

Aberration corrected environmental STEM (AC ESTEM) for dynamic *in-situ* gas reaction studies of nanoparticle catalysts

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Abstract:

Environmental scanning transmission electron microscopy (ESTEM) with aberration correction (AC) has recently been added to the capabilities of the more established ETEM for analysis of heterogeneous nanoparticle based catalysts. It has helped to reveal the importance and potentially unique properties of individual atoms as active sites in their own right as well as pathways between established nanoparticles. A new capability is introduced for dynamic *in-situ* experiments under controlled conditions of specimen temperature and gas environment related to real world conditions pertinent to a range of industrial and societal priorities for new and improved chemical processes, materials, fuels, pharmaceutical products and processes, and in control or remediation of environmental emissions.

1. Introduction

Commercial versions of the ETEM, largely based on the earlier work of the authors [1, 2, 3], are now widely used around the world in both academia and industry, and we have recently introduced [4] the important additional capabilities of aberration corrected environmental scanning transmission electron microscopy or AC ESTEM. The double (Cs, TEM + STEM) aberration corrected JEOL 2200 FS has been rebuilt at York to create the first full function environmental scanning transmission electron microscope (AC ESTEM). It has <0.1nm image resolution in both TEM and STEM modes and already provides a powerful new analytical capability which is being actively developed further. The essential proposition is to add facilities for dynamic *in-situ* studies of the heterogeneous solid state catalysis of gas reactions, with a hot stage providing controlled high temperatures and a gas environment around the specimen. The challenge has been to combine the new capabilities while retaining or improving the performance of the original full function STEM (and TEM) system with unrestricted imaging and analysis modes, including for Z-contrast STEM, a wide range of electron diffraction modes, and spectroscopy (EDX and EELS). The new system is also a full function ETEM [1, 2, 3]; now also with greatly improved diffraction and the addition of high quality EDX analysis.

2. Experimental procedure, design criteria and initial system operation results

2.1 Single atom imaging and raft analysis

The design goal has been to have all the functions available in all combinations. The proof-of-principle system, now developed further [4], has been used in preliminary experiments to image single atoms and analyse the 3D structure of reacting nanoparticle catalysts under reaction operating conditions. Specifically, single atom imaging and quantitative column analyses [4, 5] have been used effectively with Platinum on Carbon specimens in a hydrogen atmosphere of 2 to 20 Pa and at



controlled hot stage temperatures of up to $>500^{\circ}\text{C}$. Experimental HAADF Z-contrast single atom FWHM peak width resolution has been measured at $0.11\pm 0.01\text{nm}$ without contrast enhancement and $<0.1\text{nm}$ using it. These experiments show the incidence and movement of individual atoms between, and associated with, larger entities; including rafts, as well as nascent and fully formed nanoparticles with varying amounts of ordered crystallinity. The images, which were previously not attainable, reveal a significant number density (but low mass fraction) of isolated individual atoms existing on the support under real reaction conditions of gas and temperature.

