Platinum Group Metal Catalysis at the End of This Century

PROBABLE SYSTEMS AND THE PROCESSES BASED ON THEM

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At the annual meeting of the Royal Society of Chemistry, held earlier in the year at Exeter University, Dr. Acres, Director of Research, Johnson Matthey, gave some predictions about platinum group metal catalysed reactions in the year 2000. This article is based upon his lecture.

In looking to the year 2000 and the developments likely to occur in the field of platinum metal catalysis, it is at first sight perhaps tempting to suggest that both the catalyst systems as they are known today, and the processes for which they are used, will be superseded by significantly more efficient catalysts and processes allied to those operating in biochemical processes. For example, one might propose that ammonia will be synthesised at near-ambient temperature, and that methane and synthesis gas will be efficiently converted into fuels and chemical intermediates. Additionally it might be expected that the direct conversion of fuels into electrical energy will become established technology during the next 15 years. All of this, one might conjecture, would be built on an ability to model catalysts and processes from basic principles. But can and will platinum group metal catalysts develop to this stage by the turn of the century?

To answer this question it is as well to look first at some of the major catalytic processes used in the chemical industry today. These are illustrated in Table I which shows some of the better known processes, the date they were first commercialised and the relevant industry.

It is notable that many of the processes were used 50 or more years ago, that the catalyst and process conditions have not changed significantly since their inception, and that platinum group metals are used in at least half of the applications. A large number of the improvements in catalyst and process have been concerned with better reproducibility in catalyst manufacture and increased durability under reaction conditions. History, therefore, suggests that platinum group metal catalysed processes, once established, tend to remain in use with development occurring continuously rather than in quantum jumps. In some areas of the chemical industry platinum metal catalysts have replaced base metal catalysts, and this is not surprising considering the range of reactions which the six metals catalyse, see Table II.

Currently platinum group metal catalysts are unique in terms of activity and selectivity for many hydrogenation and oxidation reactions, and as a result they are being used increasingly in the synthesis of chemicals and intermediates. Extrapolating into the future, therefore, it can be said that platinum group metal catalysts will continue to be utilised at the turn of the century. If this is to be the case, it is now necessary to consider the form they are likely to take, and the new processes and systems in which they will be used by the year 2000.

Platinum Group Metal Catalysts for AD 2000 and Beyond

With the majority of catalytic reactions, one or more of the reactants is adsorbed on the catalyst surface, where reaction takes place. The products then desorb, to be replaced by further reactant. The reactants adsorbed on the

Table I
Major Catalytic Processes Used in the Chemical Industry

Industry	Application	Discovery
Petroleum refining	Catalytic cracking	1915
	Catalytic alkylation	1935
	Platforming	1950
Fertilisers	Ammonia oxidation	1838
	Ammonia synthesis	1913
Bulk chemicals	Sulphuric acid	1831
	Methanol synthesis	1924
	Ethylene oxide	1931
	Acetaldehyde	1960
	Steam reforming	1962
Plastics	Polyethylene	1955
Fine chemicals	Hydrogenation	1900
Fats and oils	Hydrogenation	1901
Pollution control	Oxidation	1949

catalyst surface form chemisorbed activated complexes in equilibrium with reactant in the non-adsorbed condition. The same is true of the products, and it is the relative strengths of adsorption of the reactants and the products which determine how fast the reaction takes place. If either the reactant or the product is too strongly absorbed on the catalyst surface then the equilibria will be biased towards the adsorbed state and the reaction will proceed slowly. If the reactant is too weakly adsorbed then the equilibrium will be biased towards the non-adsorbed state, the concentration of activated complexes will be low, and again the rate of reaction will be slow. Only when the reactants are adsorbed with intermediate strength and

