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Visualising reacting single atoms under controlled conditions: Advances in atomic resolution *in situ* Environmental (Scanning) Transmission Electron Microscopy (E(S)TEM)

Voir des atomes individuels en cours de réaction sous conditions contrôlées : Progrès récents en microscopie électronique (à balayage) en transmission environnementale in situ (E(S)TEM)

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A R T I C L E   I N F O

A B S T R A C T

Advances in atomic resolution Environmental (Scanning) Transmission Electron Microscopy (E(S)TEM) for probing gas–solid catalyst reactions *in situ* at the atomic level under controlled reaction conditions of gas environment and temperature are described. The recent development of the ESTEM extends the capability of the ETEM by providing the direct visualisation of single atoms and the atomic structure of selected solid state heterogeneous catalysts in their working states in real-time. Atomic resolution E(S)TEM provides a deeper understanding of the dynamic atomic processes at the surface of solids and their mechanisms of operation. The benefits of atomic resolution-E(S)TEM to science and technology include new knowledge leading to improved technological processes with substantial economic benefits, improved healthcare, reductions in energy needs and the management of environmental waste generation.

R É S U M É

On décrit ici les progrès réalisés en microscopie électronique (à balayage) en transmission (E(S)TEM) pour étudier *in situ* les réactions catalytiques solide–gaz au niveau de la résolution atomique sous des conditions environnementales contrôlées en pression et en température. Les récents développements de l'ESTEM ont permis la première visualisation directe en temps réel d'atomes individuels et de la structure atomique de catalyseurs solides hétérogènes dans leurs conditions de réaction. Ils donnent accès à une meilleure connaissance des processus atomiques dynamiques à la surface des solides et à leurs mécanismes de fonctionnement. Les bénéfices apportés par cette nouvelle génération de microscopes ESTEM à la science et à la technologie sont nombreux. Ils doivent conduire à la mise en œuvre de procédés technologiques améliorés, avec des retombées fructueuses en

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termes de bénéfices économiques, de soins de santé améliorés, de réductions des besoins énergétiques et de gestion des déchets.

1. Introduction

Many technological processes occur at the gas–solid or liquid–solid interface at the atomic level. Direct *in situ* observation of the nanostructural evolution at the solid surface under controlled dynamic reaction conditions of gas environment and high temperature, using atomic resolution environmental electron microscopy, is a powerful scientific tool in the materials and chemical sciences for the nanostructure dependent information [1–5]. It is often not possible to infer the dynamic state of the material from post-mortem examinations of the static material and these data often cannot be obtained directly by other means [6–12]. We are particularly concerned with properties of solid state heterogeneous catalysts of interest for gas reactions in technological processes; to better understand the fundamental reaction mechanisms and atomic scale structure–property relationships important in the development of new materials and improved processes [1].

Chemical reactions catalysed by solid surfaces in heterogeneous catalysis take place at the atomic level and play a major role in the production of industrial chemicals, energy sources and environmental emission controls [1–12]. *In situ* atomic resolution E(S)TEM under controlled reaction conditions provides dynamic information on processes which take place at the atomic level, performance-critical defect structures and sub-surface diffusion of catalytic species. However the development of E(S)TEM for directly visualising reactions under extreme conditions of gas pressures and temperatures at the atomic level is highly challenging.

Since chemical reactions take place at the atomic level, in this article we have focused on the novel development of *atomic resolution*-E(S)TEM with a new design of the *in situ* environmental cell reactor. For earlier *in situ* studies carried out with different environmental cell technology using an ex-situ reactor jig inserted inside the EM column to carry out reactions at modest resolutions, readers are referred to Ref. [13] and the literature cited therein.

We further provide examples of some recent applications that exploit atomic-resolution E(S)TEM for understanding the role of gas–surface interactions in nanocatalysts and nanomaterials in their functioning state. Temperature, time and pressure resolved studies on real systems are possible for the first time, with the aim of bridging the pressure and materials gaps at operating temperatures. The use of surface science techniques in very high vacuum with extended single crystal surfaces to model and understand the fundamentals of heterogeneous catalysis has been invaluable. However, the direct industrial application of these studies was limited by the pressure and materials gaps that exist between them. Firstly, in real systems reaction temperatures and gas pressures may exceed the regimes accessible in surface science instrumentation, secondly gas treatments may be discontinuous or at very low pressure and thirdly, practical heterogeneous catalyst surfaces are often not extended perfect single crystal faces but the complex surfaces of nanoparticles on supports.

2. Atomic-resolution environmental TEM (ETEM)

We have organised and designed over many years instruments which are dedicated to environmental cell (ECELL or gas reactor system) operations with continuous gas exposures and elevated temperatures. In our approach the ECELL facilities are integral to the electron microscope and have led to the development of the first atomic resolution ETEM for probing *in situ* gas–solid reactions directly at the atomic level under controlled gas atmosphere and temperature conditions as well as for *in situ* nanosynthesis [2–5]. In this design the gas system is made part of the microscope and regular specimen holders can continue to be used. Commercial versions of this development are now widely used in an increasing number of laboratories globally [e.g. [8,11,12]]. The latest versions can support controlled reaction environments of temperature and gas involving pressure and time resolved studies with high precision and <0.1 nm resolution.

Here we first describe the development of the method which has opened up a new field for studying gas–solid reactions at the atomic level [3]. The whole EM column in a modern high resolution (S)TEM, and not just the immediate region around the sample, has been completely redesigned for the ECELL functionality. Highlights of this development have included a novel ETEM design with objective lens pole-pieces incorporating radial holes constructed for the critical first stage of differential pumping [3]. The basic geometry is a four-aperture system, in pairs above and below the sample (Fig. 1), but the apertures are now mounted inside (and aligned with) the bores of the objective lens polepieces rather than as in previous designs placed between them with no direct alignment. To achieve this it was necessary to measure each bore optically and to construct custom bushes for each position.

