

The enduring relevance and academic fascination of catalysis

Catalysis is a subject with a surprisingly long and rich history. It seems certain that it has an even brighter future as the challenges of our society require a focus on this discipline more than ever.

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Few branches of natural science have such comprehensive and impressive credentials as catalysis. The subject is not only of ancient lineage, but also of great current practical importance; and in view of its perennial fascination and numerous enigmatic features it continues to stimulate many exciting, academically oriented adventures.

The phenomenon itself may not, like Melchizedek, have been with us forever, but it was certainly described in the works of Aristotle and also in the writings of the alchemists. It is alleged that Jabir ibn Hayyan in the eighth century outlined one of the first commercial catalytic processes by utilizing the acids produced by the combustion of sulfur to generate ether by the dehydration of alcohol — itself the product of enzymatic conversion — used since time immemorial by primitive societies and subsequently.

Both Michael Faraday and his mentor, Sir Humphry Davy, in the early nineteenth century were well aware of the catalytic properties of metallic platinum. Indeed, they chose strips of this metal as a means of giving light (in Davy's miners' safety lamp) in explosive mixtures of firedamp (methane) in coal mines¹. A little later, the German worker, Döbereiner², devised his ingenious so-called tinder box (*Feuerzeug*), the forerunner of the cigarette lighter, by using a jet of hydrogen to produce a flame when it contacted powdered platinum in air (news of Döbereiner's discovery reached England through the French mathematician and physicist, Hachette, who wrote to Faraday). Platinum was also the catalyst in the first commercial production of sulfuric acid patented by the enterprising Peregrine Phillips, a Bristol vinegar manufacturer in 1831 (ref. ³).

Arguably, the greatest single impact that catalysis has had on humans came when Fritz Haber invented his process of manufacturing ammonia from aerial nitrogen in 1909: it led, through agricultural fertilization, to the elimination of the fear of universal starvation.

Catalysis straddles large areas of chemistry, biochemistry, biotechnology, chemical engineering and molecular biology. It also holds the key to creating a secure, sustainable and environmentally responsible future.

It is well known that approximately 90% of all manufactured materials involve at one stage or another in their production at least one catalytic process: the petrochemical, pharmaceutical and agrochemical industries all depend critically on various kinds of catalytic conversions.

But is it not the industrial scientist alone who investigates the challenges of catalysis: the academic is also profoundly stimulated. How is it, for example, that molecules impinging on certain (catalytically active) surfaces at velocities of typically $1,600 \text{ km h}^{-1}$ can be converted at that surface, with high efficiency, and often with spectacular selectivity, into a desired product, whereas the same species impinging on other (inert) surfaces merely rebound with more or less retention of translational, vibrational and rotational energy?

Catalysis, by its very nature, is not only expansive, but also a topic conducive of cross-disciplinary activity and debate. It serves as a nexus that brings together numerous subdisciplines, each with its own identity: surface and solid-state chemistry, photo- and electrochemistry, solid-state physics, organic and biochemistry, materials science and engineering, chemical engineering and robotics, crystallography, and organometallic and theoretical (including computational) chemistry.

This first issue of *Nature Catalysis* reflects the diversity of the topics encompassed by catalysis. Take, for example, the paper by Barta and collaborators on the complete conversion of abundant lignocellulose into valuable platform chemicals and fuels⁴. There is an exigent need for novel ways of converting the main component of agricultural and forestry wastes into highly desirable and usable products. This study echoes, in part, an earlier venture by Wakerley et al.⁵, who devised an ingenious

method for producing hydrogen, also from lignocellulose, using a solar-driven CdS/CdO_x photocatalyst.

Solar-powered processes — be they predominantly photochemical or electrochemical, as in the reduction of CO₂ and H₂O to produce syngas (a mixture of CO and H₂) that has long been, and continues to be, a vital feature of the petrochemical industry — must, sooner or later, be implemented in more benign ways. This is why the paper by Haas et al.⁶ is so timely.