Table II
Reactions Catalysed by Platinum Group Metals

Reaction	Catalyst					
Hydrogenation	Platinum	Palladium	Ruthenium	Rhodium	Iridium	
Oxidation	Platinum	Palladium	Ruthenium	Rhodium	Iridium	
Dehydrogenation	Platinum	Palladium				
Hydrogenolysis	Platinum	Palladium	Ruthenium			
Synthesis Ammonia			Ruthenium			
Methanol		Palladium				
Hydrocarbons			Ruthenium			
Acetic acid				Rhodium		
Hydroformylation			Ruthenium	Rhodium	Iridium	
Carbonylation				Rhodium		
cis-Hydroxylation						Osmium

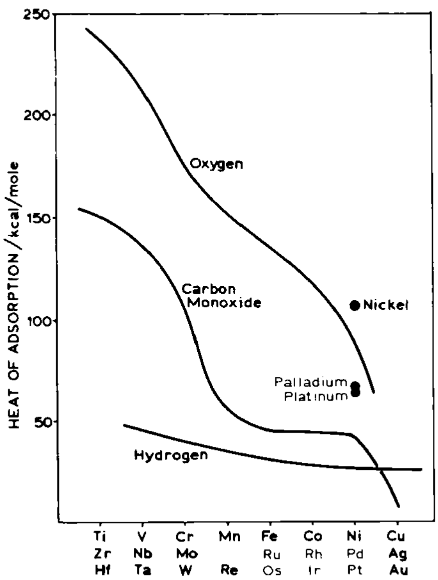


Fig. 1 Here initial heats of adsorption of oxygen, carbon monoxide and hydrogen are plotted as a function of the catalyst metal. For each reactant there is a significant decrease on moving from left to right, best illustrated here by oxygen on nickel, palladium and platinum. (After G. C. Bond, *Platinum Metals Rev.*, 1979, 23, (2), 50)

the products less strongly adsorbed will the reaction proceed at a commercially interesting rate. Heats of adsorption are related to strengths of adsorption and one test of catalytic ability is the measurement of the heat of adsorption. Figure 1 illustrates the key function that makes the platinum group metals unique as catalysts (1). Most of the commercially interesting reactants are adsorbed with moderate strength on the six platinum metals, which explains why these rare and intrinsically valuable metals are used to catalyse so many reactions in preference to more abundant elements, some of which exhibit catalytic properties.

Since the heat of adsorption and thus the strength of adsorption contribute exponentially to the activation energy, minor changes in the heat of adsorption result in major changes in the catalytic activity. This can be seen in Figure 2 which illustrates the catalytic activity of the elements of Groups VA, VIA, VIIA, VIII and IB for ethylene hydrogenation. Clearly the platinum group metals are several orders of magnitude more active than the elements of the other Groups (1).

Similar volcano-shaped curves exist for many other reactions and this illustrates the unique properties of platinum group metal catalysts. For this reason alone platinum group metals will continue to be used.

The Form of the Catalysts

To envisage the form that platinum group metal catalysts will take in the next few decades it is necessary to look at the materials currently used and then to consider how they may be improved in the future. Since they possess high intrinsic activity, the platinum group metals can be used in the form of bulk metal, indeed

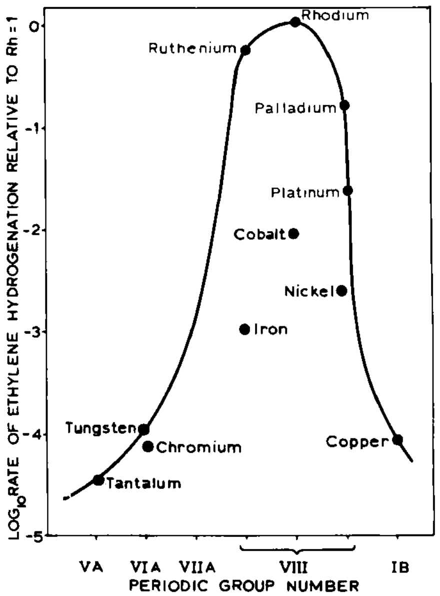


Fig. 2 The rate of ethylene hydrogenation on various metals, relative to rhodium = 1, is plotted here as a function of the Periodic Group Number. The superior catalytic activity of the platinum group metals is clearly illustrated. (After G. C. Bond, *Platinum Metals Rev.*, 1979, 23, (2), 51)

this was the system originally described at the start of the nineteenth century for ammonia oxidation. Recent progress includes the addition of promoters such as rhodium, and a better understanding of the mechanisms of sintering and metal diffusion phenomena (2, 3).