Another important feature uses the regular EM sample chamber as the controlled reaction environmental cell or reactor and is thus integral to the core instrument [3]. The ETEM can be operated either in gas environments or in vacuum (as a conventional TEM), without compromising the atomic resolution for TEM imaging but with restrictions on STEM (see later). Differential pumping systems connected between the apertures consist of oil-free molecular drag pumps (MDP) and turbomolecular pumps (TMP). This system permits high gas pressures in the ECELL sample region while maintaining high vacuum in the rest of the ETEM. A conventional reactor-type gas manifold system constructed with stainless steel modules, enables the inlet of flowing gases into the ECELL of the ETEM and is compatible with both high vacuum and gas pressure
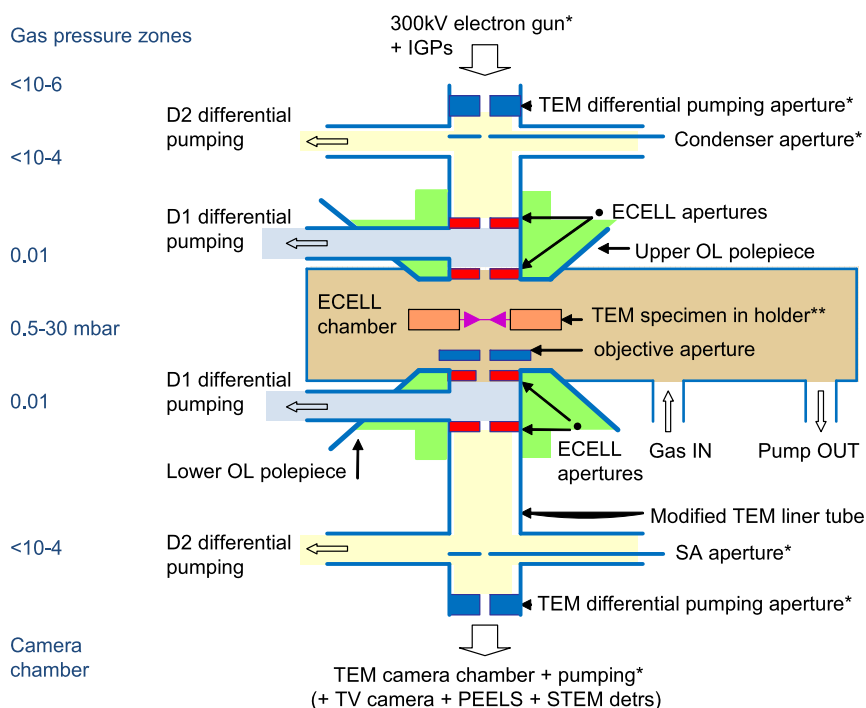
Fig. 1. (Colour online.) Schematic (not to scale) of key elements of the pioneering development of the atomic resolution ETEM design by the authors (Gai and Boyes) to probe gas–solid reactions at the atomic level [2,3]. The basic geometry of the aperture system in the pioneering development consists of radial holes through objective pole pieces (OL) for gas lines at D. The OL pole pieces are above and below the specimen holder and the lower OL pole piece is indicated. Gas inlet, the first stage of differential pumping lines (D1) between the environmental cell (ECELL) apertures, condenser aperture, a second stage of pumping (D2) at the condenser lens, selected area (SA) diffraction aperture, parallel electron energy loss spectroscopy (PEELS) and TEM camera vacuum are indicated. The sample chamber is the gas reaction cell. The atomic resolution ETEM design [3] is used for commercial production and now widely used by researchers worldwide.

conditions. The sample is in a controlled dynamic flowing gas environment similar to conditions in technological reactors, with a positive flow rate of gas. A hot stage allows samples to be heated routinely at controlled temperatures up to about 1000 °C (or higher with special holders) and a mass spectrometer is included for inlet gas analysis.

For dynamic atomic resolution studies a few millibars (mbar) of gas pressure are typically used in the ECELL but the authors' original version can be operated with gas-type-dependent pressures up to >50 mbar. Higher gas pressures compromise the resolution due to multiple scattering effects of the electron beam through denser gas layers and this depends on the gas. Electronic image shift and drift compensation help to stabilise high-resolution images for data recording (with a time resolution of the order of 1/30 s or better), on film, CCD or with the originally used real-time digitally processed low light TV (LLTV) video system. The video system connected to the ETEM apparatus can facilitate digital image processing and real-time recording of dynamic events on a time scale of milliseconds, consistent with contact times of gas molecules in chemisorptions reactions in technological reactors [9,10,12]. Minimally invasive low dose electron beam techniques are used throughout. *In situ* data under low electron dose conditions are checked in parallel 'blank' calibration experiments in which dynamic experiments are conducted without the beam and the beam is switched on only to record the final reaction end point. The aim is non-invasive characterisation under benign conditions without any contamination [1–11]. By providing the gas supply and some other facilities as part of the microscope, this arrangement allows use of a wide range of existing designs of specimen holders for flexibility, simplicity, economy and reduced set up time and cost in new scientific applications. It is essential for the specimens to be clean both to ensure the chemistry being probed is that intended and to avoid contamination build up in the electron microscope. This means a hot stage rather than beam heating must be used to heat the sample. The use of a locally intense beam to heat the sample, as used in some other work reported in the literature, means that the temperature is uncontrolled and unpredictable, there is the danger of local gas ionisation or direct beam ionisation of the sample affecting the chemistry and contamination is pretty much inevitable. Only recent designs of hot stage have low drift rates making continuous recording relatively easy but we have found that even the older designs can with care be used for extended experiments on a selected area and this approach is much preferable, if more difficult experimentally, to uncontrolled and chemically unnatural beam heating.

In our development of the atomic resolution ETEM, atomic resolution TEM, STEM, hot stage and PEELS/GIF functionalities have been combined in a single instrument. The combination is required to aid simultaneous determination of the dynamic structure and composition of the reactor contents, surface and bulk analyses, dynamic electron diffraction, with the ETEM system used as a nano-laboratory with multi-probe measurements. Design of novel reactions and nanosynthesis are possi-

ble. The structure and chemistry of dynamic catalysts are revealed by atomic resolution imaging, electron diffraction and chemical analysis while the sample is immersed in flowing controlled gas atmospheres and held at the operating temperature. For chemical microanalyses, a commercial post column Gatan PEELS/GIF or an in-column Omega filter system provides elemental analysis during *in situ* experiments with low gas pressures [1–12,14].

Under carefully controlled conditions, data from *in situ* ETEM can be directly related to structure–activity relationships in technological processes. In catalysis, this correlation is crucial in optimising the synthesis and development of improved catalysts to ensure the long catalyst life required for chemical technologies. It has been particularly useful in understanding better the surface tensions in using very small (<5 nm) nanoparticle catalysts. These may initially have attractive surface type selectivity and surface area reactivity but be subject to rapid deactivation due to migration of material and sintering into large particles often with different and less attractive properties.

Because of the small amounts of solid reactant in the microscope sample, measurement of reaction products are carried out on larger samples in an ex-situ micro-reactor operating under similar conditions to those used for the nanostructural correlation. The correlation between the dynamic nanostructure and reactivity is crucial for a better understanding of gas–solid reactions and the development of improved materials and processes.

In addition to providing direct and unparallelled insights into the dynamic evolution of structural changes at the atomic level, the E(S)TEM allows the detection, in real time, of surface as well as sub-surface structural phenomena including defect evolution, access to metastable states, changes in the chemical composition and oxidation states, monolayer segregation, and active sites on specific catalyst surfaces involved in binding gas molecules and hence influencing reaction mechanisms. These can be explored by closely mimicking the working conditions of practical reactors, allowing us a look at the real atomic world. Entire patterns of key catalyst activation, operation and aging can be studied in a range of gas and temperature regimes that provide fundamental understanding of kinetics and reaction processes. These studies enable optimisation of synthesis, processing and stability of materials. The atomic resolution ETEM development is therefore a major change from the conventional methods and is now extended into ESTEM [19,23] with key additional capabilities.

Furthermore, beyond calibration experiments, several conditions are required for successful studies using the ETEM. Electron-transparent samples are necessary and most practical catalyst powders and ceramic oxides meet this requirement. Ultrahigh-purity heater materials and sample grids capable of withstanding elevated temperatures and gases are required (such as stainless steel, Ti or Mo). The complex nature of catalysis with gas environments and high temperatures requires a stable design of the ETEM instrument to simulate the real world at the atomic resolution. For high temperature studies in gas environments samples are normally supported on finely meshed-grids of high purity Ti or Mo with experiments carried out on crystals protruding from the edge of grid bars. Carbon support films are not suitable for the highest temperature experiments.

The direct real time imaging of dynamic interactions between hydrocarbons and oxide catalysts and how the gas molecules move and rearrange the catalyst surface in selective hydrocarbon oxidation has resulted in the discovery of an atomic scale reaction site mechanism resulting from a simple atomic movement, called the "glide shear reaction mechanism" (now referred to as Gai glide shear mechanism) [2]. During the selective oxidation the glide defects are formed to accommodate the shape misfit between the reduced anion-deficient catalyst surface and the sub-surface without collapsing the catalyst structure which is critical to the sustained operation of the catalyst.

