Discussion

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Providing sustainable catalytic solutions for a rapidly changing world: a summary and recommendations for urgent future action

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In addition to summarizing the main thrusts of each paper presented at this Discussion, other urgent issues involving the role (and characterization) of new catalysts for eliminating oxides of nitrogen, for using CO_2 liberated from steel mills, for fuel cells and the need for rapid decarbonization of fossil fuels are outlined.

This article is part of a discussion meeting issue 'Providing sustainable catalytic solutions for a rapidly changing world'.

1. Introduction

Most of the topics and problems raised in this Discussion encompassed, to a greater or lesser degree, those that need urgent attention if humans are to comply with the admirable definition of sustainable development enunciated by the then Prime Minister of Norway, Gro Harlem Brundtland, in her report to the United Nations in 1986.

Meeting the needs of the present without compromising the ability of future generations to meet their own needs.

While, as a listener and participant, I was grateful to the organizers for choosing the topics that we discussed (and which I summarize in §3), I also felt that we should focus on some other urgent societal issues, such as the prospects for new catalysts to eliminate oxides of nitrogen, especially from diesel-operated vehicles [1,2];

new catalysts for the utilization of anthropogenically produced CO_2 (to form methanol, which can be used as a fuel in motor engines and as an important platform chemical [3]); the development of noble-metal-free catalysts [4] for fuel cells and a host of other conversions; and catalytic solutions for rapid decarbonization of fuels. The last-named topic is being actively pursued in Japan (a MITI report, issued in Japan recently, states that, by 2030, the economy of that country will be based on hydrogen and be CO_2-free; also, the Governor of California (which is the sixth largest economy in the world) has said (May 2017) that his State aims to rely entirely on renewable energy from 2045 onwards) and this topic is a current urgent issue among 'think tanks' in Sweden, Switzerland and Australia [5].

Nevertheless, there were several timely contributions that have already provided viable catalytic solutions for our rapidly changing world. Before proceeding, briefly to summarize these, I shall first, in §2, focus on other perceived new developments relevant to the theme of the Discussion concerning new catalysts, and their deployment and characterization in the near future. Of the four distinct new development that I identify (see §2), by far the most significant (insofar as preparing new catalysts is concerned) is the arrival of readily preparable and vast new numbers of nanoporous solids that has proved critical. As laudable as the attempts to increase the pore diameters of molecular sieve (zeolitic) solids or the efforts of the so-called surface organometallic community have been (see §2c), it is the ease with which numerous new mesoporous solids can be prepared in hierarchical form and made into powerful new catalysts that is most important and significant.

2. Some important new developments

Here I focus on:

(1) capturing solar energy in novel catalytic ways using plasmon-enhanced photocatalysts;
(2) exploiting powerful new experimental methods of characterization;
(3) capitalizing on the advantages of the current widespread availability of nanoporous materials; and
(4) decarbonizing fossil fuels.

(a) Plasmon-enhanced photocatalysis [6]

As shown in the recent joint work of investigators at Rice University and Princeton University [6] plasmon-enhanced photocatalysis holds significant promise for controlling chemical reaction rates and outcomes. Unfortunately, traditional plasmonic metals have limited surface chemistry, while conventional catalysts are poor optical absorbers. By placing a catalytic reactor particle adjacent to a plasmonic antenna, the highly efficient and tunable light-harvesting capacities of plasmonic nanoparticles can be exploited to increase drastically absorption and hot-carrier generation in the reactor nanoparticles. Swearer *et al.* [6] have demonstrated this antenna–reactor concept by showing that plasmonic aluminium nanocrystal antennas decorated with small catalytic palladium reactor particles exhibit dramatically increased photocatalytic activity over their individual components. The modularity of this approach provides for independent control of chemical and light-harvesting properties and paves the way for the rational, predictive design of efficient plasmonic photocatalysts.

