Reflections on the value of electron microscopy in the study of heterogeneous catalysts

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Electron microscopy (EM) is arguably the single most powerful method of characterizing heterogeneous catalysts. Irrespective of whether they are bulk and multiphasic, or monophasic and monocrystalline, or nanocluster and even single-atom and on a support, their structures in atomic detail can be visualized in two or three dimensions, thanks to high-resolution instruments, with sub-Ångstrom spatial resolutions. Their topography, tomography, phase-purity, composition, as well as the bonding, and valence-states of their constituent atoms and ions and, in favourable circumstances, the short-range and long-range atomic order and dynamics of the catalytically active sites, can all be retrieved by the panoply of variants of modern EM. The latter embrace electron crystallography, rotation and precession electron diffraction, X-ray emission and high-resolution electron energy-loss spectra (EELS). Aberration-corrected (AC) transmission (TEM) and scanning transmission electron microscopy (STEM) have led to a revolution in structure determination. Environmental EM is already playing an increasing role in catalyst characterization, and new advances, involving special cells for the study of solid catalysts in contact with liquid reactants, have recently been deployed.

1. Introduction

During the past decade, major advances have occurred in electron microscopy (EM) largely because of spectacular instrumental, detector and computational developments. First, there is the arrival of aberration-corrected (AC) high-resolution electron microscopes of both the...
transmission (TEM) and scanning transmission (STEM) kind. This, in turn, has enabled almost routine measurements to be made at sub-Ångstrom-unit resolution, as illustrated in figure 1 of the individual atoms in elemental silicon [112] direction [1]. In addition, direct electron detectors have now become available and they, in turn, have revolutionized electron crystallography (EC) especially cryo-electron microscopy of macromolecular entities.

Moreover, as a result of improved electron spectrometers, it is now possible to record the electron energy-loss spectrum (EELS) at high-resolution of individual atoms and ions in a given structure and, thereby, determine their valence state and detailed atomic environment, as well as measure high-resolution vibrational spectra of the structure to which the atom or ion is bound [2,3]. Furthermore, electron tomography (ET), especially when using AC-STEM microscopes of the type schematized in figure 2, has now become a quite popular and powerful addition to the armoury of the electron microscopists [4–6].

In addition, when beam damage is inflicted by the primary electron beam, the procedure of compressed sensing, as described in a recent paper [7] can be invoked. Given that energy-dispersive detectors for X-ray analysis are now a regular feature of modern electron microscopes, as well as electron spectrometers, it is readily possible to record several distinct signals, so that it is legitimate to talk of multi-dimensional EM, as described more fully elsewhere [4,5]. In other words, EDS (energy-dispersive X-ray signals) and EELS signals, as well as images and diffraction patterns can all be simultaneously recorded.

All the above remarks apply to static imaging. But there have also been revolutionary developments in ultra-fast four-dimensional (4D) EM—three dimensions (3D) of space and one of time—most of these being brilliantly pioneered and exploited by Zewail and co-workers [8–13]. An illustration of the power of 4D EM is given in figure 3 taken from the paper read to this Society by Zewail [14] in 2010.

Even prior to the arrival of the new developments in EM in the last decade, considerable progress had been made using EM to characterize heterogeneous catalysts [15–18].
Figure 2. (Left) The STEM and associated detectors; high-angle-annular dark-field (HAADF) annular dark-field (ADF), and bright-field (BF). If the BF detector is removed, transmitted electrons can pass through a spectrometer to form an energy-loss spectrum. The tilting of the specimen performed in electron tomography (ET) experiments is illustrated schematically. $\theta_A \approx 10$ m rad; and $\theta_H \approx 50$ m rad. (Right) Set-up for the precession electron diffraction.

High-resolution electron microscopy (HREM) had uncovered many important matters of direct relevance to heterogeneous catalysis, and it is instructive to refer to just three of them here:

(i) **The enigma of strong metal support interaction (SMSI)**

At one time, it seemed puzzling to observe that catalytically active nanoparticles of precious metals, such as Rh, lost their activity after use at high temperatures. It seemed implausible when it was suggested that the support could be so mobile as to encage the active metal catalyst. But HREM studies showed convincingly that this was indeed possible in situations where the interaction between the metal and its support, typically Rh on TiO$_2$, was strong (figure 4).