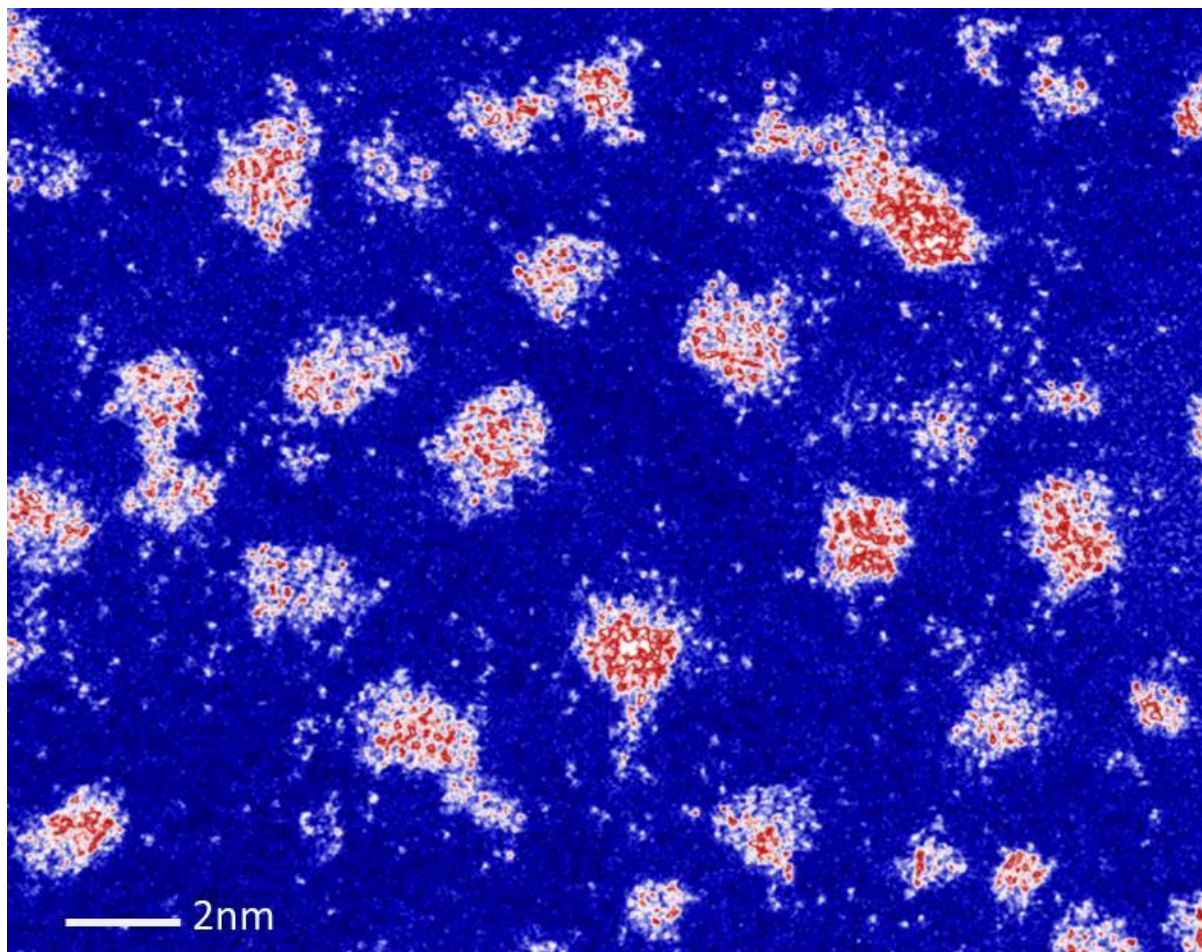


Fig.1: HAADF STEM image of Pt atoms and 1-2 atom thick relatively disordered rafts in an as deposited model Pt on C catalyst in the AC ESTEM with the H_2 gas modifications operational.

The significance of these results is several-fold. Firstly, they reveal migration of individual atoms or in some cases very small clusters between and also located in-between larger units on the support, and indicative of particle growth mechanisms. Secondly, they themselves predominantly have support and gas atoms rather than other metal atom as nearest neighbours. They will therefore inevitably have different energy levels and properties to the same type of atom bound into a nanoparticle crystal structure, or even a raft, and there surrounded with at least some of the nearest neighbours being its mates. This may be a very different environment and may lead either to de-activation or potentially much more active and perhaps differently reacting properties with different reaction type selectivity as well as volume activity. These properties will depend on the nature and strength of the support interaction, as will the site stability of the ‘reaction’ atom. Thirdly, the geometry of highly dispersed atoms is equivalent to a very high or ultimate surface area catalyst which is at least potentially very effective. Finally, in part the significance of the direct imaging of these species is that although perhaps present as a high number and activity density, and therefore importance, they may form a

very small mass fraction and would otherwise remain undetected by other methods of analysis, such as most conventional HRTEM or conventional surface science methods. In essence they are a new component of the reaction pathway to be taken into account in understanding and improving catalyst activity and selectivity by design on a rational basis and better informed by the new data now made available with the development of (AC) ESTEM.

2.2. Nanoparticle development in hydrogen

After heating in hydrogen at 400°C or higher the previous partially ordered rafts, mostly 1-2 atoms thick and with edges always single atom high, are replaced by the ordered high density crystallinity of nanoparticles of Pt, usually with cube form and edges made up of cliffs several atoms high [4]. The particle geometry is extracted from quantitative analyses of Z-contrast HAADF STEM images, using analysis based on the original Crewe work [5] rather than more modern approaches [12]. We analyse reliably only within each image frame because the video signals are normalised within each frame. This can be most easily done where there are individual atoms to act as clear reference signals but also on the basis of the identification of multiple discrete levels. Results are similar to those originally reported by Crewe [5] with linear response, as here, for column heights of up to >10.