Alternatively, of course, supported catalysts may be employed and here the range of supports and hence of support surface chemistry is so large that preparation techniques become all important (4). In this field great improvements are being made, and these promise to convert the present art of catalyst preparation into a science.

Platinum on alumina catalysts have been one of the workhorse catalysts of the refining and chemical industries for the last thirty-five years, but even they can still be improved. Impregnation technology has changed as the reaction between the platinum salts and the alumina surface has become better understood. Now other platinum group metals and even base metals can be incorporated to improve catalyst performance. For high temperature applications, phase changes in the alumina can be slowed down by the addition of stabilisers. Additionally, current trends suggest the use of other oxide supports particularly titania and zirconia, while the use of molecular sieves as supports is still at an early stage of development. For demanding applications in liquid phase catalysis, platinum on carbon catalysts have reached a high degree of sophistication. It is now possible to control the platinum crystallite size and its dispersion on the carbon support accurately, and to forecast exactly the metal location within the support structure.

New reaction possibilities have been opened up by the recent application of platinum group metal homogeneous catalysts to industrial processes. In the 1960s it was widely thought that homogeneous catalysis had great potential, promising operation under mild conditions, with benefits of high activity, selectivity and durability. Some of this early enthusiasm has had to be tempered by practical experience; none-the-less industrial application has been very successful. Today rhodium catalysed hydroformylation of propylene to n-butylaldehyde takes place at low temperature (90 to 120°C) and low pressure (7 to 25 atm). The catalyst, which is dissolved in triphenyl phosphine at a concentration of 200 ppm rhodium, is very active, highly selective and durable. By the year 2000 the range of such reactions is likely to be expanded using either very dilute solutions or supported catalyst systems.

In heterogeneous catalysis the control of activity/selectivity is dependant on controlling the crystallite size of the catalyst, such crystallites containing many metal atoms. On the other hand homogeneous catalysts are usually single metal atom species. It is now possible to bridge these two technologies by using metal cluster compounds containing a number of metal atoms, for example $[H_2Rh_{13}(CO)_{24}]^{3-}$ and $H_2FeRu_2Os(CO)_{13}$. Platinum group metals readily form such cluster compounds which may be used as conventional homogeneous catalysts, supported homogeneous catalysts or precursors in the preparation of heterogeneous catalysts. In each of these three systems the metal-metal bonded structure is retained to impart new and unusual properties. For example with heterogeneous catalysts it is anticipated that very close control of crystallite size with multi centre adsorption will be achieved. With homogeneous cluster catalysts the adsorption may be further modified by the ligands, so changing the activity/selectivity abilities of the catalyst. This novel technology offers exciting new possibilities in catalyst design which are likely to be important for both new and established processes by the end of the century (5).

Environmental Control Catalysts

One of the more recent developments in the application of platinum group metal catalysts is for environmental control, and in particular control of the emissions from motor vehicles. This is at present the largest single application of platinum group metal catalysts and it is likely to expand in the future.

As is now well known, motor vehicles

burning hydrocarbons as fuel emit in their exhaust fumes, in addition to water and carbon dioxide, a quantity of other compounds especially carbon monoxide, nitrogen oxides and unburnt hydrocarbons; in ultra violet light these form a photochemical smog.

So far engine modifications alone have not reduced the pollutants sufficiently but catalytic systems have been developed for this purpose. Two systems are presently in use and likely to form the basis of emission control systems for petrol/alcohol fuelled cars in the future (6). The first system removes carbon monoxide and hydrocarbon pollutants over promoted platinum based catalysts. In the second system carbon monoxide, hydrocarbons and nitrogen oxides are controlled catalytically by a platinum-rhodium catalyst containing base metal promoters. These two catalyst systems represent some of the most advanced catalyst technology available, and to date over 100 million units have been purchased.