(ii) **Existence of surface structures different from the underlying (bulk) structure**

Figure 5 clearly illustrates the reality of situations where the bulk catalyst is fundamentally different from that which exists at the surface. In the oxidation catalyst of composition La$_2$CuO$_4$, which smoothly converts CO to CO$_2$ in O$_2$, the catalytically active phase does not exhibit this stoichiometry or structure, but a different, simpler one, the C-phase of La$_2$O$_3$. It would be instructive to re-examine this catalytic system using annular dark-field EM, just as was done recently by Pennycook et al. [20]. In the hands of these investigators, AC-STEM has enabled atomic resolution imaging at significantly reduced beam energies and electron doses. It has also made possible the quantitative determination of the composition and occupancy of atom columns using the atomic number (Z)-contrast annular dark-field (ADF) [21] imaging available in STEM.
Figure 3. 4D electron imaging in real, Fourier and energy spaces. The conceptual design of Caltech’s UEM-2 is presented on the right; a single-electron trajectory is depicted within the UEM. The atomic-scale (femtosecond) temporal resolution characteristic of the apparatus allows for the visualization of dynamical processes in real time. Shown on the left are typical UEM frames of real-space images and diffraction patterns, together with three-dimensional maps of femtosecond-resolved electron-energy-loss spectra (FEELS). Image reproduced from [14].

Figure 4. Typical example (after [19]) of strong metal-support interaction, designated SMSI. When the Rh/TiO$_2$ catalyst is raised to an elevated temperature in H$_2$ (approx. 500°C) the support is seen to climb over the Rh, thus diminishing its catalytic activity.

Pennycook et al. [20] employed rapid scanning to both drive and directly observe the atomic-scale dynamics, using combined high-resolution imaging and high-resolution EELS, in the transformation of Mn$_3$O$_4$ into MnO. This EM study clarified the complex atomic mechanism involved in the changes at the oxide catalyst.

Such is the power of modern STEM instruments that my colleagues (Midgley, Collins et al.) have been able to observe a thin veneer on the surface of crystallites of CeO$_2$, where the Ce$^{III}$, rather than the normal Ce$^{IV}$ ions predominate.

(iii) Atomic structure of ultrafine metal nanoparticles and the catalytic significance of crystallographic twinning

An early study [22] by my colleagues and me of the structure of nanoparticles of Pt catalysts revealed a strong propensity for twinning (figure 6). Very recent work by Behrens et al. [23]
have convincingly shown—see figure 7—that the catalytic activity of nanoparticles of Cu in the methanol synthesis reaction are crucially governed by the number of twin boundaries that exist in the Cu particles [23]. (In this case, it is also thought that minute traces of Zn$^{\delta+}$ ions, preferentially accumulated at the termini of the twin planes, play an important role in the catalytic turnover.)

I now turn to the two main themes of this article:

(a) single-atom heterogeneous catalysts and
(b) nanoporous oxidic catalysts of the single-site variety.

2. Single-atom heterogeneous catalysts

In the study of nanoparticle and nanocluster mono-metallic [24,25] and bimetallic [26] heterogeneous catalysts over the years, it has long been suspected that individual atoms, detached from the nanoparticles (containing $10^4$ to $10^7$ atoms) or nanoclusters (containing 4 to 20 atoms), were the true loci of catalytic action (figure 8).

Recently, several studies [27–37] have provided incontrovertible proof that individual atoms are indeed capable of effecting a number of catalytic reactions, especially selective hydrogenations, as well as the water-gas shift reaction:

$$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2.$$  

Examples are shown in figures 9 and 10. Details of these studies are given in the work of Flyzani-Stephanopoulos et al. [31,32,36,37] of Zhang et al. [27–30] and Perez-Ramirez and co-workers [34], see also Christopher et al. [38] and Thomas & Leary [39] From these studies, it is quite clear that individual atoms of the platinum group metals are the active centres for catalytic turnover. (We note, in passing, that in many of the reactions for which nanoparticles of Au on various supports are the catalysts, Fu et al. [40,41] showed that the nanoparticles were spectator species, and that it was Au–O moieties that served as catalytically active centres.)
Figure 6. HREM images of ultrafine nanoparticles of Pt are seen to be rich in twin boundaries.