2.3. Pumping systems

A key attribute of the new ESTEM instrumentation, like that of the previous ETEM development, is to sustain a controlled gas pressure around the specimen while retaining the full functionality and performance, including <0.1nm imaging resolution, of the core instrument; both for use in the catalyst applications and to allow the parallel use for high vacuum studies of the same piece of high capital investment simply by not turning on the gas supply. Use of a common gas/no-gas microscope configuration ensures minimal need to open the column after initial modifications and contributes to system reliability. The gas pressures for the ESTEM on the JEOL column are achieved with a series of beam line apertures and stages of differential pumping similar in principle to the configuration used for the original ETEM [2] on the 300kV Philips/FEI column but modified in detail to fit the 200kV JEOL system now employed and to provide the novel ESTEM functionalities. Each design is opportunistically adapted to reduce the need to modify the specific core column being used. A key part of both systems is the use of aggressive gas tolerant turbomolecular pumping systems with appropriate new manifolds and with the necessary engineering to ensure full compatibility with <0.1nm image resolution in both TEM and STEM modes. New fixed beam line apertures and differential pumping stages support design gas/vacuum pressures over a 10^{10} x range from up to 100Pa at the sample in the middle of the column down to 10^{-8} Pa in the FEG at the top.

TMPs supplement the ion pumping on the FEI column and replace it entirely on the JEOL one, with a completely oil-free dry pumping system including an additional ion pumped stage before the UHV Schottky FEG. The various pumping modifications for gas have the incidental and slightly paradoxical effect of also improving the basic vacuum of the system (at least in the authors' versions) with the effect of significantly reducing specimen contamination effects in regular high vacuum operations. With the hot stage above 300°C contamination is almost completely avoided anyway. The use of the controlled temperatures of a hot stage, rather than uncontrolled beam-heating, is essential to have calibrated temperatures related to the real world outside the microscope and to reduce as far as practical distorting reaction mechanisms through charged particle effects, as well as to remove contamination with specimens which may initially be less than completely clean. Experiments with aggressively cleaned test specimens suggest most contamination is introduced with the sample rather than being machine derived. The high differential temperatures and associated migration of species across a very locally beam heated sample only add to contamination problems with less than ideally clean samples.

3. Gas pressure calibrations

Gas pressures at the sample have been measured with N₂ gas flow rates through an aperture in the tip of a modified specimen holder and the results calibrated in a separate system held at a succession of independently measured pressures. In the initial proof-of-principle system the manifold pressures were found to be reduced by almost exactly a factor of 100x, or from from mbar to Pa, and have so far been operated mostly in the range 2-20Pa. In the more developed system now being introduced pressures should be able to be increased to 100Pa, to the point with heavier gases the limit is expected to be gas type dependent scattering of the e-beam by gas interactions rather than by the earlier pumping system throughput limitations. Pressures measured at the sample with the test specimen holder built for purpose are calibrated against a gas type insensitive diaphragm gauge in the gas inlet manifold to the microscope.

Compared to the periodic dose methods in surface science UHV analytical methods, the ESTEM can support continuous gas flows and much higher pressures. Somorjai [6] has suggested that the criteria for surface reactions define the ‘high pressure’ region as being 0.1Pa and higher. This corresponds approximately to a gas supply of 1000 monolayers per second, which should ensure a good level of coverage for a reacting surface. The ESTEM operates with gas supply pressures at least one order of magnitude higher than this and often 100-1000x for up to mega-monolayer gas supply per second. While this is not as high as some industrial reactor processes, which may extend to >100bar, it is clearly much higher than is usual in many other types of analytical systems.

