogenation. Microscopic and chemical techniques are being used in the investigations. The amounts of the different macerals present play a large role in determining the properties of coals.

The scientists have found that metal halide catalysts, such as stannous chloride, may penetrate right through grains of solid coal, a millimetre and more in size, at temperatures well below 380°C — the temperature at which major hydrogenation reactions commence. In the case of stannous chloride, tin and chlorine, no longer present as the stannous compound, move progressively through vitrinite, a maceral that becomes plastic on heating. Tin sulphide is formed as sulphur is scavenged from the vitrinite. No such penetration occurs in another maceral, inertinite; it is usually hydrogenated to only a minor extent.

Some catalysts do not have the same mobility as the metal halides, and probably differ in both behaviour and chemical role. A number, such as those based on molybdenum, become ineffective after a time in the presence of some elements — vanadium, for example — that may be found in coal (they are said to be

'poisoned'). However, a major reason for the de-activation of catalyst pellets is that they may become coated with coke-like material derived from the coal.

One of the catalysts used for coal hydrogenation during World War II was red mud, a waste produced in copious quantities during the refining of bauxite to alumina. To complete the hydrogenation, molybdenum- or tungsten-based catalysts were used.

At the Division of Applied Organic Chemistry in Melbourne, a team led by Dr Peter Wailes recently tested red muds from the alumina refineries at Gove, N.T., and Weipa, Qld, as hydrogenation catalysts. Both performed well, the Gove red mud giving the better result. This is probably because its chemical make-up gives particles of bigger surface area (about 37 sq m per g as against 20 sq m per g for the Weipa product).

Red mud is regarded as a 'throw-away' catalyst; its great advantages are its cheapness and ready availability. The whole hydrogenation job can be done using the molybdenum-based catalysts that the Germans employed to finish off the process. However, molybdenum is expensive, and the world's known resources are quite small. If hydrogenation takes off as a commercial process, it will almost certainly be as a two-stage operation using something cheap like red mud for the first stage and a more effective, but more expensive, catalyst for the second.

To give an idea of the quantities involved, it has been estimated that a plant producing 100 000 barrels of oil a day would consume 40 000 tonnes of coal and 2000 tonnes of red mud a day. Unfortunately, hydrogenation plants cannot solve

the environmental problems associated with red mud; they may just shift part of the disposal problem away from the alumina refineries.

Flash pyrolysis

The main interest of the Division of Applied Organic Chemistry in the molybdenum-based catalysts relates to CSIRO's flash pyrolysis project (see the box). The prospects for producing liquid fuels by rapidly heating coal in the absence of air (flash pyrolysis) and then hydrogenating the tar product are being examined in this major research effort. The conditions required for the hydrogenation step are less extreme than those applying when coal is dealt with directly. But drawbacks of this route from coal to petrol include the need to find uses for the char and gases that are produced along with the tar during pyrolysis.

Dr Helmut Weigold and Applied Organic Chemistry Division colleagues are examining the operation of various molybdenum-based catalysts (some of them designed at the Division), and seeing how differences in catalysts affect the hydrogenation product. Typically, the catalysts are sulphides of molybdenum and cobalt, or molybdenum and nickel, on porous alumina supports. The cobalt and nickel promote the molybdenum's activity.

Crude, residues, and shale oil

Industrial development of such sulphide catalysts has concentrated on improving their performance in oil refineries, where their main role has been in removing sulphur from crude oil. At the Division of Materials Science, Dr Kerry Pratt and his

The pyrolysis project

The CSIRO flash pyrolysis project (see *Ecos 5* and *Ecos 16*) is proceeding as planned. At the Division of Applied Organic Chemistry in Melbourne, construction has started on a continuously operating hydrogenation plant with a capacity 50 times greater than that of the plant now in operation. It will produce about 3 kg of synthetic crude oil per hour from tar produced by the flash pyrolysis rig at the Division of Process Technology in Sydney.

A similar hydrogenation plant is under construction beside the pyrolysis rig, so that the problems of coupling the two major steps in the coal-to-oil conversion process can be examined. The scientists

also aim at establishing how tar fresh from the pyrolyser responds to hydrogenation. It is hoped that the results will be better than those obtained with tar that has stood around for some time, because the pyrolysis product tends to deteriorate as some of its low-molecular-weight constituents recombine.

The main problem encountered in tar hydrogenation so far is a build-up of coke on the catalyst. Dr Wailes and his colleagues at the Division of Applied Organic Chemistry are looking for ways to overcome this. Possibilities include subjecting the tar to some form of pre-treatment or controlling heating during

hydrogenation to limit coke formation.

The new hydrogenation plant is the largest planned for construction at the Division. Its hydrogen requirement — 50 litres per minute — is a striking illustration of the size of the operation.

The plant will provide the scientists with information on the problems of scaling-up. Variation of the operating conditions together with detailed examination of the product — its chemical constitution and physical characteristics — should show how the best possible product can be produced. Tests will be carried out with tars derived from a variety of coals and with many different catalysts.

colleagues are studying the structure and mode of action of these catalysts. The idea is to find out the functions of all the ingredients, in the hope that this will make it possible to design effective catalysts for purposes other than sulphur removal. At present very little is known about how they work.

Sulphide catalysts can be used to crack and hydrogenate (hydrocrack) the residue of heavy molecules remaining after crude oil has been distilled. This enables petrol and other useful fuels to be made from the residue, something that is not done in Australia at present but would result in the production of more fuel per barrel of crude.

Another role for this type of catalyst is in shale oil processing, and Dr Pratt is looking at this. Here one of the main requirements is to remove nitrogen, rather than sulphur, and modifications to existing catalysts may be needed to make the process proceed efficiently.

Cracking and reforming

Other types of catalyst being studied in the Division include 'cracking' and 'reforming' catalysts used in oil refineries, and mentioned earlier. An aim of the work on cracking, being conducted by Dr Pratt, is to find efficient ways to cope with the higher metal content of the heavier imported crude oils that Australia will use increasingly as our own oil reserves diminish. Work on reforming catalysts, being carried out by Dr Karl Foger, seeks to improve the efficiency of that part of the refinery operation by development of more selective and poison-resistant catalysts. This should help reduce the losses occurring on the road from crude oil to high-octane petrol.

Robert Lehane

More about the topic

Coal liquefaction — chemistry and catalysis. T. Mole and K. C. Pratt. *P.A.C.E.*, 1979, 32, 12–17.

A chemical engineering overview of heterogeneous catalysis. K. C. Pratt. *Chemical Engineering in Australia*, 1979, 4, 38–44.

Coal hydrogenation using 'throw-away' catalysts. L. Bagnell, T. Mole, P. C. Wailes, and H. Weigold. *CSIRO Division of Applied Organic Chemistry Technical Paper No. 5*, 1979.

Some aspects of behaviour of tin (II) chloride during coal hydrogenation in the absence of a solvent. M. Shibaoka, S. Ueda, and N. J. Russell. *Fuel*, 1980, 59 (in press).