At the Dalian Institute of Chemical Physics much work has been carried out, using individual atoms of the platinum group metals (Ir, Pt especially) supported on non-stoichiometric FeO\textsubscript{x}. Wei \textit{et al.} [29] have demonstrated that single-atom catalysts (SACs) of Pt on FeO\textsubscript{x} are excellent catalysts for the chemoselective hydrogenation of a variety of nitroarenes to their amino products (without hydrogenating benzene rings or carbonyl groups attached to them) under mild conditions, typically at 40°C, with contact times ranging from 10 to 120 min, conversions of 90–100% and selectivities from 90 to 99.7% [29].

Later, Lucci \textit{et al.} [32] showed how effective their so-called ‘single-atom alloys’—see also [40]—where isolated, individual atoms of Pt on a Cu support can selectively hydrogenate 1,3-butadene to 1-butene, an industrially important reaction used to eliminate impurities of the diene in propylene gas that is extensively utilized for polymerization (figure 9).

SACs are, in effect, the \textit{reductio ad absurdum} of the single-site heterogeneous catalysts that are well known in other contexts [42–44]. The key question, so far as their longevity is concerned, is how stable and secure is the solitary catalytically active atom on its support? Clearly, the nature of the bonding between the SAC and its support is crucial. An ingenious way of boosting the stability and minimizing the tendency for surface diffusion was devised by Perez-Ramirez and co-workers [34] and further discussed by Thomas [35] My group at Cambridge with Midgley,
Leary, Furnvial et al. [45,46] have recently been collaborating with Perez-Ramirez et al. to investigate such systems as Ir on C₃N₄—the support described by Vilé et al. [34]—which, in its graphitic form, has monatomic depressions into which SACs like Pd fit snugly (figure 10).

This catalyst is active in the three-phase selective partial hydrogenation of alkynes in flow mode, and both in activity and selectivity surpasses those of nanoparticle Pd. In our joint work with the Perez-Ramirez group, we have been able—thanks to the assistance of Dr Ramasse at Super STEM in Daresbury—to image several SACs composed of one or other of Ir, Pt, Ru and Pd on C₃N₄ supports. One micrograph (figure 11) reveals individual atoms of Ir on C₃N₄, with a slight tendency for the Ir atoms to form loosely attached pairs.

In collaboration with Vajda et al. in the US, and Ramasse, UK, my colleagues and I have recently studied [48] the energetics of single atoms of Cu on a graphene oxide. This sample was prepared by Vaja & Toy [49] using a novel ‘cluster’ deposition method of laying down atoms and their clusters, in soft-landing mode, on to the chosen support. The micrograph (figure 12) shows well-separated individual atoms of Cu that are rather loosely bound to the graphene oxide. We have studied the diffusion of these single Cu atoms across the surface at ambient temperature. The observed behaviour exhibits anomalous symptoms, which are still the subject of investigation.

Processes such as surface diffusion are not only important in heterogeneous catalysis, but also in epitaxial growth and in the phenomenon of Ostwald ripening [50,51].

(a) Catalytic and optical properties of discrete Pt nanoparticles bound to nanoparticles of colloidal Au

This subsection is not directly concerned with heterogeneous catalysis per se [7]. The dendritic Pt nanoparticles visible in figure 13 are active, proven plasmonic catalysts, but the prime reason
Figure 8. Illustrative examples of minute clusters of Au on a titania support (top) and on an activated carbon support (bottom). Sub-nanometre clusters (white circles) of size approx. 5 Å diameter and containing 10 Au atoms are observed, together with individual Au atoms (black circles). (Micrographs kindly provided by P. L. Gai).

for discussing them here is to illustrate the importance of both electron tomography (ET) [52] and compressed sensing [53] as vitally important techniques in the electron microscopic investigations of nanoporous and plasmonic catalysts. Full details are given in [52]. For a pedagogically interesting example of direct observation of catalytic conversions promoted by surface plasmons, see the work of Novo et al. [46] on Au nanocrystals.

3. Nanoporous oxidic catalysts of the single-site variety

This is very much the age of nanoporous solids. Not only has the number of distinct kinds of mesoporous silicas increased enormously in the past few decades, but there has also been an almost exponential growth in the number of nanoporous metal oxides, both simple and mixed: TiO₂, ZrO₂, GeO₂, MgO, Cr₂O₃, Al₂O₃, etc. (table 1). Furthermore, there are nanoporous covalent solids, nanoporous carbons, not to mention the 200 or so structurally distinct kinds of zeotypes (embracing alumino-silicates and alumino-phosphates). In addition, over 30 000 distinct types of metal-organic-frameworks (MOFs) have now been identified, some of which exhibit quite high thermal stability. So far as the solid-state chemist devoted to the design of ever-more powerful single-site catalysts is concerned, very many of the numerous nanoporous solids currently available possess high crystallographic order.