Other applications of atomic resolution-ETEM include carbon nanotube growth [15] and solid state reaction mechanisms [16]. A specialised specimen holder based approach [17] with windows for extended gas pressures but generally lower image resolution and some analytical limitations can also be accommodated, but it has higher barriers to new types of experiment; each of which may require a complex custom holder design.

The atomic resolution ETEM [3] is used for commercial production by TEM manufacturers and used by numerous researchers internationally leading to scientific and technological advances with significant real world benefits. It has contributed to the invention of a catalytically controlled, breakthrough in situ nanocoating process for titania pigments for high strength polymer applications, improved catalysts and processes [12].

3. *In situ* studies with the most recent generation of aberration-corrected (scanning) transmission electron microscopes

3.1. About the newly developed Aberration Corrected Environmental (Scanning) TEM (AC-E(S)TEM)

Heterogeneous gas–solid catalyst reactions occur on the atomic scale and there is an increasing indication that single atoms and very small clusters can act as primary active sites in chemical reactions. Enhancing the atomic resolution ETEM, we have therefore developed the first double aberration corrected environmental (scanning) transmission electron microscope (AC E(S)TEM) for novel studies of nanoparticle catalysts with sub-angstrom (<0.1 nm) resolution in gas atmospheres at working temperatures described below. It extends high vacuum (and ETEM) analyses with full analytical facilities and unrestricted high angle annular dark field (HAADF) imaging of single atoms, small clusters and nanoparticles in dynamic *in situ* experiments with controlled gas reaction environments at initial operating temperatures up to >500 °C. HAADF is also required to set up the STEM corrector.

Aberration correction is particularly beneficial in dynamic *in situ* experiments because there is rarely, if ever, the opportunity to record from a scene which may be continuously changing, a systematic through-focal series of images for subsequent data reconstruction. In these applications it is necessary to extract the maximum possible information from

Table 1

Generic objective lens parameters for the narrow gap ultra-high resolution UHR and intermediate gap Midi type of polepieces used in the York E-instrument [19].

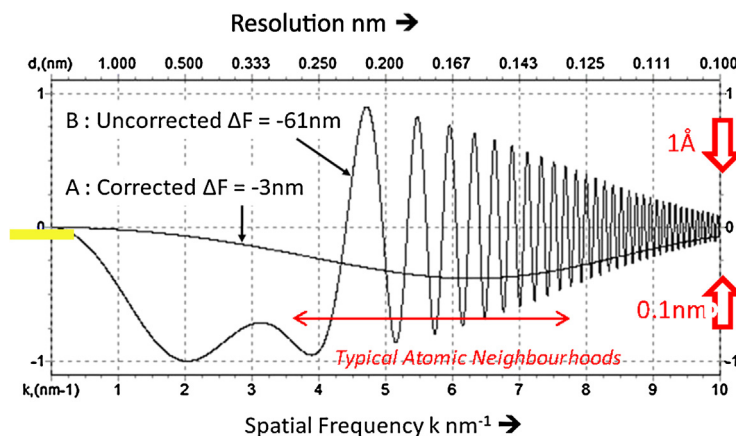| Polepiece type	Gap range (mm)	Uncorrected Cs (mm)	Uncorrected Cc (mm)	Cc with Cs AC (mm)	Std hot stage fits?
UHR	2.2–2.5	0.5–0.6	1.0–1.2	1.4	No
Midi	4.3–5.4	1.0–1.2	1.2–1.4	1.6	Yes

Fig. 2. (Colour online.) Calculated contrast transfer functions (CTFs) for an aberration corrected (A) imaging conditions of the HRP version of the double aberration corrected JEOL 2200FS FEG TEM/STEM at the University of York (UK) [19]. (CTF for the uncorrected conditions is shown in (B) for comparison.)

each single image in a continuously changing sequence. It is also desirable to limit the electron dose exposure to ensure minimally invasive conditions and to avoid secondary effects such as contamination. Based on these considerations we proposed aberration corrected dynamic *in situ* electron microscopy [18]. The novel *in situ* development and its applications to nanoparticles and in the development of new energy efficient nano-catalysts of interest in energy, emission control and medicines, are described in the following sections.

To observe changes in the nanostructure as a function of operating temperature under controlled *in situ* reaction conditions in an aberration corrected environment, we have employed the following procedures (Gai and Boyes [19,20]). The need to accommodate special specimen holders in an aberration corrected instrument has been one of the more important criteria driving our specification of a double aberration-corrected (2AC) electron microscope, namely, the JEOL 2200FS (2AC) FEG TEM/STEM operating at 200 kV, in the Nanocentre at the University of York. Currently all the aberration corrected-ETEMs use the earlier atomic resolution-ETEM design of Gai and Boyes [2,3] described in the preceding sections.

Since aligning the sample into a zone axis orientation is a prerequisite for atomic resolution electron microscopy of crystalline materials, an increased specimen tilt range is also desirable. Both these conditions benefit from the larger gap (HRP/Midi) objective lens pole piece [19,20], shown in Table 1 [19,20].

The Cs (C3) CEOS aberration correctors (Haider et al., [21]) on both the STEM probe forming and TEM image 'sides' of the instrument were used to provide the desired expanded specimen geometry with minimal effect on the 1 Å and below imaging performance of the system. The effect of the increased polepiece gap on Cs in this range is much more evident ($\times 2$) than on Cc ($\times 1.2$); but of course Cs is now corrected (Cs ~ 0).

The advantages of the configuration we have adopted, include promoting a HRTEM contrast transfer function (CTF) extending to higher spatial frequencies and resolution in the data; allowing image recording at close to zero defocus, including to strengthen and simplify interpretation of information at internal interfaces and external nanoparticle surfaces; analysing small (<2 nm) nanoparticles and clusters on supports, using high-resolution TEM as well as HR STEM; facilitating HAADF STEM and extending HAADF STEM resolution to 1 Å (0.1 nm) and below [22]. As well as benefiting from improved resolution at 1 Å and below, it becomes important to be able to set the conditions to avoid the previously intrusive contrast transfer function (CTF) and defocus sensitive oscillations in image contrast in the spatial resolution range from 1 Å to 3 Å. This is where atomic neighbourhoods in crystals lie in low index projections and it is especially important in studying the atomic scale detail of the surfaces of ultra-small nanoparticles, atomic scale defects and internal interfaces. It is a key topic of interest in nanoparticle studies, e.g. in considering the possible origin of sintering mechanisms important in heterogeneous catalyst design including control of processing, activation, operation, and deactivation mechanisms. Calibration experiments were performed according to procedures described in previous sections.