A particularly interesting account of biocatalysis is reported in this issue by Zakharchenko et al., whereby using a well-controlled magnetic field as a trigger, a cancer drug may be delicately released on demand⁷. And an interesting combination of enzymatic and photocatalytic conversion involving in situ generation of H₂O₂ from water is given by Zhang and colleagues⁸. Ever since the pioneering work of Barber⁹ and others¹⁰ on the catalytic splitting of water into hydrogen and oxygen, much attention has been given to the exploitation of bioinspired soluble manganese clusters that simulate the behaviour of the ubiquitous Mn₄CaO_x cluster. Here, too, Maayan et al.¹¹ report the synthesis and characterization of a novel Mn₁₂-based cluster that functions as a stable, homogeneous electrocatalyst for the oxidation of water at a pH of 6 and with an exceptionally low overpotential.

With the prospect of abundant future supplies of hydrogen, generated from renewable sources of energy, it is desirable to explore a means of effecting hydrogenations of key organic substances using readily available, inexpensive catalysts. The work of Bauer et al.¹² described herein, does just that; and it is exemplified by imine hydrogenation using simple, alkaline earth metal catalysts. Such work constitutes an attractive alternative to the use of more expensive, and often environmentally aggressive, transition metal-based catalysts.

For a considerable time, the petrochemical industry has utilized shape-selective conversions, using acidic zeolitic

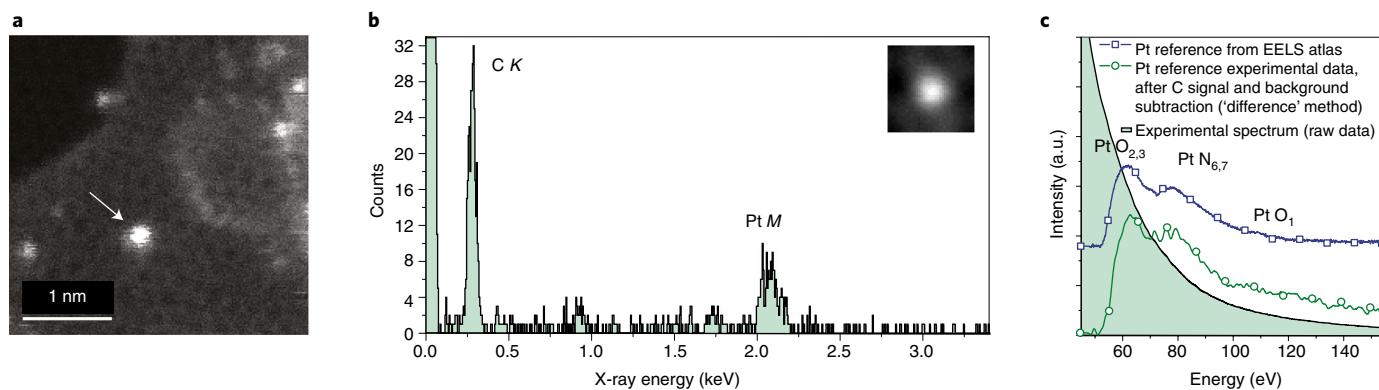


Fig. 1 | Catalyst characterization. Advances in characterization techniques, such as aberration-corrected scanning electron microscopy, and their associated detectors have made it relatively simple to characterize single-atom catalysts. **a–c**, A scanning electron microscopy image (**a**), X-ray emission spectrum (**b**) and electron energy-loss spectra (EELS; **c**) of a single Pt atom. Inset in **b**: image of a single atom of platinum. (For further discussion of electron microscopy see ref. ⁴⁶.) Figure reproduced from ref. ⁴⁴, Royal Society of Chemistry. Originally reproduced with adaptations from ref. ⁴⁵, with permission from AIP Publishing LLC and Q. M. Ramasse.

catalysts to generate polymeric and other intermediates and products¹³, a typical example being the Badger process in which ethene and benzene are converted to ethylbenzene, the precursor of styrene. In this issue, Chowdhury et al. report¹⁴ the use of bioethanol in place of ethene as one of the reactants — soon non-fossil sources of benzene will also need to be utilized — and in doing so they have pinned down the identification of surface ethoxy species (akin to those described some time ago by Zamarev and co-workers¹⁵ in the Boreskov Institute, Novosibirsk).