In addition to the availability of microporous oxidic solids (with pore diameters up to approx. 14 Å diameter), there is a multitude of mesoporous solids possessing pore diameters from 15 Å upwards to several hundred Å units. Some of these (mesoporous) solids exhibit chirality, and can
Figure 9. (a) STM images showing atomically dispersed Pd atoms at a Cu(111) surface and hydrogen atoms that have dissociated and spilled over onto the Cu surface. (i) Pd is alloyed into the Cu(111) surface preferentially above the step edges as evidenced by the rumpled appearance of the upper terrace (scale bar 50 Å). (Insert) Atomic resolution of the Pd/Cu alloy on the upper terrace showing individual, isolated Pd atoms in the surface layer appearing as protrusions (scale bar, 20 Å). (ii) Schematic showing dissociation and spillover at individual, isolated Pd atom sites in the Cu surface layer. (iii) Islands of H atoms imaged after hydrogen uptake appear as depressed regions on the clean Cu(111) lower terrace (scale bar, 50 Å). (Insert) High-resolution image of individual hydrogen atoms on Cu(111) (scale bar, 20 Å). Images recorded at 5 K. (b) Mechanistic aspects of the selective hydrogenation of 1,3-butadiene to 1-butene using a platinum-copper nanoparticle catalyst at the single-atom limit (by kind permission of M. Flytzani-Stephanopoulos).

be prepared as homochiral polymorphs, but to a much lesser degree than the porous MOFs now widely available.

It is chemically rather straightforward to introduce well-defined single catalytically active sites into these nanoporous hosts, and the various ways of doing so (either during formation or by post-synthesis modification) have been described elsewhere [42–44,66,69]. One of the key features of nanoporous, well-ordered solids is that they possess very large surface areas. It means, therefore, that the number of catalytically active sites—spatially well separated from one
Figure 10. Schematic of a single-atom Pd catalyst comprising isolated Pd atoms on a solid support of C$_3$N$_4$ (carbon, grey, nitrogen, purple), which acts as a catalyst [34] for hydrogenation reactions. Strong bonds to the nitrogen atoms firmly anchor the Pd atoms in roughly triangular pores in the stacked, two-dimensional layers of the support, see also [35].

Figure 11. HREM image of individual Ir atoms bound to a C$_3$N$_4$ support (after [47]).
another so as to secure uniformity of performance—is very large per unit mass (or volume) of the
designed catalyst.

From the very early days of the study and use of pentasil zeolites, like ZSM-5 and ZSM-11
(termed MFI and MEL in the International Zeolite notation), EM has played a progressively more
powerful part.

Even before the 3D, X-ray-derived crystal structure of ZSM-5 was determined, HREM had
unequivocally established [70] the nature of the distribution of the pores and general internal
porosity of this important catalyst. In the ensuing 20 years, my group had evolved [15] a well-
deﬁned set of procedures for the structural elucidation of microporous and mesoporous catalysts
and molecular sieves by HREM.

(a) Full structure determination by electron crystallography

Thanks largely to the subsequent work of my former colleague, Osamu Terasaki, [71,72]
numerous structural determinations have been made by EC of very many mesoporous silicas,
and of the corresponding mesoporous carbons prepared, such as CMK-1 and CMK-4 (derived
by moulding with organic material such as sucrose, as described by Ryoo [73,74]). The 3D
structure model of MCM-48 (which has interesting mesopores that facilitate intra-crystal diffusion
of reactants), shown in figure 14 was determined by EC. The prime advantage of using the EC
technique for mesoporous silica—and for several other ordered nanoporous solids—compared
with traditional X-ray single crystal diffraction, is that HREM images can be taken and the phases
of crystal structure factors (CSFs) are immediately available from the Fourier transform of the
image. Additionally, the stronger interactions (by several orders of magnitude, approx. $10^4$)
of electrons with matter compared with X-rays, enables very small crystals, down to several tens of
unit cells in size, to be investigated.
Figure 13. Volume rendering visualizations of the four Pt-decorated Au nanoprism studies by electron tomography. (a,b) Planar approximately 7 nm thick Au nanoprism with lower and higher amounts of Pt NP growth, respectively (total thickness approximately 15 nm). (c) Smaller (edge length approx. 110 nm) but thicker (approx. 14 nm) Au nanoprism with extensive Pt NP growth (combined thickness approx. 25 nm). The inset orthoslice reveals well-defined convex \{111\} facets of the Au nanoprism. (d) Pt—Au nanoprism with twisted morphology [7].