The increasing use of diesel engined vehicles in the U.S.A. has resulted in proposed legislation to control the emission of particulate pollutants, and again the challenge has been taken up by catalyst technology. A platinum-rhodium alloy catalyst has been developed which reduces particulates; and polyaromatic hydrocarbons and odour have been largely eliminated from the exhaust stream (7). As long as internal combustion engines remain in use, catalytic emission control is likely to be necessary.

Although accepted solutions have been found to the problem of controlling the pollution from motor vehicles, the control of the pollutants that form "Acid Rain" will require altogether more radical approaches. The emission of both sulphur dioxide and nitrogen oxides from power stations provides a situation in which the two pollutants act synergistically to create a problem bigger than that posed by the two pollutants alone. The removal of sulphur dioxide has a number of solutions including catalytic fuel desulphurisation in which the sulphur is removed from the fuel before it leaves the refinery. Nitrogen oxides, however, are potentially a bigger problem, as they are formed from atmospheric nitrogen during the combustion process. Measurement of man-made nitrogen oxide emissions in the U.S.A. during 1980 revealed that stationary fuel combustion, consisting of coal fired power generation and hydrocarbon fuelled turbines together with domestic and commercial boilers, produces 52.2 per cent of these emissions while mobile sources such as motor vehicles create 45.6 per cent. The relationship between nitrogen oxides formation and flame temperature is shown in Table III.

Clearly, the way to reduce nitrogen oxide emissions is to reduce flame temperature or even eliminate the flame completely. Already experimental gas turbines using catalytic combustors instead of conventional flame combustors have been run successfully. The use of catalysts in a Rover gas turbine engine (8) virtually eliminated nitrogen oxide emissions without loss of engine efficiency. This technology is applicable to oil or gas fired burners and is likely to constitute a major new use of advanced platinum group metal catalyst technology, derived from existing, highly successful car emission control catalyst systems.

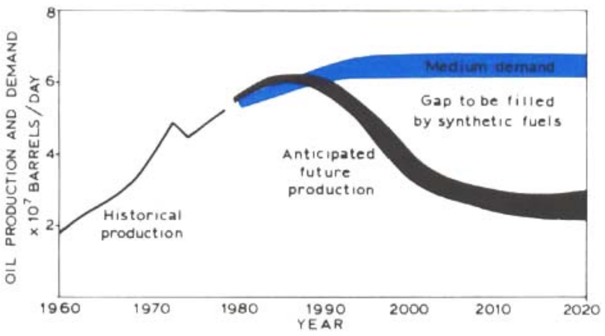
The catalytic engine is an exciting application of catalytic combustion technology (9). The benefits of this system include the ignition of leaner mixtures to give better fuel economy and reduced emission of pollutants, while ignition at

Table III

Formation of Nitrogen Oxides at Elevated Temperatures

Temperature °C	Equilibrium concentration of nitrogen oxides, ppm	Time of formation of 500 ppm nitrogen oxides, s
1093	180	—
1316	550	1370
1538	1380	16.2
1760	2600	1.1
1982	4150	0.117

Fig. 3 Sometime before the end of this century the demand for oil is expected to exceed the supply. Possible production and demand curves for the Western World, based upon predictions by Shell, show a substantial gap which will have to be met by the use of alternative fuels



optimum compression ratio improves fuel economy further. An additional advantage is that the engine can operate normally on a range of conventional hydrocarbon fuels, or even on alternative fuels such as methanol. This is one of the new concepts in advanced platinum catalyst technology which has possible applications towards the end of this century.