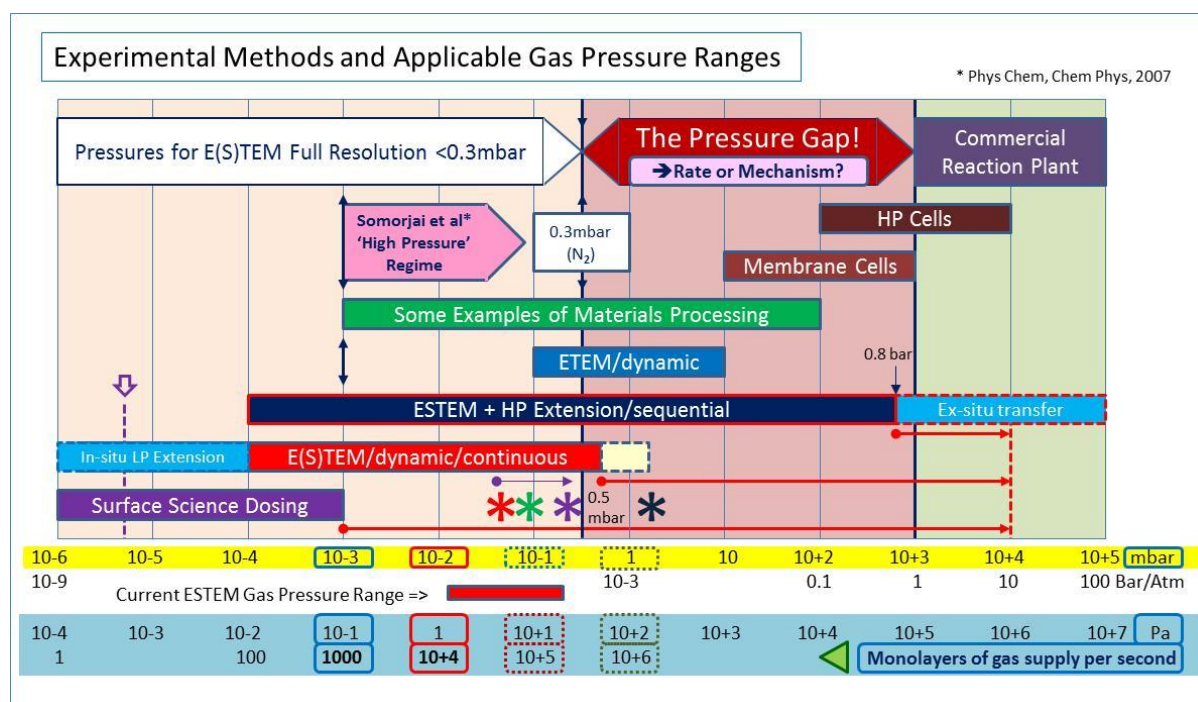


Fig.2. Chart of applicable gas pressure ranges for selected different gas reaction analytical methods. Such data are inevitably somewhat subjective and are intended to be illustrative rather than necessarily accurately definitive for all applications. In the chart E(S)TEM refers to the open version with the gas supply and pumping microscope-based as promoted and used by the authors of this paper, and widely adopted by others for ETEM.

Some of the information about how the ESTEM fits into the pressure landscape is summarised in Fig.2. Higher pressures, to several bar, have been reported for *ex-situ* reaction EM transfer systems [7], window specimen holders [8], and in laboratory and especially synchrotron x-ray analyses.

In the current practice the intent is to use E(S)TEM for real world related gas reaction studies and in part to close the ‘pressure gap’ through the scientific understanding generated. The applicability of this approach depends on whether the main effect is on reaction rate – when it is OK – or whether the reaction mechanisms are changed significantly and studies at modest pressures are not indicative of

results in the real reaction. The sense is that a gas supply to the sample surface of between 10,000 and 100,000 or more monolayers of gas per second currently used in the new E(S)TEM will be sufficient to flood the solid surface and ensure stable reaction conditions, but this will depend on the (often mS or more) residence time of each gas molecule at reaction sites on the catalyst surface.