Such conditions allow datasets to be obtained for 3D CSFs from HREM images taken down different zone axes. The structure of MCM-48 determined in this way (figure 14) exactly follows the so-called G-surface with a thickness of approximately 13 Å. The wall separates the structure
A typical set of HREM images of MCM-48, taken with incident electrons parallel to [100](a), [110](b), and [111](c), is shown in figure 14, with the corresponding Fourier diffractograms (FD) inserted in each image. These FDs are complex in general and their moduli is a function of wavevectors. From the extinction rules, the space group was found to be la3d. (Fuller details of how contrast transfer functions are incorporated into the final determination are given in the many papers of Terasaki—see, in particular [71]). An ordered nanoporous carbon formed from MCM-48, such as CMK-1 or CMK-4, has had its structures determined also by EC as outlined above. CMK-1 and CMK-4 are prepared by impregnating calcined MCM-48 with sucrose solution in the presence of sulfuric acid. After drying the resulting mixture, the impregnation step is repeated, before the whole is carbonized under vacuum at approximately 1170 K. Finally, the silica template is dissolved at 373 K in aqueous NaOH, leaving the final CMK product [73].

(b) Other methods of elucidating nanoporous structures by high-resolution electron microscopy

It is not necessary to go through detailed structural determination of the type described for MCM-48 above in order to gain fresh insights that are crucial for an understanding of catalytic action [15]. Thus, a few HREM images taken down one or two zone axes can reveal the essential nature of the structure of the zeolitic catalyst. We cite two examples:

First, the selective oxidation catalyst developed by the Exxon Central Research (ECR-1) Laboratory; Second, the Brønsted-acid catalyst known as ZSM-23, developed by the Mobil Company.

As seen in figure 16, ECR-1 turns out, from HREM imaging, to be an intimate twin of the well-known natural zeolites mordenite and mazzite, shown in projection in figure 16a. And the zeolitic catalyst ZSM-23 is a recurrently twinned version of the synthetic zeolite Theta-1 (TON) (figure 16b).
Figure 14. HREM images of MCM-48. Incident electrons are parallel with [100] (a), [110] (b), and [111] (c). Corresponding Fourier diffractograms (FDs) are inserted in each image (by kind permission of O. Terasaki).

The framework-substituted microporous alumino-phosphates selective oxidation catalysts [44] are rather beam-sensitive and not amenable to the EC method described above for MCM-48. A combined approach entailing computation and HREM imaging was used [76] to solve this structure of Co-ALPO-36, which has very many catalytic uses [44].

(c) Summarizing verdicts on the value of high-resolution electron microscopy in elucidating structures of zeolitic catalysts

Up until the early 1980s, there was much confusion in the open and especially the Patent literature concerning identification of a large number of new zeolitic catalysts. One classic example involved the debate between the US companies Union Carbide and their new zeolite, termed silicalite, and the Mobil Company and their new zeolite, ZSM-5. Were their structures distinct? The definitive answer came partly from a combination of powder X-ray diffraction, and, especially, from magic angle-spinning $^{29}$Si NMR. It was unequivocally established, [77,78] that, structurally, silicalite and ZSM-5 were identical so far as the tetrahedral sites were concerned. ZSM-5 simply had some $\text{Al}^{3+}$ isomorphously replacing $\text{Si}^{4+}$ sites, whereas silicalite was ‘pure’ $\text{SiO}_2$. Silicalite I was structurally identical, but compositionally distinct from ZSM-5, and silicalite II was
Figure 15. Two views of the structure of the zeolite MCM-48 determined by electron crystallography (EC). (Reprinted with permission from Thomas et al. [15]. Copyright © American Chemical Society.)

likewise related to ZSM-11. The former microporous catalyst has what the International Zeolite Association describes as a MFI framework, the latter an MEL framework. Earlier investigations had speculated that an almost infinite series of pentasil zeolite catalysts could exist between various sequences of the end-members ZSM-5 and ZSM-11. EM duly confirmed that this was a reality. My colleague, Millward and I showed [79,80] that various sequences of ZSM-5, intimately connected at sub-unit cell level, with ZSM-11 were readily visible in HREM images (figure 17).