Fig. 2 is a CTF plot which illustrates that in practice, it is possible with Cs aberration correction to combine demonstrated spatial resolution better than 1 Å using the HRP lens polepiece with the large ~ 4.3-mm gap [19,20] needed to accommodate a standard hot stage (Gatan model 628 variants); and with it in operation. This is an example of using Cs aberration correction to combine the limited added space required for *in situ* experiments with a high level of imaging performance with which such facilities were previously incompatible; and thereby to extend considerably application specific and relevant
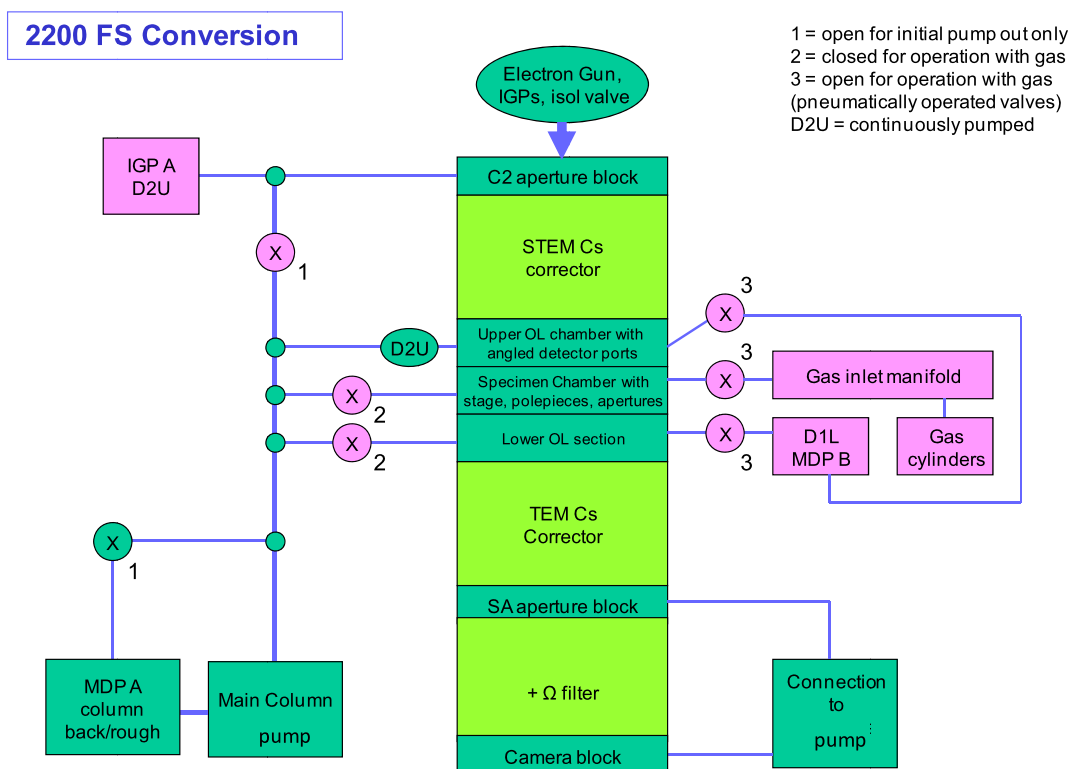
Fig. 3. (Colour online.) A schematic of the double aberration-corrected E(S)TEM development carried out in-house at the University of York.

TEM and STEM experimental capabilities. In this range the Cc is relatively insensitive to the lens gap dimension but stability issues remain important.

The (2AC) E(S)TEM system at York is configured to be tolerant to out-gassing of hot samples and as a key foundation for controlled gas environment experiments [19,20] by using a combination of turbomolecular and molecular drag pumps for the main column evacuation systems. Ion pumps continue to the used (and added) pre-FEG and in the regular gun itself. A schematic of the E(S)TEM development using the JEOL double AC 2200FS carried out in-house at York is shown in Fig. 3 [19,20]. The instrument configuration is considered to be beneficial for *in situ* developments with additional capabilities [20]. In our case both capabilities are combined on the remotely controlled electron microscope platform. Despite the *in situ* modifications, single atom imaging has been possible in practical catalysts under reaction conditions (Boyes and Gai et al., [23]). The permanently mounted ECELL developments retain or enhance the full performance of the original core instrument with proven <0.1 nm resolution and single atom sensitivity in imaging; with or without gas flowing. With the permanently mounted instrument-based and fully integrated environmental cell capability the gas conditions apply for all regular specimen holders and there is also full compatibility of the shared use, undedicated, (E)(S)TEM instrument for regular high vacuum TEM and STEM operations in other applications (which also benefit from the improved column pumping systems).

The first applications have been reported [23] on the initial proof-of-principle version of the double aberration corrected E(S)TEM, innovatively modified in York to provide both ETEM, and for the first time ESTEM, with full analytical functionalities. These include introducing controlled conditions of gas environment and high temperature with uncompromised high angle annular dark field Z-contrast ESTEM imaging, low background EDX microanalysis, AC ESTEM EELS and wide angle electron diffraction analyses of nanoparticle structures and wider crystallography. TEM and STEM correction montage procedures (Zemlin tableaux) and image resolution to better than 1 Å have been maintained with the hot stage and gas environments in the *in situ* double AC-E(S)TEM, including with power connected and the samples held at elevated temperatures >500 °C [23].

Details of this approach have been published previously [19,20,23]. TEM Cs aberration correction also allows use of the previously unattainable combination of conditions with small amounts of negative Cs and positive defocus [24] to create a new high contrast imaging mode for atomic resolution studies. For high angle annular dark field (HAADF) imaging of single atoms and multiple analytical modes in STEM, the main benefit of aberration correction is a smaller and more intense probe; aiding resolution and contrast with the potential for reduced electron dose and for combining analysis with high resolution imaging.

The new AC E(S)TEM system operates in both (E)STEM and (E)TEM modes with 1 to >10 Pa gas pressures; in the latter case for a gas supply of >100,000 monolayers per second (>0.1 mbar) measured directly at the sample position with
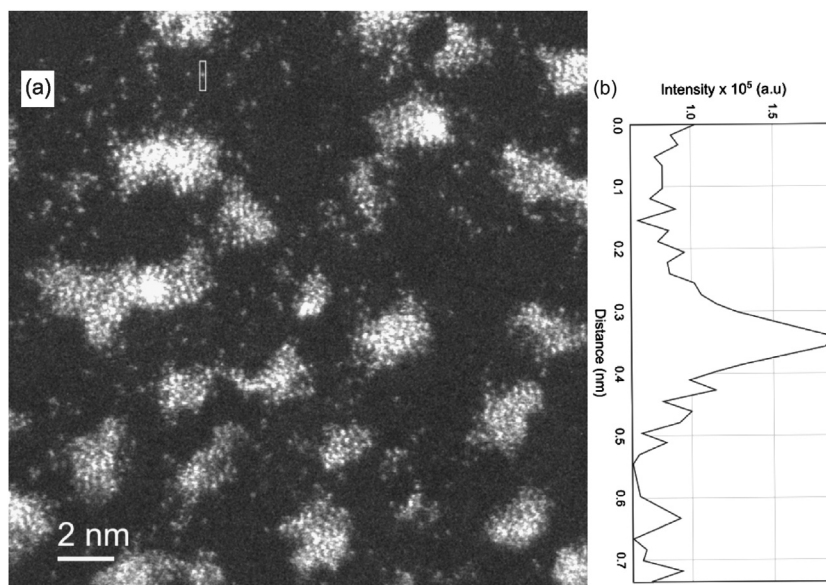
Fig. 4. (a) Single atoms of a Pt/C catalyst in aberration corrected ESTEM (HAADF) developed at the University of York [19,23]. (b) Intensity profile of a single atom in (a) is illustrated. The atom is marked in the top left hand corner. Single atom images measure about 100 pm (0.11 ± 0.1 nm) in diameter.

inlet gas pressures up to a few mbar. This is in contrast to the usual high vacuum STEM analytical environment. This gas supply should generally be adequate to flood the sample surface with gas coverage. The system supports analysis of key intermediate phases of catalysts which may be metastable with respect to gas atmosphere, temperature and time. They may be critical to understanding catalyst mechanisms, and to designing new ones [1], but they are not reliably accessible with ex situ or high vacuum methods of analysis.