Synthetic Fuels and Chemicals

The imminence of the long foreseen gap between oil demand and production is a matter of some dispute, but on one thing all authorities are agreed; sometime, probably towards the middle or end of the 1990s, a gap will develop between the demand for oil and the ability to supply it. One such forecast is shown in Figure 3. By the year 2000, in this scenario, there will be a shortage of oil and the need for alternative fuels to bridge the gap will be great. Luckily the interconversion of natural energy sources into fuels and chemicals can potentially be mediated by catalytic processes. This will be a major challenge to catalyst technology in the year 2000. As an example of the use of the platinum group metals in this technology to improve synthetic fuels let us consider the Fischer-Tropsch reaction in which $C_5 - C_{35}$ hydrocarbons are selectively manufactured from synthesis gas (carbon monoxide + hydrogen). Two metals of Group VIII may be used to catalyse the Fischer-Tropsch reaction, namely iron and ruthenium. A comparison of iron and ruthenium as catalysts is shown in Figure 4 and it is noticeable that ruthenium is more selective, producing a narrower fraction centred on $C_8 - C_{11}$ which is suitable as a petrol fraction.

The use of ruthenium supported on HZSM-5 zeolite gives a petrol fraction with no

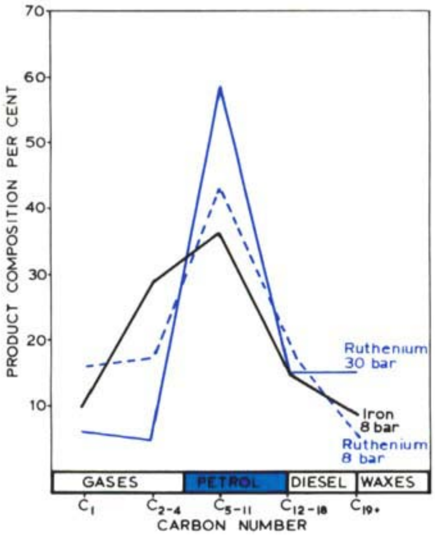


Fig. 4 Improved fuels can be manufactured from synthesis gas by the Fischer-Tropsch reaction using either an iron or a ruthenium catalyst. At a reaction pressure of 8 bars, ruthenium (at 235°C) is more selective for the production of liquid fuels suitable for use in spark ignition engines than iron (at 260°C), while if the pressure is increased to 30 bars ruthenium catalyses an even more selective fraction

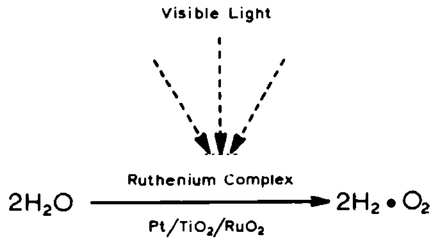


Fig. 5 Over recent years there has been an abundance of research seeking to harness light as a source of useful energy, the system illustrated here being one of the more successful attempts to decompose water into hydrogen and oxygen. Much remains to be done and the task is, perhaps, one of the most challenging facing scientists

hydrocarbons larger than C_{12} and the selectivity is essentially unaltered when the ruthenium loading is decreased from 5 per cent to 1 per cent metal. Based on this, one may expect to see advanced catalyst systems capable of selectively producing a wide range of fuels and feedstocks.

Fuel Cells

Fuel cells produce electricity by the direct combination of fuels without the limitations imposed by burning fuel, raising steam and rotating a conventional turbine generator (10).

Catalyst technology for the hydrogen/air cells using either alkaline or acid electrolytes is now well established. Highly dispersed platinum on carbon catalysts exist in which the metal is dispersed in an almost atomic state. The normally used catalyst has metal crystallites of about 20Å diameter. The limiting factor with these cells is not platinum technology but capital costs. Examples of currently used fuel cells are the Space Shuttle 12 kW unit and the Combined Heat and Power 40 kW unit. This latter unit, incorporating a reformer and an inverter, uses methane or naphtha as fuel and is on extended field trials in both the U.S.A. and Japan. The big brother to the 40 kW unit is the 4.8 MW Peak Lopping Station which again uses natural gas as fuel, with an incorporated reformer. Units have been installed in New York and Tokyo. The principal benefits of these units are high efficiency and environmental compatibility.