In a study of the photocatalytic production of ethylene from acetylene, these workers enhanced the selectivity of the hydrogenation (with H_2) by a factor of 40 or so. They describe [6] their photocatalytic work as involving heterometallic antenna–reactor complexes. They recall that, traditionally, heterogeneous catalysis has relied upon weakly light-absorbing metals such as Pd, Pt, Ru, or Rh to lower the activation energy for chemical reactions [7]. They, however, showed that coupling a plasmonic nanoantenna directly to catalytic nanoparticles enables the light-induced generation of hot carriers within the catalyst nanoparticles, transforming the entire complex into an efficient light-controlled reactive catalyst. In Pd-decorated Al nanocrystals, photocatalytic
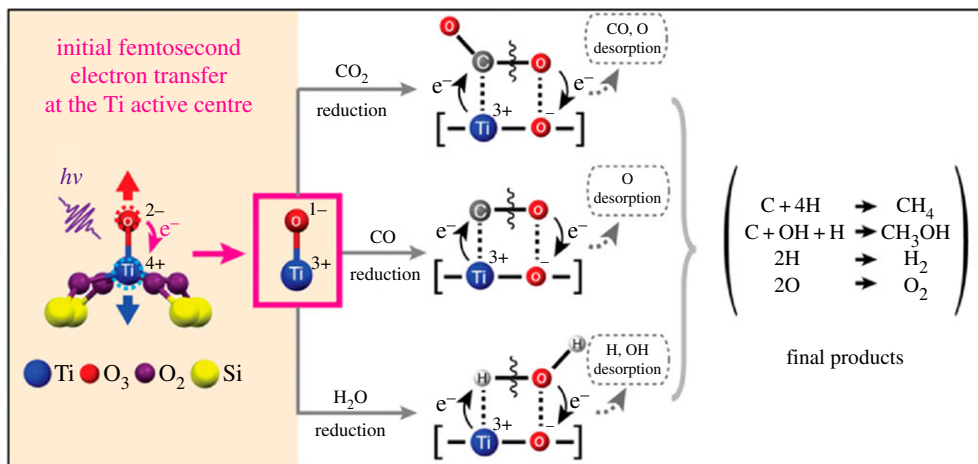
Figure 1. When a femtosecond pulse of light is shone at the absorption frequency of the titanyl active centre of Ti^{4+} single-site photocatalyst, it is found, by 4D ultrafast electron microscopy [14,15], that a $Ti^{3+}-O^-$ ion pair is transitorily formed. This active pair (picosecond lifetime) is the locus for the ensuing reduction processes, indicated in the middle, that lead to the final products, shown at the extreme right. (From Yoo et al. [16].)

hydrogen desorption closely follows the antenna-induced local absorption cross section of the Pd islands, and a supralinear power dependence strongly suggests that hot-carrier-induced desorption occurs at the Pd island surface.

In another interesting and novel study (from Rice University) Halas et al. [8] capitalized upon plasmonic heating combined with fermentation and thermal distillation so as to produce cellulosic bioethanol in an entirely novel sustainable manner.

(b) Exploiting new experimental methods of characterization

In recent years, major advances have been made in exploiting both in situ and ex situ methods of studying catalysts. It was clear from the early pioneering work of Tamaru [9] that in situ methods of probing catalysts could reveal far more than any technique that focused on either 'pre-natal' or 'post-mortem' examinations of the catalyst. The necessity to exploit in situ methods has been emphasized repeatedly by others—see Thomas [10,11]—and the arrival of synchrotron radiation sources has accelerated the rewarding application to catalytic science of this tunable, powerful source of electromagnetic radiation. Since the early 1990s it has become routinely possible to record in parallel both the short-range chemical nature and structure of an active site and the long-range crystallographic order of its surrounding matrix [12].

With the current availability of free-electron lasers, and their associated femtosecond-scale temporal resolutions, in situ studies of biocatalysts have been enormously facilitated, thanks to the work of Chapman, Spence, and their collaborators using the Stanford University synchrotron facilities [13]. The merit of exploring structural changes at the femtosecond timescale is that it reveals the mechanistic details of the making and breaking of bonds. But even when the time resolution is much lower, as in the Diamond facility in the UK, a good deal of useful topographical information pertaining to optimal size ranges of nanoparticle catalysts for Fischer–Tropsch reactions can be retrieved, as shown in the paper by Beale (see §3) in this Discussion.