3.2. AC ESTEM of Pt nanocatalysts

Here we report initial experiments with the method for supported Pt nanocatalysts important in catalyst technologies and energy. Dynamic *in situ* applications include direct studies of single atom migration in a model system with supported metal particle heterogeneous catalysts under controlled gas and temperature operating conditions related to industrial applications; and in future studies planned to be taken directly from them. The samples for the initial studies reported here were prepared by sputtering Pt onto a carbon film support. At each stage before transfer into the microscope the sample and holder were mildly plasma-cleaned in an external unit (Diener Femto) with an Ar/25% O_2 gas mixture. We have established that in our system contamination issues of specimens during microscopy are dominated by the received state of holders and specimens, and their preparation and transfer; with little detected contribution from the 10^{-8} mbar range background microscope vacuum environment or the high purity gases. The situation is eased by preliminary 'beam showering' [25], or by using a hot stage [1–6,12]. In initial operations avoidance of problems with specimen-based contamination required a slightly higher hot stage temperature for STEM ($\sim$350 °C) than for TEM ($\sim$300 °C). We minimise beam effects in the design of experiments [1,23], and the effect is checked by beam blanked experiments and by reference to previously unexposed areas of the same sample; with the latter a better defined condition for STEM than TEM.

The images in this section are all high angle annular dark field (HAADF) using the original JEOL (upper) STEM detector. The recording conditions for the STEM data were magnifications of 8–12MX with 512 and 1024 line frames and sampling at 0.015 or 0.03 nm; i.e. at 6× or 3× over sampling of the 0.1 nm digital imaging resolution element, using pixel dwell times of 19 or 38 μs (with 50 Hz line synchronisation). Some images were also recorded with faster frame integrations. The incident probe had a calibrated 24 mrad convergence semi-angle and the collection angles for HAADF imaging were 110 mrad and 180 mrad, respectively, for the inner and outer diameters of the detector. Short sequences of images recorded at reduced frame times and pixel counts were also assembled into a video to analyse and demonstrate the dynamic—and in some cases competitive—nature of the processes involved.

Fig. 4 shows single atoms and clusters of a Pt sample sputtered on to a carbon support with a corresponding HAADF AC ESTEM image intensity profile of a single atom recorded at 25 °C. The very thin (1–2 atoms high), raft-like, clusters are made up primarily of partially ordered {111} spacings with a general ⟨110⟩ texture. The FWHM for the single atom image peaks are 0.11 ± 0.1 nm in the full-range video signals and <0.1 nm with expanded contrast and shifted black level. In AC ETEM (rather than HAADF ESTEM) images of similar areas it is difficult to discern the single atom positions accurately; or in some cases even to detect small particles at all against the background support image. This is generally impossible without aberration correction and this may explain in part why these features, and especially the population of single atoms
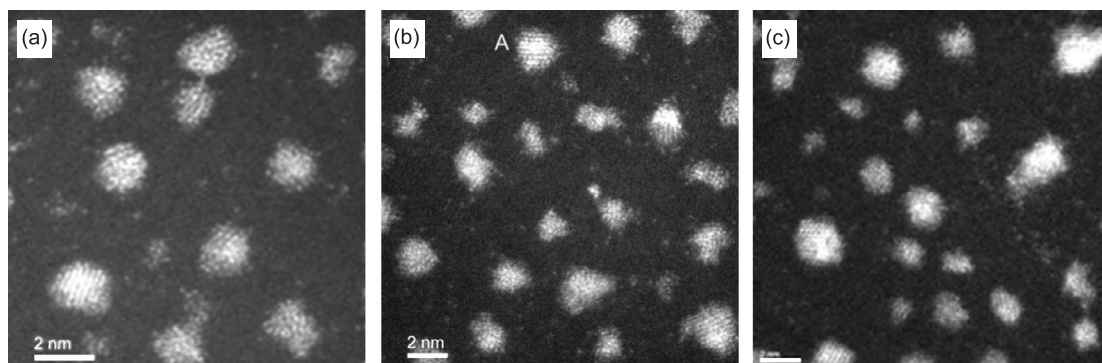
Fig. 5. Dynamic ESTEM imaging at the single atom level in hydrogen gas and operating temperatures (a) 25 °C (gas pressure measured *at the sample* is 2 Pa). Single atoms are detected 'loose' on the support between the nanoparticles and the development of a more structured and 3D particle forms with faceting is observed in the presence of the gas. (b) Dynamic ESTEM imaging with increased faceting of Pt nanoparticles hydrogen gas at 400 °C. An increasingly facetted particle is shown, e.g. at A with 0.23 nm (111) lattice plane spacings. (c) Dynamic ESTEM imaging at 500 °C in hydrogen gas showing further faceting of nanoparticles. (Scale bars are 2 nm.)

(of other species in other reports), have only recently been identified in vacuum studies [26], and for the first time by the authors with gas [23]. The migratory single atoms on the support between the more substantial clusters have recently been imaged for the first time in a controlled gas and temperature environment [23], as described in the following sections. This observation is important in understanding the mechanisms of catalytic reactions and in characterising deactivation processes.

Fig. 5(a) shows a sequence of single Pt atoms and clusters, some of which are seen to be substantially modified and evolving into well-ordered 3D single crystal particles (such as A in the figure), on a carbon support in 2 Pa of hydrogen gas at 25 °C. Under these conditions even at 25 °C the internal structure of some of the particles becomes highly ordered with a strong ⟨110⟩ texture and external surfaces faceting into {111} faces. In Fig. 5b at 400 °C in hydrogen, as well as more ordered particles there is clear evidence of residual single atoms still present on the support away from the nanoparticles. Fig. 5c shows further development of nanoparticle structures imaged in hydrogen at 500 °C after 30 min exposure to the reaction conditions of gas and temperature. This image shows far fewer distinct single atoms are recorded and their typical contrast is greatly reduced. There may be more questions of mobility and the image sampling frequency rather than thermal diffuse contrast, or they may indeed report an actual absence of 'loose' single atoms. More three-dimensional particles are observed at higher temperature compared to the initial observations of as deposited raft-like structures before exposure to hydrogen. They are accompanied by more facetted particle perimeters based on regular single crystal internal forms for the Pt particles. Full resolution in both ETEM and ESTEM (the latter only with custom electronics) was retained with the hot stage operational to >500 °C. The images illustrate the tension which exists between facetted crystalline nanoparticles which have inherent stability and more free form ones with a higher proportion of low co-ordination surface atoms. The latter are likely to be both more reactive but also more dynamic and less stable in form, and therefore probably less consistent in chemical reactivity. Further work is required to establish whether there are actually fewer single atoms on the carbon substrate surface between the distinct nanoparticles, as it appears from the images, or whether at this temperature the single atom mobility is now much faster than the STEM imaging frequency and they are not resident at a single position long enough to be imaged by this method.