We note in passing that the exceptionally powerful [81] selective oxidation catalyst, TS-1, has isomorphous substitution of Ti$^{4+}$ in place of Si$^{4+}$ (figure 18).

New, and highly interesting kinds of zeolites continue to be synthesized, the catalytic properties of which remain to be fully explored. Thus, from Corma’s group in Spain, multi-pore zeolites have been synthesized (and some of their catalytic applications examined) [82]. Also, there is the report of a multi-dimensional extra-large [83] pore zeolite with $20 \times 14 \times 12$ ring channels, [82] which, as yet, has been produced in coexistence with GeO$_2$ and the structure of which has been solved (by Zou et al. [71]) using ET and rotation electron diffraction. In the characterization of these two new types of nanoporous catalysts, EM plays a major part.

As well as the straightforward aluminosilicate nanoporous (predominantly microporous) solids, there are also increasingly prominent organo-silica hybrid mesoporous solids, such as the one described by Inagaki et al. [84] shown in figure 19, and the fascinating range of organic–inorganic zeolites produced by the ENI company in Italy (see [85] and references
therein) where they incorporate simple organic groups (mainly -CH₂-) into known zeolite frameworks. To date, to quote Millini & Bellussi [85] the attention has been primarily focussed on the preparation and structure characterization of the materials and little information has been published on the possible applications of these hybrid crystalline phases. It is fully realized, however, that because of the presence of an abundance of well-defined C–H bonds—in both the Japanese and Italian

**Figure 16.** (a) HREM reveals that zeolite ECR-1 is a sub-emit-cell level intergrowth (recurrent) of mordenite and magzite layers. (b) Schematic of ZSM-23 structure, revealed by HREM to be a recurrently twinned version of the zeolite theta-1 (TON). (Reprinted with permission from Thomas et al. [15]. Copyright © American Chemical Society.)
Figure 17. (Top) Schematic drawing of an example of seven recurrent ZSM-5 structures interspersed by one ZSM-11. (Bottom) HREM images with accompanying diffraction patterns of various parts of a ‘nominally pure’ ZSM-5 specimen.

Figure 18. Isomorphous substitution of Si by Ti in TS-1 (after Bellusi et al. [81]).
organicsilica hybrid mesoporous crystal

An ordered mesoporous organicsilica hybrid material with a crystal-like wall structure.

Figure 19. (a–c) A typical organo-silica hybrid microporous crystal, of the type yet to be exploited in heterogeneous catalysis—see text (after Inagaki et al. [84] see also [85]).

preparations—it is possible to insert functional groups that are able to coordinate metal complexes for specific redox reactions or chiral junctural groups for enantioselective conversions that are not feasible in conventional zeolites. This is potentially a rich area of future investigation, and can extend the work of Thomas et al. in grafting enantioselective catalysts on to mesoporous silicas [44,86].

(i) An illustrative example of electron tomography yields topography of heterogeneous catalysts

My colleagues and I have previously drawn attention [87] to how, using the set-up depicted in figure 2, high-angle-annular dark-field (HAADF)-STEM tomography of a supported heterogeneous catalyst reveals a great deal both about the topography of the support and the distribution of the nanoclusters and nanoparticles catalysts upon it. We first draw attention to the bimetallic (Pt-Ru) nanocluster catalysts supported on mesoporous silica where such nanocatalysts may be almost invisible using conventional bright-field TEM, yet can be readily distinguished from the lighter support using HAADF-STEM imaging, [21] owing to the strong Z-dependence of the HAADF signal. From the ET reconstruction, as outlined elsewhere, [87] the pore volume, surface-area, mean diameter, overall porosity and catalyst loading can be determined. The surface dimension of the pore network was found to be fractal in nature. Moreover, by classifying the surface curvature of the support, the nanocatalysts were found to be anchored at ‘saddle points’ on the support surface (figure 20a). In another example (figure 20b), a combination of AC-STEM and HAADF-STEM tomography identified the propensity for Au nanoparticle catalysts on a titania support to reside in crevices between the individual titania grains.

