Ways and means. past, present and future, of open aperture ESTEM for atom-by-atom gas reaction catalyst research

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Assured natural chemistry dynamics require controlled gas environments and temperatures, rather than high vacuum, and minimally invasive e-beam conditions. There are operational advantages and disadvantages of open aperture 'gas-in-microscope' (1,2,3) (vs windowed 'gas-in-holder' (4)) approaches to environmental scanning transmission electron microscopy (ESTEM) (3). A JEOL 2200 FS with CEOS Cs correctors for TEM image and STEM probe has been rebuilt in-house to add gas reaction capabilities. The project reconfigures for full STEM the serial differentially pumped aperture gas containment method developed for the original atomic resolution ETEM (1,2). The design is widely used commercially and has led to a big expansion in this field of EM applications, with 100s of publications. TEM environmental studies have a much longer history at modest resolution (nms), with notable science (5) on defect analysis in oxide catalysts and a good review of the earlier work (6).

Until recently (3) STEM, with its imaging and analysis advantages, was restricted to high vacuum instruments involving *ex-situ* sample transfers; now augmented with auxiliary 'gas-in-holder' systems (4).

The York ESTEM was purposefully designed for single atom resolution dynamic in-situ gas reaction HAADF imaging and analysis under controlled conditions of a continuously flowing (vs much surface science) gas atmosphere, high temperatures and sub-Angstrom (<0.1nm) resolution, as Fig.1.

Since the reaction gases are in the microscope, independent of the holder, we can use a wide range of existing (often zero cost and set up time) specimen holders, including double tilt units for crystallography, MEMS, 3mm furnaces, and tomography or FIM needles (7). There is a clear electron beam path through the instrument; with a very thin support film, e.g. <5nm of carbon. With dual correctors, a wider lens gap can be used; adding flexibility in design (thickness) and operations (double tilt). Similarly, the original ETEM (1,2) restrictions on STEM HAADF Z-contrast imaging and EDX analysis are avoided; supporting dual gas and enhanced vacuum use of a single full function machine and large capital investment.

The 'gas-in-holder' with windows (4) uses higher (not always required/desirable) gas pressures of ~1bar; but still far below some >100bar real reactors. The surface science literature (8) defines 'high pressure' as being >0.001torr; orders of magnitude below the Pa-mbar range in the ESTEM. At Pa levels the continuous gas supply at the specimen surface amounts to ~10,000 ML/second; with coverage determined by residence time. In the recent York study of the Cu/Cu_2O system (9), Pa gas pressures drive either arm of the REDOX reaction pathways to completion - to reduced Cu metal or oxidised Cu_2O - with oxidation end-point nanostructures similar to those achieved in *ex-situ* reactions at 1bar (9).

The future of E(S)TEM includes lower beam voltages and intensities, with improved illumination controls and detection systems, and faster frame rate ADF STEM (or ADF TEM (10)). It depends on excellent mechanical alignment of the various differential pumping apertures to the optics - a key aspect of the modern E(S)TEM designs (1,3) - and inherently favours open aperture systems and lower gas pressures.

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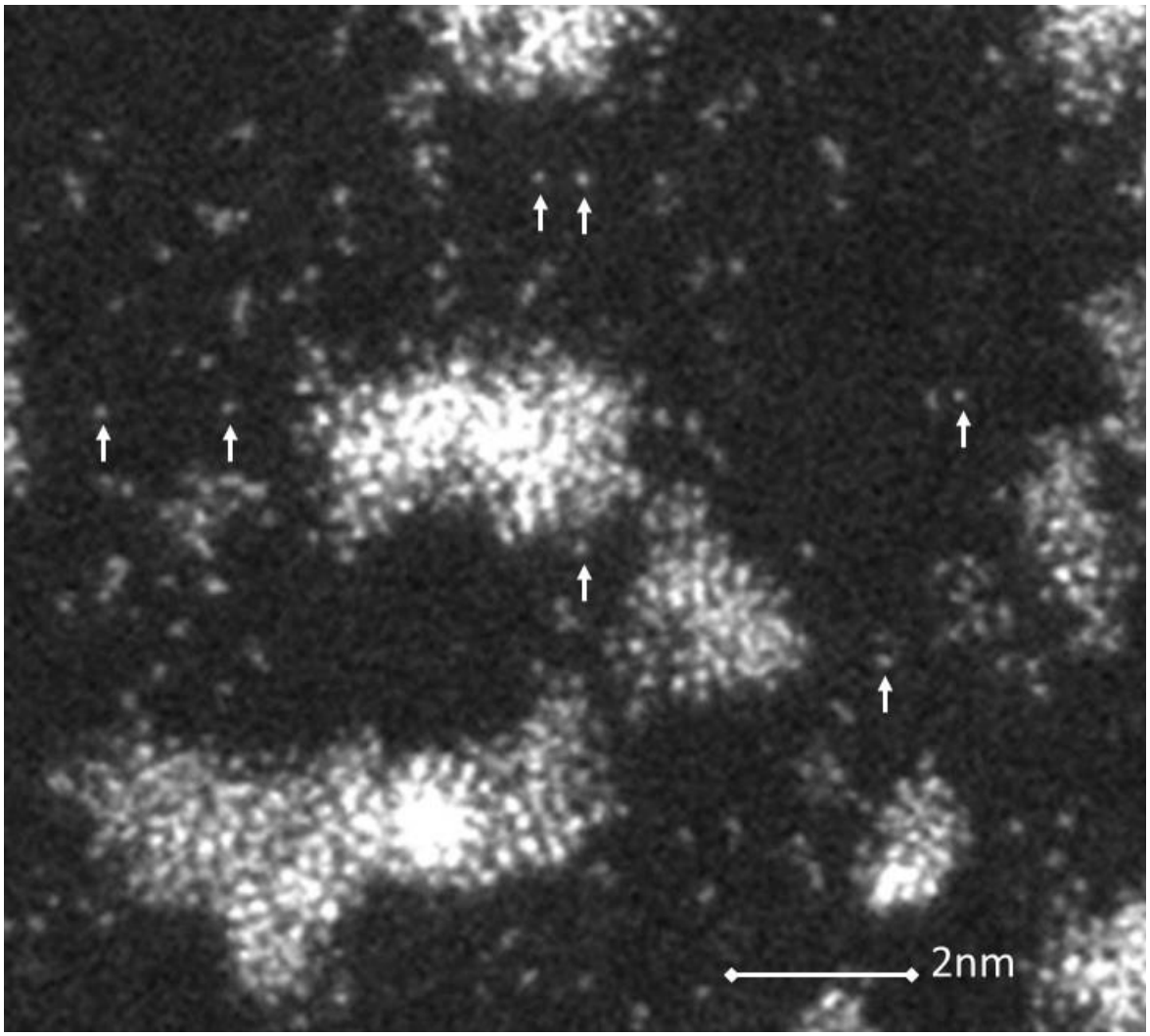

Fig.1: Single atom resolution ESTEM HAADF image of single atoms (a few are arrowed) individually isolated on the support on statistical kinetics or systematic pinned site basis, clusters and nascent partly crystalline particles of Pt on a carbon support film in the early stages of sintering in a 3Pa flowing H_2 environment using a modified furnace hot stage with replacement low noise electronics.