The original HAADF publication by Crewe et al. [27] already included quantitative measurements of a restricted number of atoms in each column (up to $n \sim 10$ atoms per column). The sensitivity and precision of these analyses has improved (to $n > 30$) with careful methods using higher resolution aberration corrected instruments [28–30]. Here we identify single atoms in a similar way to Batson et al. [28] with preliminary illustrative data in Fig. 6. They show discrete levels in the video signals from single atoms; with multiple (n up to 4 but more typically 1–2) 'layers' of atoms in the initial clusters; based on a linear model [27] for intensity with n (for $n < 10$). The particles more developed at higher temperatures have been analysed by video intensity of discrete columns of atoms in a regular crystal structure (Fig. 7) and show a thicker form of particle (n up to 8 ± 1 measured) than the flatter and more raft-like forms of the initial clusters ($n = 1$–2) (Figs. 4(a) and 5(a)). A detailed analysis of atom column intensities in the selected nanoparticle from Fig. 6 shows particle edge 'cliffs' made up of minimum columns containing multiple ($n > 4$) atoms; compared to the initial rafts with greater area and tapering to single atom high edges. To reduce the effects of signal auto-levelling in the electronics, the video signals are only compared within each frame where single atoms can be used for reference to calibrate the local video signal and the results are then normalised between frames. The error bars reflect noise in the signals with the limited statistics of the individual measurements but analysis of the column intensities support the blocky form of the selected appropriately oriented particle (Fig. 6). Adsorption of hydrogen (or even oxygen) gas atoms or molecules onto Pt atoms, or conversely onto the support, would change the Z-contrast ($\sim F(Z^{1.7})$) only marginally.

Sintering plays a key role in the deactivation of heterogeneous solid state catalysts with nanoparticle active phases but the dynamic behaviour at the single atom level is not well understood and even less well controlled in practice. There are
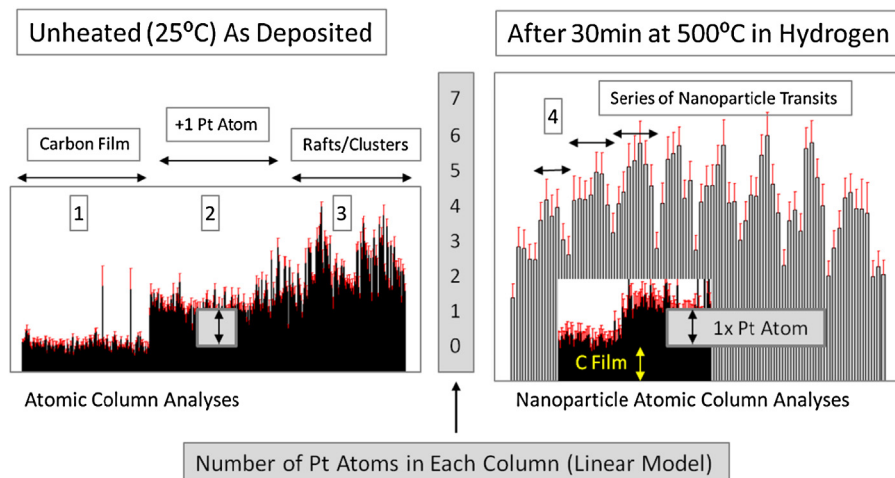
Normalised STEM HAADF Intensities

Fig. 6. (Colour online.) Plots of STEM HAADF intensities normalised to single Pt atom contrast (2) for atomic column height analyses across (a) as deposited single atoms (2), clusters and rafts (3) on the unheated carbon support film (1) at ambient temperature (25 °C) and (b) in transits across crystalline nanoparticles 1.5–2 nm in size (4) after exposure to hydrogen at 500 °C for 30 min and analysed under those conditions.
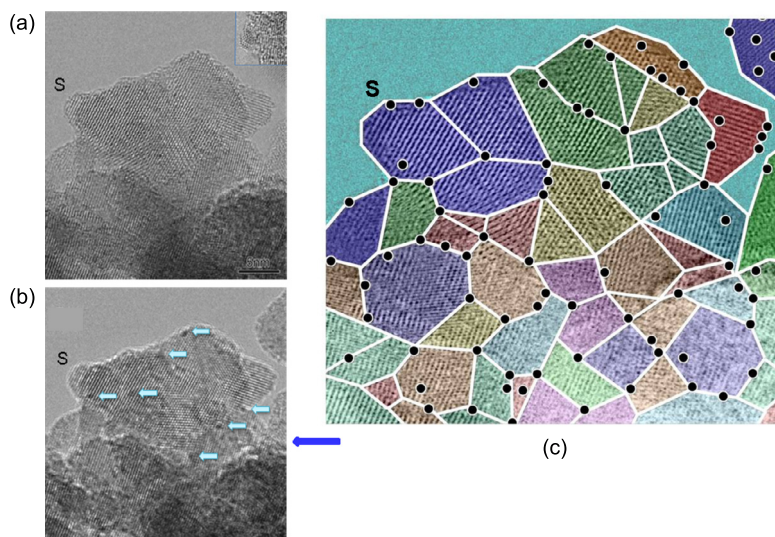

Fig. 7. (Colour online.) (a) Atomic resolution images of the 15WZA sample reacted at ∼700 °C (scale bar: 12 mm = 5 nm) (AC-ETEM). Darker clusters are just discernible. Image (b) shows slightly negative defocused (under-focused) image of the crystal (near the area S) revealing the clusters. (c) Schematic of the clusters (with single atoms) anchored at grain boundaries of nano-zirconia.

reports with gold [31] that the particle shape changes are driven by adsorption of gases on metal surfaces based on modest resolution ambient temperature TEM experiments (plus in this case any additional energy contribution from the electron beam). We have now carried out single atom studies in hydrogen and oxygen gases using AC ESTEM to obtain an atomic level view of the sintering behaviour.

In situ hydrogen reduction in Fig. 5(c) shows the presence of fewer single atoms on the support than in (a), with clusters and increased faceting of the nanoparticles. This indicates that the nanoparticles act as a source of potential ad-atoms and clusters. This has important implications in catalysis and in understanding the role of nanoparticles generally. In hydrogen reducing environments low co-ordination surface atoms are replaced by surface facets through local rearrangements to minimise surface energy [23,32]. Whilst overall loss of surface area and hence activity is often the result of Ostwald ripening, the existence of single atoms and small clusters on the surface of the support during the intermediate stages has important implications for catalysis, with recent work attributing excellent catalytic performance to the presence of single atoms and clusters [32,33]. This decrease in the low co-ordinated sites may explain the often observed initial drop in the activity of nanocatalysts [32]. Through the use of a support material with an abundance of anchoring sites, migrating atoms may
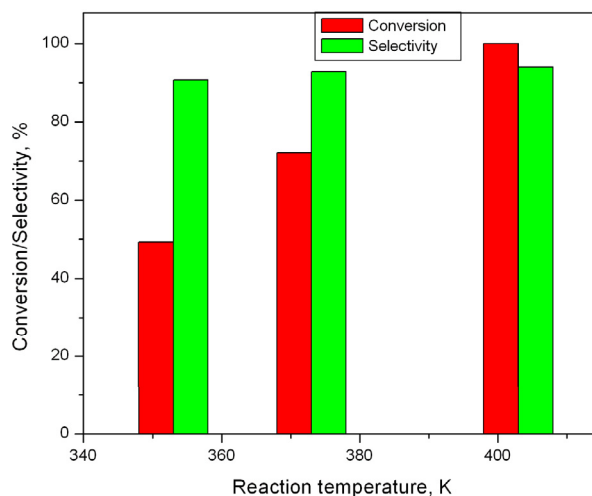
Fig. 8. Excellent Conversion of 4-hydroxyacetophenone oxime and selectivity of *N*-acetyl-*p*-aminophenol medicine as a function of reaction temperature over the catalyst clusters (with single atoms). Solvent = benzonitrile; time = 12 h; oxime = 0.9 mmol; catalyst = 20 mg.

be stabilised and provide further active sites for adsorption, with the nanoparticles acting as reservoirs and recipients of ad-atoms and migratory clusters [34].