Femtosecond resolution of the early events in photo-assisted water splitting (as well as the reduction of CO_2 to either methane or methanol) can be gleaned from the judicious use of 4D ultrafast electron microscopy, the technique pioneered by Zewail and his associates [14,15]. An illustration of how 4D ultrafast electron microscopy illuminates the fundamental photocatalytic steps in the use of a single-site Ti^{4+} active centre in the catalyst JDFL-1 is shown in figure 1.
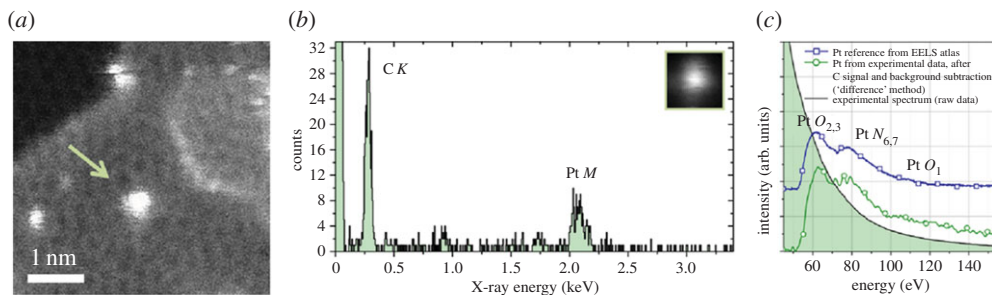
Figure 2. Present-day aberration corrected electron microscopes (see text and [19,20]) can identify single atoms of Pt on a graphene support (a). Also shown are X-ray emission (b) and electron (+) energy-loss spectra (c). (By kind permission of Q. M. Ramasse.) (Online version in colour.)

What 4D ultrafast electron microscopy enables us to do is to identify the initial femtosecond-scale electron transfer at the Ti^{4+} active centre—a Ti^{3+}–O^- pair is formed and has a lifetime in the picosecond range [16]. Subsequent reactions, depending upon whether the reactant is CO_2, CO or H_2O (figure 1) then follow to yield the final products shown in the figure. As pointed out by Gray [17], a pioneer in the utilization of solar energy and photocatalysis, this work has revealed, for the first time, snapshots of early events in water splitting (as well as CO_2 reduction) catalytic cycles.

Aberration-corrected, high-angle, annular-dark-field scanning transmission electron microscopy (AC-HAADF-STEM) [18–20] has also made very valuable contributions to the *ex situ* characterization of heterogeneous catalysts. In recent work on single-atom heterogeneous catalysts (SAHC) pursued by Perez-Ramirez, Flytzani-Stephanopoulos and others [21–26] AC-HAADF-STEM studies have been invaluable (figure 2). The mere existence of the phenomenon of SAHC opens up the possibility of replacing tens of thousands of atoms of platinum-group metals (PGM) by one atom, thereby effecting considerable economy in the use of PGMs for a wide range of chemical catalytic conversions (see also [27]).
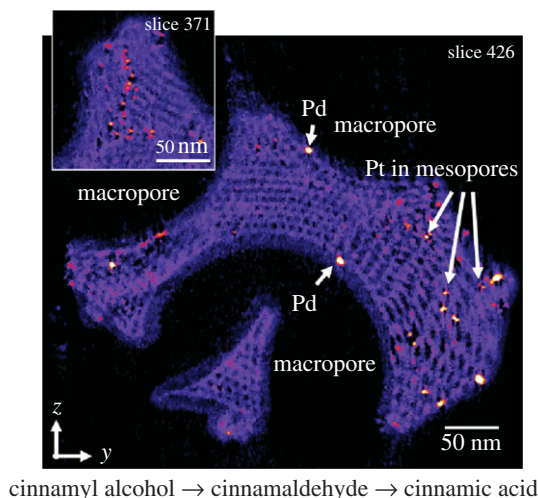
(c) Capitalizing on the widespread availability of nanoporous materials

From the earliest efforts involved in the preparation of highly active solid catalysts, high-surface-area solids have been extensively employed. Often, minute nanoparticles of active metal catalysts, especially Pt and Pd, have been supported on high-area, zeolitic or amorphous silicas or amorphous carbons. The purpose in so doing has been to maximize the number of active sites and hence the activity of the prepared catalyst. In petrochemical contexts, zeolitic supports for PGM catalysts have figured eminently [28,29]; and, of late, larger-pore zeolitic solids have been prepared [30] to enable larger hydrocarbon molecules in petrochemical feedstocks to be transformed within the interior of the solid catalysts.

Nowadays, however, thanks to much progress in exploiting large structure-directing template molecular entities [31] as well as other strategies [32], it has become feasible to prepare an extensive range of nanoporous solids (especially oxidic ones), the pore diameters of which may be controllably altered to fall in the range of 20 to 500 Å [7,33]. It has been estimated that over half the elements of the periodic table can now be prepared as nanoporous oxides, or halides or sulfides (or in their natural states).