A breakthrough in the use of fuel cells is likely to occur if one that directly uses a readily available fuel can be developed. Possibilities exist for using methanol as a direct fuel; already a prototype golf cart is operating which uses a direct methanol cell. Similar cells also exist for portable consumer electronics, for example video cameras. However, the exploitation of these cells is currently limited by the catalyst technology, since the activity and durability of the platinum-ruthenium on carbon catalysts is relatively low. This forms a major challenge to platinum group metal catalyst technology, which must be met if methanol fuelled cells are to be widely exploited.

Photocatalytic Hydrogen

Finally a speculative look at the year 2000 in terms of a challenging goal that requires advanced platinum group metal catalyst technology, namely the visible light induced decomposition of water. One of the systems investigated is highlighted in Figure 5.

The process uses a sensitiser plus a dual function catalyst. Briefly, the decomposition mechanism involves the excitation of a ruthenium compound dissolved in water by visible light, resulting in the transfer of electrons from this compound to a platinum + ruthenium catalyst. The electrons migrate to the platinum covered areas of this catalyst where they split water and produce hydrogen; at the same time oxygen is formed at the ruthenium covered areas. One of the many problems that will have to be overcome if this system is ever to find application is the spatial separation of the hydrogen and oxygen generating centres so that the two gases can be recovered in pure form.

Summary and Conclusions

It is clear that industrial processes which at present make use of platinum group metal catalysts will continue to do so into the next century, although it is expected that both the catalysts and the processes will have been improved by continuous development. Hopefully, further deterioration in the environment will be prevented, and both existing and foreseen platinum metal technology has much to contribute to this.

By the year 2000 diminished reserves of gaseous and liquid fossil fuels will be conserved by the more efficient use of fuels, as in the catalytic engine, while fewer losses will occur when electrical energy is generated directly from the fuel. Chemicals and fuels will be manufactured from more widely available feedstock, principally synthesis gas produced from coal using platinum group metal catalysts.

Although widely used at present, platinum group metal catalysis will undoubtedly have an even greater role to perform at the start of the next century.

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Platinum Anti-Cancer Drugs

More than 30,000 cancer patients in the United States of America are now being treated each year with a combination of drugs which includes Cisplatin. This combination is particularly effective against testicular cancer but Cisplatin is also approved by the Food and Drug Administration (F.D.A.) for first line therapy of ovarian and bladder tumours. These three tumours affect over 60,000 of the 800,000 new cancer cases reported in the U.S.A. each year. Marketed by Bristol-Myers of New York—who in their 1983 Annual Report to stockholders included a special report on the search for new anti-cancer drugs—Cisplatin is now the leading anti-cancer drug in the U.S.A. and is also registered widely in Europe and most recently (1984) in Japan. The compound resulted from a research programme started at Michigan State University in 1965 and sponsored by Rustenburg Platinum Mines and Johnson Matthey. It was developed into a viable product by way of a major project by Johnson Matthey in association with universities, institutes and hospitals in the United Kingdom and in the U.S.A. To produce the drug, Johnson Matthey Inc. set up a special unit at West Whiteland, Pennsylvania in 1978, built to standards approved by the F.D.A. The bulk drug is supplied to Bristol-Myers for conversion to the final dosage form, suitable for patients treated intravenously, although alternative treatment routes are being investigated.

Work on less toxic analogues of Cisplatin, namely Carboplatin and Iproplatin, was reported at the Second International Platinum Group Metal Chemistry Conference at Edinburgh, in July 1984. As with Cisplatin, research on the chemistry and pharmacology of these two compounds was progressed by Johnson Matthey through collaborative projects with U.K. institutions notably the Royal Marsden Hospital/Institute of Cancer Research (London) for Carboplatin, and the Christie Hospital/University of Manchester Institute of Science and Technology for Iproplatin. Bristol-Myers have licensed these compounds from Research Corporation and Johnson Matthey, respectively. A major comparative clinical study for these compounds and Cisplatin is now in progress in parallel with the registration procedure for Carboplatin in Europe. Preliminary results show promising activity against a number of other tumours suggesting that a greater proportion of cancer patients will benefit from platinum chemotherapy in the late 1980s.

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