Low co-ordination surface atoms enhance the catalytic activity of small nanoparticles [23,32,33] and through the in situ ESTEM, the stability of these active sites has begun to be studied as a function of gas environment and temperature as well as in high vacuum. Minimisation of surface energy leads to the removal of under co-ordinated surface atoms in favour of facets, and such a process is proposed to contribute to the often observed initial drop in activity of nano-catalysts. The new ability to analyse the population of single atoms individually dispersed on the support may also introduce new catalytic capabilities with a different gas-dependent stability profile. As well as maintaining the catalyst surface area by preventing deactivation through sintering processes, it is clear that understanding the evolution of the identified active sites at the atomic scale is also needed. It should lead to the development of more active, more durable, and more economically and environmentally attractive catalysts.

The dynamic observations of single atoms in reducing environments at working temperatures suggest that low coordination surface atoms and 'loose' single atoms are key to understanding the activity and selectivity performance, stability, activation, activity, deactivation and possible reactivation of heterogeneous gas–solid catalysts. The AC ESTEM microscope system [23] introduces the capability for systematic studies of the science of catalyst nanostructures with single atom sensitivity and (0.1 nm) atomic resolution of underlying crystal structures under representative operating conditions of a gas environment and controlled high temperatures. It has the potential to account for every atom in a reacting nanostructure.

4. A wide field of applications in catalysis science

4.1. Medicines in healthcare

The modern healthcare industries require efficient catalytic processes but the progress is often hampered by the difficulty in detecting and anchoring active sites on the catalyst surface. In heterogeneous catalysis the identification and stabilisation of the active site during the transformation of the precursor to the active catalysts are important to prevent sintering and deactivation of the catalyst and require the integration of dynamic *in situ* imaging at the atomic level with reactivity studies [34]. Solid acid catalysts with strong acidic properties are of interest in key catalytic processes [35,36]. An example of the usefulness of AC-ETEM in the development of new clean routes to medicines in healthcare is described in the following sections. *N*-acetyl-*p*-aminophenol (paracetamol or acetamenophen) is one of the important non-steroidal anti-inflammatory drugs (NSAIDS) or medicines commonly used by humans because of its analgesic properties. Its preparation involves reacting 4-hydroxyacetophenone oxime to obtain the ketoxime. The conventional homogeneous catalytic process to produce it involves a processing step with fuming sulphuric acid which produces unwanted wastes. An efficient heterogeneous process for the production of the medicine is therefore desirable. Zirconia-based solid acid catalysts show better activity for the production than many other solid acid catalyst systems, including zeolites [34].

Nanostructural and physico-chemical studies towards a clean, low temperature heterogeneous catalytic process for NSAIDS on tungstated zirconia nanocatalysts have been reported [34]. The dynamic precursor transformations to the active catalyst, have been directly visualised using AC-ETEM and the observations are quantified with catalytic activity studies for the NSAIDS which are illustrated in Figs. 7 and 8, respectively. The observations using negative defocus imaging in AC-ETEM combined with HAADF-STEM have provided direct evidence for surface WO_x clusters with dimensions $\leqslant 0.35$ nm and W single atoms located at grain boundaries at the surface of the zirconia nanoparticles. The correlation between the
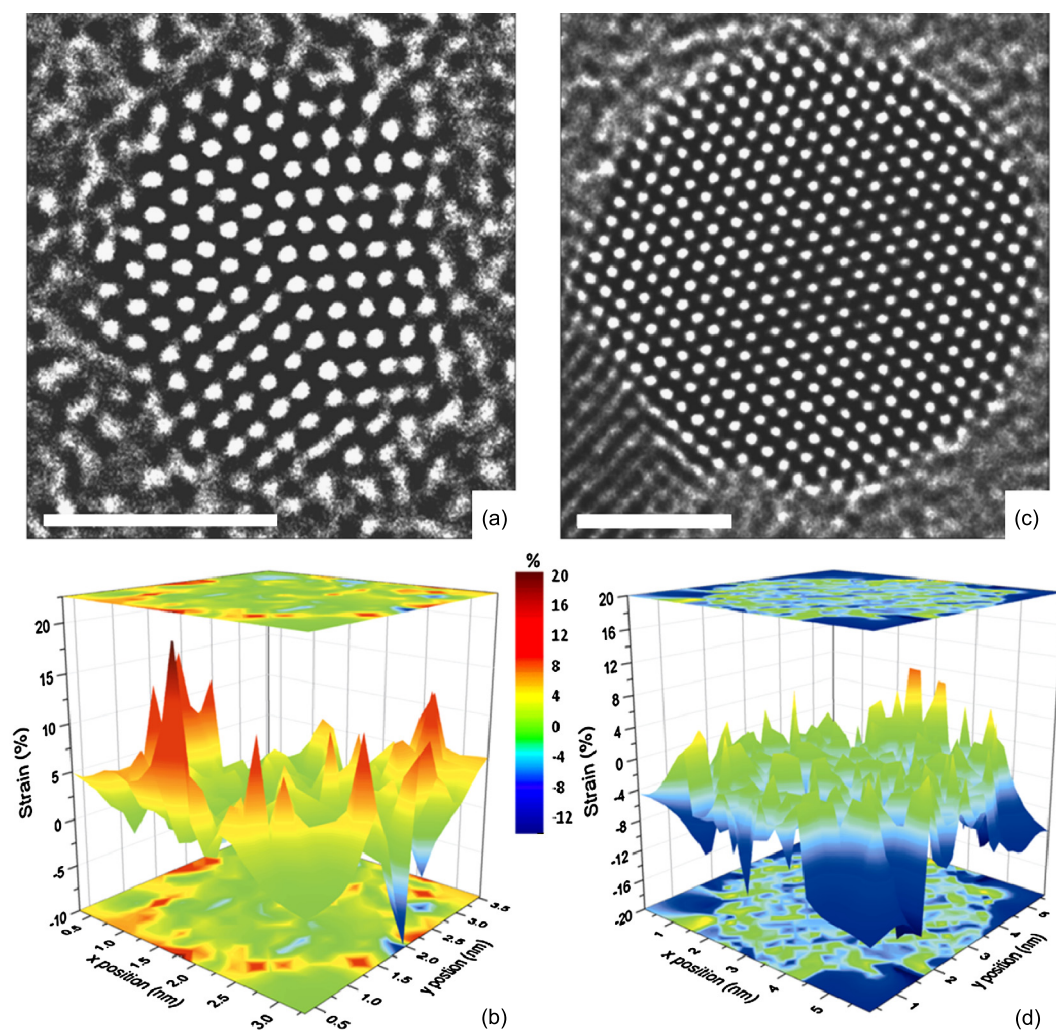
Fig. 9. (Colour online.) AC-TEM images of a decahedral gold nanoparticle (a) and single crystal gold nanoparticle (c). The corresponding 3D strain distributions are shown in (b) and (d), respectively. Scale markers indicate 2 nm.

nanostructure and activity of catalysts with different W loadings indicate that the surface WO_x clusters and W, create Brønsted acid sites, highly active for the low temperature reaction. Fig. 8 illustrates excellent performance (both conversion and selectivity to the medicine) at 400 K. The results further elucidate that the anchoring of active sites at grain boundaries of the zirconia nanoparticles prevents undesirable coalescence of the active species and improves the catalyst stability and performance to make more product [34]. This is a type of creative nanostructural solution to restraining deactivation which it is hoped to apply more widely.