This enables numerous new types of functionalized solid catalysts to be prepared, because a wide variety of organometallic precursors can be sequestered into the nanoporous host [34]. Moreover, active sites can be inserted as surface features in the interior of nanoporous solids that can be synthesized without the use of organometallic precursors [24] (see also [26]).

Nanoporous silicas are particularly good hosts for preparing enantioselective catalysts [35]. But the advent of metal–organic frameworks (MOFs) has made it even easier to produce highly

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cinnamyl alcohol → cinnamaldehyde → cinnamic acid

Figure 3. Slice of an electron tomogram of a hierarchical macro/mesopore siliceous oxidation catalyst containing Pd and Pt nanoparticles. (By kind permission of P. A. Midgley, A. F. Lee, and R. K. Leary *et al.*—see also [39].)

effective chiral catalysts, as demonstrated by Lin and associates [36,37]. The great advantage in using the appropriate chiral MOFs for enantioselective conversions arises because, by adroit choice of the chiral organic components of the MOF, homochiral crystals can be easily prepared. (A zeolite that crystallizes in a chiral space group will generally yield an almost equal number of crystals of opposite chirality, and hence be of little value in boosting *ee* values.)

Much activity is now centred on preparing nanoporous hierarchical structures, in which macropores and mesopores coexist and are intergrown. My colleagues and I, using electron tomography—as described elsewhere [38]—have confirmed the validity of Lee *et al.'s* strategy [39] in endeavouring to place nanoparticles of Pd at the inner walls of the macropores of their hierarchical siliceous host (to oxidize aerobically cinnamyl alcohol to the aldehyde) and nanoparticles of Pt inside the mesopores, into which the aldehyde (unlike the alcohol) can enter to be further converted to cinnamic acid (figure 3).

This kind of strategy (K. A. Wilson, A. Lee, M. Isaacs 2017, personal communication), in which so-called spatially orthogonal acid/base catalysts are used, is good for the production of biodiesel. In effect, acid sites in the macropores serve to protect the basic sites by *in situ* removal (esterification) of free fatty acid impurities from triglycerides in the stream of feedstocks.

(d) Decarbonizing fossil fuels

A US Department of Energy report by M. Steinberg, emanating from the Brookhaven National Laboratory, Upton, NY in 1987, focused on 'Fossil fuel decarbonization technology for mitigating global warming'. This 30-year-old report deals eloquently with many of the factors now responsible for our changing world, in particular, the various options available for the reduction in the anthropogenic production of CO_2. In a prescient manner, it advocated various ways of preventing CO_2 from entering the atmosphere arising from the utilization of fossil fuels as a source of energy. Apart from discussing, *inter alia*, improvements in efficiency of conversion and utilization of energy, it also dealt with the decarbonization of fossil fuels and the sequestration of carbon from fossil fuels.

This topic is now of pressing importance, so much so that numerous papers are currently being published to tackle the central issue of decarbonization and the inevitable move towards the hydrogen economy [5,40]. Thus, workers at the Institute of Advanced Sustainability Studies

(IASS) in Potsdam, Germany [40] are recommending that renewed attention be given to methane cracking as a bridge technology to the hydrogen economy.

As mentioned earlier, in both Japan and California, and in other countries also, the aim is to function with a hydrogen economy from about 2030 onwards. With continuing advances in the use of renewable energy, hydrogen production becomes increasingly more feasible, and, already, there are growing numbers of hydrogen refilling stations in the US, Scandinavia and the Far East. With fuel cells of constantly improving efficiency, hydrogen is converted to water and electricity in a pollution-free manner.

Public and private transport is increasingly dependent on the use of hydrogen fuel cells. And while the future supply of H_2 can be met, it is the on-board storage of H_2 that is the key factor that will govern further utilization of H_2-fuel cell vehicles. While compressed H_2 can and is being used in many vehicles, it is desirable, using catalysis, to devise ways of liberating H_2 rapidly from a safe, benign H_2-storage material. This is a major challenge, which could be met by rapidly decarbonizing fossil fuels (such as liquid-range hydrocarbons) by processes such as

$$C_n H_{2n+2} \rightarrow nC + (n + 1)H_2.$$

Significant progress in this direction has been made by a group led by P. P. Edwards, based in the University of Oxford. This group [41,42] uses readily available inorganic catalysts (such as Fe or Ni or alloys thereof), supported on silicon carbide which, with microwave assistance, rapidly produces high-purity H_2. The elemental carbon that is a by-product can be used as constructional material, such as carbon black, or simply, and safely, buried (burying the elemental carbon in a safe manner is much less costly than burying or otherwise sequestering CO_2).