Some current trends and challenges

Inevitably, personal preferences and subjectivity loom large in any assessment of what now are regarded as the prime factors in the quest for sustainable catalytic solutions for a rapidly changing world. To members of the general scientific public, the following topics would, I surmise, appear on most individual's list of priorities where catalysis must play a vital role: the elimination of oxides of nitrogen and particulates, especially from diesel-operated vehicles; new catalysts for the utilization of anthropogenically produced CO₂; the development of noble metal-free catalysts for fuel cells and a host of other conversions; and new catalytic methods for the rapid decarbonization of fossil fuels. The last-named topic is being actively pursued in Japan at present, and is a current urgent issue among numerous think tanks¹⁶.

My own list of priorities is as follows: capturing solar energy in novel catalytic ways using plasmon-enhanced photocatalysis; exploiting powerful new experimental methods of catalyst

characterization; capitalizing the advantages of the current widespread availability of nanoporous and nanocrystalline materials; and decarbonizing fossil fuels. Each of these is discussed below.

Plasmon-enhanced photocatalysis

It has been shown by Japanese workers several years ago that plasmon-enhanced photocatalysis holds significant promise for controlling both the rates and outcomes of chemical reaction¹⁷. These workers recognized that traditional plasmonic metals (such as Al) exhibit limited surface catalytic chemistry, while conventional catalysts (typically TiO₂) are poor optical absorbers of visible light. By placing a catalytic 'reactor' particle adjacent to a plasmonic antenna, highly efficient and tunable light-harvesting capacities of plasmonic nanoparticles can be exploited to increase substantially absorption and hot-carrier generation in the reactor nanoparticles. In this way, one can boost the absorption of visible light with an absorption maximum at localized surface plasmon resonance (wavelengths 530–600 nm). The precise size and shape of the gold nanoparticles determine the actual range of absorption. Swearer et al.¹⁸ have recently demonstrated this antenna–reactor concept by showing that plasmonic Al nanocrystal antennas decorated with small catalytic Pd reactor particles exhibit dramatic photocatalytic activity over their individual components. In another interesting study, Neumann et al.¹⁹ capitalized on plasmonic heating combined with fermentation and thermal distillation to produce cellulose bioethanol in a sustainable manner. In essence, this plasmonic excitation approach enables many important catalytic

conversions to be carried out at much lower temperatures than was possible hitherto.

Catalyst 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 Tamaru²⁰ 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 others²¹ 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 matrix²². Free-electron lasers, and their temporal resolutions, permit in situ studies of biocatalysts, as demonstrated in the work of Chapman, Spence and co-workers at Stanford University²³.

Femtosecond resolution of the early events in photoassisted water splitting can be gleaned from the judicious use of four-dimensional (4D) ultrafast electron microscopy, the technique pioneered by Zewail²⁴. Such is the power of 4D ultrafast electron microscopy, it enables one to identify the initial (femtosecond scale) electron transfer at, typically, a Ti⁴⁺ active centre into a Ti³⁺–O[−] pair, which has a lifetime in the picosecond range²⁵. As pointed out by Gray²⁶, 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 CO₂ reduction) catalytic cycles. The only downside to 4D ultrafast electron microscopy is that it can never be fully exploited for in situ studies in view of the necessity for the catalyst to be held in a good vacuum. New developments in attosecond pulse studies may, possibly, be able to circumvent this limitation, with consequential huge bonuses. With attosecond (10⁻¹⁸) timescales, the mobilities of the electrons in the catalytic processes may perhaps be accessible.

Notwithstanding the present inability to harness 4D ultrafast electron microscopy for in situ studies of catalysts, there are numerous other techniques that are suitable for such purposes, including Fourier-transform infrared, Raman (either the 1D or 2D kind) and neutron scattering spectroscopy²⁷. And synchrotron radiation becomes ever-more applicable, not only because of the great applicability of free-electron lasers, mentioned earlier²³, but also because progressively lower X-ray wavelengths (for example, less than 0.5 Å) are available, and this, under ideal conditions, enables the position of hydrogen atoms attached to metals to be readily located.