4.2. Gold nanoparticles

Many nanoparticles (such as Au, Ag) are used in catalytic oxidation reactions. Ultra small gold nanoparticles of 2–5 nm are known to be highly active catalysts, particularly for the low temperature oxidation of carbon monoxide [37]. The origin of the surprising activity of nano-gold in this size range is still not fully understood. Previous work considering size related causes identify under co-ordinated surface atoms as the source of activity. Here we introduce an entirely new mechanism for reactivity of multiply twinned gold nanoparticles in the relevant size range, resulting from their inherently strained nature on the atomic scale. The recent work [38] using dynamic AC-ETEM and density functional theory calculations shows how multiply twinned nanoparticles (MTPs) in the critical size range differ from single crystal particles and from larger particles with much less strain; providing insights into their properties.

Fig. 9(a) and (b) shows AC-TEM images of a multiply twinned decahedral gold nanoparticle in (a) and a minimally strained single crystal particle (c), with corresponding strain distributions ((b) and (d)). Scale markers indicate 2 nm. Through the introduction of truly quantitative analysis of atomic column displacements observed by aberration corrected electron microscopy [38], we detail the significant surface strain inherent to the decahedral structure. An average surface
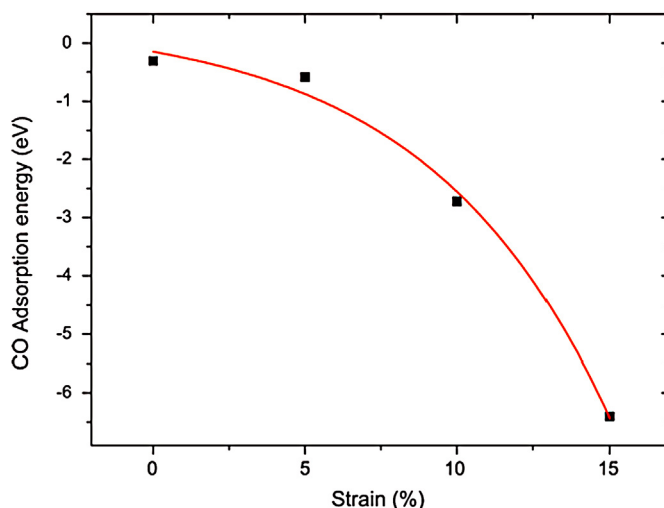
Fig. 10. Results of DFT calculations of CO adsorption energy vs. strain as a function of normalised distance from the 'central' fivefold axis. The data indicate that the strain at the gold nanoparticle surface can significantly enhance its catalytic performance.

strain of 5.6% is found, with many nearest neighbour distances between surface atoms expanded by more than 10%. Such expansive strain has a similar effect to reducing co-ordination number on the *d*-states of gold surface atoms. Density functional theory (DFT) calculations based on the experimentally observed lattice expansion confirm the significantly enhanced reactivity of such inherently strained nanoparticles (Fig. 10). This appears to be the first study of the effect of intrinsic radial strain on the catalytic properties of multiply twinned gold nanoparticles. Through quantifying the amount of strain at the surface and calculating the enhanced adsorption energies for CO resulting from band structure modifications, it is shown that such effects may be among the most important in gold catalysis. The new mechanism for understanding CO oxidation is important in environmental control and energy systems. The studies provide new aspects of fundamental understanding in heterogeneous catalysis and other chemical reactions over nanoparticles more generally, and should lead to better processes.

5. A fascinating bundle of novel instrumental advances for future experiments in gas and liquid phases

Other important developments include sample holder based developments. One approach for *in situ* environmental studies is to employ a thin-window cell, consisting of a TEM sample holder by JEOL which encloses the specimen and a volume of gas between two electron transparent thin films such as carbon [31] or more recently Si_3N_4 membranes [17]. Such reaction cells with electron transparent windows can also be used to separate the fluid phase from the EM vacuum and can in principle be applied in a regular EM. Different window cells for studies at high temperature and room temperature are also possible. Other development includes the application of MEMS technology to construct specimen holders with gas containment and high gas pressures (to >1 bar) [17]. With window cell systems, it would be desirable to achieve accurate temperature measurements at the sample, tilting to crystallographic zone axes for orienting samples and analysing defect structures. Hydro-desulphurisation mechanisms have also been investigated [39].

Innovative sample holders for *in situ* TEM and STEM including for use in gases and liquids have been developed by researchers and companies. The latter include DENS solutions, JEOL, Protochips Inc. and Hummingbird. Nanofactory (NF) and Gatan have AFM (atomic force microscopy)–TEM holders with miniaturised AFM in tip of a TEM holder which provide AFM capability and TEM in a single experiment. The NF–TEM holder enables *in situ* probing of electrical and mechanical properties of nanostructures. The different holders are summarised in a recent book entitled *In situ Microscopy at High Resolution* [40]. A JEOL sample holder has been used to study reducing and oxidising gas effects on nanoparticles at room temperature [31].

In situ TEM of nano-indentation of nanoparticles to study deformation behaviour has been reported recently [41]. Many commercial hydrogenation and polymerisation processes are derived from liquids at operating temperatures and the associated chemical reactions still occur on the sub-nanometre molecular scale. Recent advances in biological catalysis and molecular electronics also take place in liquid environments. Probing reactions in solutions at the atomic level is therefore of great importance in the development of advanced catalytic technologies and a wet holder for studies of polymerisation reactions in wet-ETEM has been developed [42,43]. Water vapour is also a major component in selective hydrocarbon oxidation or in advanced fuel cell reactions. Recently Yoshida et al. have reported atomic scale studies of Pt/C catalysts in hydrogen, oxygen and with water vapour [44]. Pt/C catalysts are important in fuel cell technology [45]. See also the contribution by T. Schuh and N. de Jonge in the present volume.

6. Conclusions

Dynamic *in situ* experiments under controlled reaction conditions of temperature and gas (or liquid) environment can be very efficient and productive of data in scanning a range of experimental conditions in a single session, and in mechanistic studies. Moreover as is often the case in catalysis, the key data for the rational design of new materials can only be obtained from dynamic *in situ* studies (EM or otherwise). The emphasis in E(S)TEM is on dynamic *in situ* studies of reaction mechanisms under controlled, near real world, conditions of environment and temperature with full analytical capabilities; with minimally invasive electron microscopy for analysis. We have now removed the previous compromises in (S)TEM performance with the E(S)TEM functionality added. The limits on the systems are a maximum gas pressure in the mbar range dictated by electron scattering and finally leakage into the gun. Other important developments are based on sample holders and include thin window cells consisting of a TEM sample holder that encloses the sample and the gas phase between two gas-tight electron transparent thin films, and the application of MEMS technology to construct specimen holders with gas containment and high gas pressures (>1 bar) or liquids.

Aberration correction is particularly beneficial to *in situ* studies. Its benefits include being able to capture in a single image a full range of spatial frequencies without Cs-induced contrast reversals and minima in the CTF of an uncorrected EM, and minimisation of electron delocalisation effects in TEM images. These effects are most important in structural discontinuities such as defects and surfaces which play a key role in materials properties and chemical activity. Using the novel ESTEM development single atom dynamics in industrially important supported platinum nanocatalysts in gas environments at operating temperatures and atomic level have been demonstrated. The results have important implications in catalysis and the role of nanoparticles in catalytic reactions.

Acknowledgements

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