3. Summarizing comments

As my colleague, Professor Oyama, has made reference in his summary to all of the speakers who read papers at this Discussion, I shall focus on only a relatively small fraction of them. At the outset, however, I wish to draw attention to some of the thoughts that I voiced in the Royal Society Discussion on 'Catalysis making the world a better place' held in June 2015. Reference [43] should be consulted to see the overlap between the perceived urgent prospectus of actions then and now.

(a) Session 1 on catalysis for clean energy

The first paper in this session, by Professor Hardacre, dealt with non-thermal plasma-activated catalysis for low temperature operations. It is encouraging to see such efforts being made using plasma chemistry and plasma physics, topics that were first exploited (in the 1830s) by past giants of this Society, namely Faraday (starting from his carbon arcs that generated plasmas), later by Sir William Crookes (in the 1890s) using his eponymous Crookes tube, and then by a Foreign Member, Irving Langmuir, who clarified the nature of non-thermal plasmas that Hardacre *et al*. have now capitalized upon. The important feature of this work is that it enables desirable chemical reactions to take place at much lower temperatures than under the usual thermally activated conditions. Subject to adroit future exploitation, Hardacre's work could well lead to more efficient means of generating energy, and to using it more economically.

Dr Jacob's presentation dealt mainly with mechanistic aspects of the partial oxidation of alkanes. But in her opening remarks she disclosed what the future predictions and assumptions of the Exxon Mobil Company are, in regard to the materials it perceives will figure eminently in 2050 and beyond. *Inter alia*, that company believes that oil will still be a key player in the energy markets, and that partial oxidation of methane would be evermore important in the next few decades.

Predictions of this kind are often controversial. And I made the observation that, depending on what future severe governmental and inter-governmental edicts will be, it may transpire that

oxidation of alkanes, with consequential production of CO_2, be phased out and banned in the coming decades or sooner (see §2).

Furthermore, many organizations and individuals feel that, in order to comply with the Paris inter-governmental recommendations of 2 years ago, it is now urgently necessary to 'decarbonize' fossil fuels, and to use only the H_2 that is so liberated during the process of decarbonization as a source of energy.

Another comment from the floor, by K. Kendall [44] (see also [45]) pointed out that the H_2-fuel cell approach is already well developed in China, especially in regard to using fuel-cell equipped buses (and cars) in the towns, cities and megacities of that country. Already, Japan, for the last several decades, has used H_2-fuel cells to provide heating in schools, hospitals and supermarkets. And there are companies in the USA now that use H_2 fuel cells for long-distance transportation on North American roads.

The paper by Professor Pacchioni was a compelling account of how computational chemistry, allied to experimental investigations, constitutes a viable path towards optimizing the properties of oxides such as TiO_2 or ZrO_2 in biomass conversions. He showed, in particular, that pre-reduction of these oxides is an important step in producing effective catalysts for converting abundant quantities of biomass, especially lignocellulosic materials, into useful platform chemicals.

X-ray tomography, the subject of the next presentation by Beale, like electron (and neutron) tomography, is a potentially powerful method of producing three-dimensional images of a wide variety of solid products, as the review by Midgley *et al.* demonstrated in 2007 [46]. Synchrotron-based X-ray tomography, as executed, for example, by Le Gros *et al.* [45] at Berkeley on biological systems, has proved especially powerful for *in situ* studies. Its use by Beale was directed at the shape and size range of a variety of Fischer–Tropsch catalysts.

(b) Session 2 on catalysis for clean water

Dr Edwards' interesting presentation, which, *inter alia*, disclosed just how much water human beings in the developed world used, per day, focused on the use of H_2O_2 as a means of cleaning contaminated water. Efforts to design and produce new catalysts, other than these based on the precious metals now in use, were described. But other, more recent advances made by her and her colleagues could not be disclosed because of commercial sensitivity.