Nanoporous materials

In capitalizing on the current widespread availability of nanoporous materials, it is relevant to recall, that, from the earliest days of heterogeneous catalysts, high-area solids were extensively used. Often minute nanoparticles of active metal catalysts, such as Pt, Pd and Ni were supported on high-area, zeolitic or amorphous silicas and amorphous carbons. This was because, by so doing, maximal numbers of active sites, and hence of turnover numbers, could be produced in this way. Nowadays, owing to much progress in exploiting structure-directing molecular entities²⁸ as well as other strategies²⁹, it is feasible to prepare an extensive range of nanoporous solids (especially oxide ones), the pore diameters of which may be controllably altered to fall in the range of 20 to 500 Å (ref. ³⁰). (Over half of the elements in the periodic table can now be prepared as nanoporous oxides, halides, sulfides or in their native states). All 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 host³¹. In addition, active sites, of a well-defined identity, can be inserted as surface features in the interior of nanoporous solids without use of organometallic precursors³². Nanoporous silicas are particularly good hosts, especially

the hierarchical ones where micro-, meso- and macro-channels coexist, for preparing enantioselective catalysts; but the advent of metal-organic frameworks has made it even easier to produce highly effective chiral catalysts, as demonstrated by Lin and co-workers³³.

Nanostructured oxidic catalysts, as artificial photosynthetic systems, are also especially useful³⁴ for the direct conversion of CO₂ and H₂O to fuel. Such catalysts need to exhibit turnover frequency and density (hence size) commensurate with the solar flux at ground level (1,000 W m⁻² and air mass 1.5) to avoid wastage of incident solar photons. For example, a catalyst with a turnover frequency of 100 s⁻¹ requires a density of one catalytic site per square nanometre. Moreover, the catalyst needs to operate close to the thermodynamic potential of the redox reaction so that a maximum fraction of the solar photon energy is converted to chemical energy. Stability considerations favour all-inorganic oxide materials, and previous work^{35,36} points to IrO₂ nanoclusters (approximately 2 nm diameter) as a very good candidate. However, Ir is the least abundant metal on Earth. For this and other reasons, Co₃O₄ nanocrystals were selected, on the basis of their stability under use, the modest overpotential, and the mild pH and temperature conditions, as a viable integrated solar fuel conversion system³⁴.

While on the subject of nanomaterials, there has recently been a plethora of papers devoted to single-atom catalysts — see the special issue of *Catalysis Science and Technology* edited by Mitchell and colleagues³⁷. Single-atom catalysts involve the use of catalysts (normally heterogeneous ones, but there are gas-phase examples³⁸) that consist of isolated metal atoms stabilized on appropriate carriers. Their rapid development has arisen in part because of continued advances in characterization techniques, such as aberration-corrected scanning transmission electron microscopy (Fig. 1), but also because of the quest to maximize atom efficiency through downsizing from the metal nanoparticles traditionally applied in heterogeneous catalysts to single atoms. This is an especially fertile area that has active groups worldwide; and several literature reviews have recently appeared^{39,40} (see also Fei et al.⁴¹ in this issue). A great deal is likely to be heard of this fertile area of catalysis in the years ahead.

Decarbonization of fossil fuels

Finally, a word about the role of new catalysts in the arrival of the hydrogen economy — which both Japan and

California are dedicated to reach from about 2030 onwards. One key obstacle at present devolves on the question of a safe, reliable means of storing hydrogen. Another is to devise a catalyst that can rapidly release hydrogen (with little or no impurities) from the storage material. If these problems can be solved — and China, in its megacities especially, is dedicated to the construction of fleets of hydrogen-driven fuel-cell vehicles — it will herald the demise of fossil fuels, and CO₂ will no longer be produced from transportation and fuels. In connection with this, polymer electrolyte fuel cells are unquestionably here to stay. They will play a crucial role in the already foreseeable hydrogen economy by generating energy through the catalytic combustion of hydrogen. And enhanced performance of polymer electrolyte fuel cells can be achieved using the recently demonstrated⁴² lung-inspired approach to their design.

A vital step forward would be the facile decarbonization of fossil fuels, whereby materials such as oil, waxes, diesel and petroleum fuels could be catalytically dehydrogenated. Promising advances in this direction have been achieved by Edwards and colleagues at the University of Oxford⁴³. □

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