Very recently, my colleagues (Midgley and Leary) have examined by electron tomography the novel catalysts of Lee, and colleagues, at the University of Aston. These are composed of a macroporous host which also contains mesopores. Electron tomography confirms that minute Pt nanoparticles reside largely within the mesopores and the larger Pd nanoparticles within the macropores.
Figure 20. (a) Electron tomographic (ET) reconstruction of (Pt, Ru) nanocluster catalyst supported on a disordered mesoporous silica. The visualization of the silica has been colour-coded according to the local Gaussian curvature [87]. The nanocluster catalysts (red) appear to prefer to anchor themselves at the (blue) saddle points. (b) Surface-rendered visualization of an ET supported on titania (blue). The nanocluster catalysts are located in the crevices between titania crystallites confirmed by the AC-STEM image in panel (c) (Thomas et al. [87]).

(ii) A striking example of the determination of the structure of a complex solid oxide catalyst by aberration-corrected scanning transmission electron microscopy

It has been known for some time that there are complex oxides, containing several distinct elements (e.g. Mo, V, Nb, etc.), that can selectively oxidize propane directly to acrylic acid in air or O₂, and ammoxidize the same reactant to acrylonitrite, each of these products being extensively used

\[
\text{CH}_3\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_2=\text{CH-COOH}
\]
CH₃CH₂CH₃ → CH₂CH-CN.

In a definitive paper by my former colleagues, Buttrey and co-workers [88], reviewed later by me [89], the essential nature of this complicated catalyst could be discerned from an analysis of the HAADF-STEM images taken down the [001] axis (figure 21).

It was even possible to read off the atomic coordinates and site occupancies from their EM study.

4. Epilogue

There are several other important applications of EM to the study of heterogeneous catalysts. For example, there are the advances in environmental TEM that have occurred beyond the work described by Zewail and me in Chapter 4 of our book [11] by investigators, such as Gai et al. [90], Helveg and co-workers [91], Grunwaldt et al. [92] and Browning [93], and the ingenious recent study of Park et al. [94]. The last named group constructed a special cell (composed of windows made of graphene) to enable them to follow freely rotating Pt nanoparticles in a liquid
environment. This constitutes a breakthrough in the potential that EM has for the future study of heterogeneous catalysts that function in a liquid (or gas-liquid) environment (figure 22). And this approach, coupled with *in situ* synchrotron X-ray diffraction [95] has already been profitably exploited in charting the development of intracrystalline mesoporosity in commercially important zeolitic catalysts.

**Figure 22.** Schematic illustration of *in situ* TEM imaging of Pt nanocrystals freely rotating in a so-called ‘graphene liquid cell’ (GLC), and 3D EM density maps calculated from individual Pt nanoparticles in solution (after Park *et al.* [94]).
Several other categories of heterogeneous catalysts, like the core-shell bimetallic ones of minute dimension, the designed bimetallic [Au-Pd] nanoparticles for efficient photocatalytic production of hydrogen [96], and the wide range of oxidative and other nanocatalysts investigated at the Max Planck Institutes in Berlin and Muelheim [97], are all now addressable using the highest ever attained spatial and chemical resolution. The EM approach has already reached its climax so far as aberration-correction is concerned. Now the territory of catalytic significance that needs to be charted is that involving progressively faster time resolution. In this connection, it is instructive to recall the very last joint work that Zewail and I did on elucidating the nature of the catalytically active site in a multiply-bonded Ti[iv]oxo unit in a low-coordinate titanosilicate photocatalyst [98,99].

Zewail and I and our colleagues, using his classic 4DEM approach [98], activated this catalytically active centre by laser-induced electron transfer to form a stretched [single bonded] Ti[iii]oxo unit. The femtosecond dynamics revealed exceptional Ti-O bond disruption, making
the oxo very basic for interaction with a proton on water or on the carbon of carbon dioxide. Commenting recently on this work the eminent photochemist, H. G. Gray, said [100]: ‘This groundbreaking work has given us [for the first time] snapshots of early events in water splitting [as well as carbon dioxide reduction] catalytic cycles!’

Many more adventures in 4D-EM can also be expected simply by pondering the wealth of variants of ultra-fast EM depicted in the characteristically evocative and spectacular illustration contained in one of the last publications [101] of Ahmed Zewail (figure 23).

Competing interests. I declare I have no competing interests.

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Author profile

Apart from his work in the development and exploitation of electron microscopy in solid-state chemistry, John Meurig Thomas has designed and characterized in situ numerous heterogeneous catalysts. He was awarded the Royal Medal of the Royal Society for Physical Sciences in 2016, for his pioneering work in single-site heterogeneous catalysts and their use in green chemistry and clean technology.

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