In Professor Neurock's presentation, detailed kinetic formulations and models were given, which convincingly accounted for the kinetic power dependencies (of O_2 and H_2) under various conditions. This was an elegant presentation, which greatly elucidated the mechanism of the catalytic synthesis of H_2O_2 under a variety of different conditions.

The important topic of destroying organic and inorganic pollutants, from aqueous environments, was masterfully described by Professor Anderson. He showed how, by ion-implantation methods, the band structure of catalysts such as TiO_2 was so changed that they better facilitated the destruction of pollutants. Anderson also made reference to the usefulness of using plasmon stimulation of certain solids to facilitate the reactions that destroy pollutants in aqueous environments. As mentioned in §2, it is felt that much progress can be expected soon in low-temperature catalytic reactions by harnessing plasmon excitation.

(c) Session 3 on catalysis for sustainable materials

The first paper in this session, by Professor Davidson, demonstrated how successful he and his colleagues have been in preparing selective and robust polymerization catalysts for sustainable bioplastics. As the global demand for plastics is set to triple over the next 3 decades, decoupling production of plastics from fossil feedstocks is becoming increasingly important. Hence, the use of bio-based resources for the production of plastics is now of great importance. Polylactides (PLAs), produced via catalytic ring-opening polymerization of lactide, are some of the most promising alternatives to petrochemically derived plastics for commodity application such as packing and

fibres. In his impressive talk, Davidson outlined the development of zirconium-based catalysts for industrial PLA production. He also adumbrated the design of new stereo-selective catalysts and the development of new synthetic strategies for control of polymer architecture.

Integration of new biocatalysts with process design was the topic of Professor Woodley's lucid presentation, in which, *inter alia*, he demonstrated that biocatalysts using enzymes for chemical synthesis and production offer selective, safe and sustainable catalysis.

Protein engineering to create highly selective transaminases as biocatalysts in cascade reactions was the topic that Professor Bornscheuer focused upon. This was a highly illuminating account of progress that he and others have achieved in recent years. One of the remarkable facts that he disclosed was that there are thousands of detailed structures in the Protein Data Base (held at Rutgers University), the biochemical function of which are, as yet, unknown and unexplored. He also reported that there are millions of gene sequences in databases ripe for future exploitation.

Pursuing a theme that overlapped to some degree with the presentation of Professor Woodley, Professor Regina Palkovits focused on efficient utilization of renewable feedstocks, and in particular the role of catalysts and of process design. She emphasized, with appropriate examples, the fact that renewable feedstocks exhibit a multitude of functional groups necessitating selective de-functionalization strategies in low-temperature liquid-phase reactions in highly polar solvents.

(d) Session 4 on catalysis and climate change

The first paper in this session, presented by de Leeuw, combined theoretical and experimental investigations of cubane-structured iron sulfide minerals as potential catalysts in the transformation of carbon dioxide into organic molecules. It was interesting to note that, in her work on the mineral greigite (Fe_3S_4), some pyruvic acid was produced; but it is not clear how the $C-C$ bond present in this material is formed.

Professor Charlotte Williams gave a fascinating account of new ways to construct catalysts for selective polymerizations of mixed reactants. In the course of this work she has devised effective ways of incorporating carbon dioxide into polymers formed from such reactants as anhydrides and epoxides. In so doing, she has evolved methods of producing 'memory polymers', in which the organic products can be repeatedly stretched by substantial amounts, and yet, on gentle heating, are able to relax to their original dimension and shape. The thermoplastic elastomers and shape-memory materials described by her are likely to find many future applications in materials science.

Dr Paul Collier's industrial perspective on catalysis and climate change focused on the development of sustainable processes for industry. In particular, he highlighted recent progress in the manufacture of methanol, nitric acid and ammonia, with a view towards making them environmentally benign. His opening illustrations (shown in fig. 6 of his presentation) drew attention to four distinct 'global drivers', namely: population growth; health and nutrition and ageing populations; natural resource constraints; and environmental factors and climate change regulation. The way in which these four factors impinge upon the chemical industry was discussed in detail by him, with all the important consequences being listed in illustrations (fig. 7 of his presentation).

It was interesting to learn from Dr Collier that it might well be economically and environmentally rewarding in future for the catalytic production of nitric acid (by the oxidation of ammonia) be better effected over a platinum catalyst, rather than vanadia that is now in universal use.

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