4. Discussion of technical issues

4.1. Specimen contamination

Outstanding issues include, most importantly, specimen cleanliness and its effect on reaction pathways and energetics. This is more important for dynamic in-situ experiments than for simple characterisations. Pre-cleaning holders, supports and with some care actual samples has been found beneficial as is avoiding e-beam artefacts; especially contamination build-up. A proper solution will require contained preparation and transfer of samples under a protective atmosphere of gas, but not vacuum, without exposure of the actually or potentially reactive samples to air and/or moisture or other contamination. Activation in the microscope of protected catalyst species, as is often used in a real reactor, is a promising pathway. Samples from industrial reactors and even, as we study, ones extracted from real world reaction environments including extended, e.g. 36,000 mile, exposure in a vehicle exhaust system [9], will often be subject either to initial or handling induced material which turns into electron microscopy 'contamination', even if it is itself from the real world operating environment of the catalyst. This may well limit the use of such materials as specimens for *in-situ* studies; although requiring extensive characterisation of the materials in their original forms. In the application it may also lead to some catalyst poisoning deactivation. In this case, and for other reasons, we resort to using model systems better to identify mechanisms and establish operating parameters more clearly than is possible with more complex choices. The simple systems have increased value when related closely to identified issues with real world reaction mechanisms.

4.2. Zone axis analyses

In practical terms an intrinsic problem with using real catalysts as samples is the need for systematic zone axis orientation for the most informative analyses of crystalline nanoparticles of both the active phase and the support if either is so structured. So far most oriented nanoparticles are found in this state due to the difficulties in orienting them in practice, since even with the best stages nanoparticles inevitably move while being tilted. This requires access to apparently simultaneous, but in practice seamlessly multiplexed [10], signals from both real (for position) and reciprocal (for orientation) spaces. Fortunately in STEM – but not in TEM with lens setting hysteresis and therefore inaccurate and slow mode switching – a convergent beam electron diffraction pattern and an image can be recorded – if not optimised – with the same lens settings. Scans are simply switched from field scan to spot analysis with appropriate signal unscrambling; assisted by the different reciprocal space annular zones in which bright field, crystallographic and Z-contrast signals predominantly emerge from the sample exit face. Suitably shaped and sized detectors can be used to pick up the majority signals at the respective radii in reciprocal space. The system has been demonstrated on a dedicated STEM and is in process of being implemented on the York ESTEM. Variations on the theme should allow the beam dose for diffraction to be reduced. This is particularly important for ESTEM which is used as far as possible to study systematic gas and hot stage temperature induced effects. However, like most other forms of electron microscopy, damaging beam-specimen interactions will in the end set the basic limit to the validity of the applications. We need to take all practical steps to minimise the broadly defined 'damage' in gas reaction studies with wide applicability to industrial practices.

4.3. Hot stages

Hot stages for controlled specimen temperatures is an area of rapid development. We continue to use the conventional furnace heating holders, in our case from Gatan [11], because they support use of 3mm disc specimens when required, including ones prepared by evaporation or ion-milling. For high

resolution STEM (but not required for TEM) we operate with a replacement Keithley 2614B power supply and independent temperature monitoring. With this type of holder there is inevitably substantial specimen position drift with temperature changes; albeit often predominantly in one direction. With skill and experience, manual or electronically assisted position stabilisation is often possible. A big advantage of these holders is the accompanying thermocouple on the furnace body to monitor temperatures even in the presence of enough gas to modify the readings in the way Pirani gas conductivity gauges work. Recent developments for small amounts of ultrafine (only) powder samples use MEMS technology [13] with much smaller dimension thin film heaters, faster response times and much less reported positional drift with temperature change. The double tile holders required for the most informative zone axis of individual nanoparticles selected for detailed analysis should especially benefit from the new technology when available in this form. However, after a suitable period for position stabilisation it has proved possible using custom electronics for STEM to use the standard Gatan 628 heating holder for sub-angstrom ($<0.1\text{nm}$) TEM and STEM imaging at modest temperatures up to $>500^\circ\text{C}$.

4.4 Parallel chemical studies

Although the AC ESTEM is equipped with a quadropole mass spectrometer this is more for vacuum system maintenance and reaction gas management than reaction product evaluations; in large part due to the very small amount of catalyst being used and the associated furnace and holder environment artefacts or potential artefacts. Current practice [1] is to conduct parallel reaction studies in an *ex-situ* reaction rig with a larger amount of catalyst material, but true parallel in-situ studies of product would clearly be beneficial in addition if not in total replacement.

5. Conclusions

We have constructed the first full function AC ESTEM system and have used it with 0.1nm resolution for single atom, raft and crystalline nanoparticle studies, demonstrating the capability of the facility and compatibility of the same instrumentation for gas studies and parallel high vacuum analyses.

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