

Recent Progress with AC E(S)TEM and Application to Single Atom Catalysis

Pratibha L Gai^{1,2,4}, Leonardo Lari^{1,2}, Michael R Ward^{1,2}, Thomas Martin^{1,2}, Robert W Mitchell^{1,2,4}
David Lloyd^{1,2}, Alec LaGrow^{1,2}, Ian Wright^{1,2}, and Edward D Boyes^{1,2,3}.

York JEOL Nanocentre¹ and Departments of Physics², Electronics³ and Chemistry⁴, University of York, York, YO10 5DD, UK.

The development of atomic resolution ETEM [1,2] and now of the E(S)TEM [3,4,5] with 0.1nm image resolution in both modes has required managing multiple scientific and engineering issues. The projects have built on the foundations laid by earlier contributors to the field, most notably Hashimoto and co-workers [6] and Swann [7], with lower resolution TEM imaging developments which nevertheless supported outstanding science. Notably this included studies by Swann of the reduction of haematite to iron [8] and the untangling by Gai [9,10] of the critical contributions of surface defects in the oxidation catalysis of hydrocarbons. The latter work led to a redefinition of the basic criteria for the design of the catalyst, understanding of the commercial process mechanisms and economic operating parameters [11].

With the recent in-house development at York of the novel E(S)TEM system, we have been able for the first time to combine controlled hot stage temperatures and a gas environment around the sample with full (AC) STEM capabilities. These include single atom sensitivity in HAADF imaging, so far down to Z=29, wide angle electron diffraction and full EDX analyses in a double (TEM + STEM) aberration corrected version of the JEOL 2200 FS (S)TEM. The new functionality has been added without reducing the core capability of the original instrument and in important ways, including the vacuum and pumping systems, augmenting it. These developments achieve the goal of continuous dynamic in-situ studies of gas-solid chemical reactions with atomic resolution. There is access to key intermediate phases which may be metastable with respect to reaction conditions of gas and temperature, as well as being susceptible to side reactions if exposed to air during sample transfer for ex-situ studies. Surface science studies are usually either at low gas pressures (>0.1Pa is described as 'high pressure' in this literature [12]) and/or uses discontinuous dosing. The ESTEM operates with continuous gas flows and pressures at the sample of a few Pa to a few mbar with even 1Pa corresponding to a gas supply of 10⁴ monolayers per second with the actual supply also depending on the sticking coefficient. The York system is also compatible with enclosed specimen holder based thin window cells for higher pressures or hydrated atmospheres. The 'open' architecture of the ESTEM with multiple added stages of powerful differential pumping across a series of beam-line apertures supports the >10⁹ pressure differential between the specimen and the FEG. It also separates the specimen holder design from the gas supply system and supports use of the full existing range of specimen holders which are available. These now include double-tilt hot stages for greater flexibility for proper crystallographic analyses for imaging, diffraction and other forms of analysis down to the single column level. It has been possible to modify the original Gatan 628 furnace hot stage design, with the considerable advantage of retaining the 3mm disc specimen capability [13], and replace the electronics for 0.1nm resolution and single atom imaging but this can be achieved only after a soak time of several minutes and high magnification area retention requires dexterity in control inputs [Fig.1]. On the other hand, MEMs technology provides high lateral stability, both short and long term, and is ideal for particulate catalyst samples placed directly onto the filmed windows, ones custom covered with the correct chemistry or using the regular catalyst support particles in a similar way. The geometry of both types of hot stage have been adjusted to support EDX analysis; with the furnace holders at up to ~400°C and the MEMS ones demonstrated to >650°C [Figs.2,3].

Initial applications of the new system include investigations of the incidence of single atoms on the support between nanoparticles or pre-particle rafts [Fig. 1] and their relevance to catalyst performance [4,5]. Single atoms may be expected to have different properties to those embedded on sites making up crystalline nanoparticle surfaces, or associated with rafts, and it is prudent for the potentially highly reactive single atoms to be treated and analyzed in-situ under controlled reaction conditions, or at least preservation conditions, rather than after ex-situ reaction and transfer through air into a conventional high vacuum electron microscope. Limits are set on the method by the potentially invasive e-beam; to varying degrees in TEM and STEM modes, as a function of the gas atmosphere and its support.

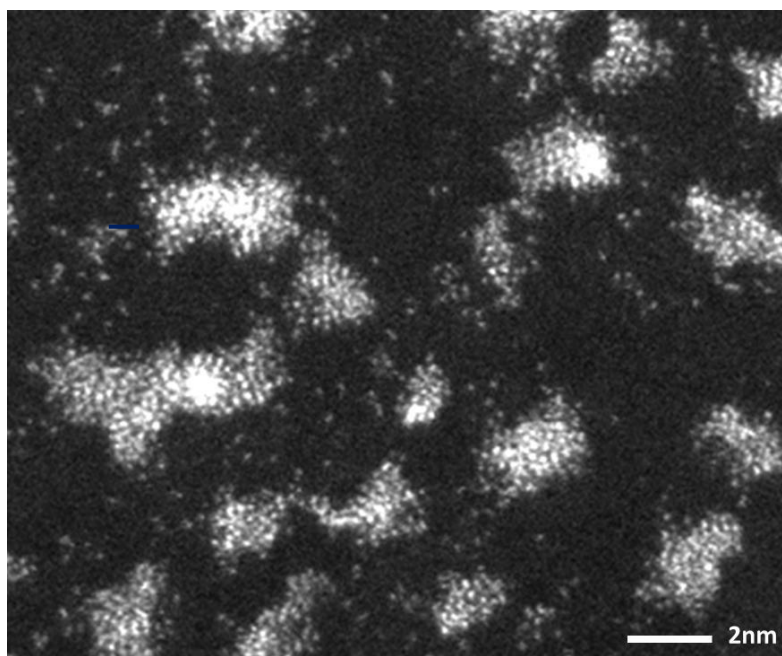


Fig.1: Single atom and raft imaging of Pt under reaction conditions (Pt/C/H₂); atoms imaged at 0.11±0.01nm diam in HAADF ESTEM

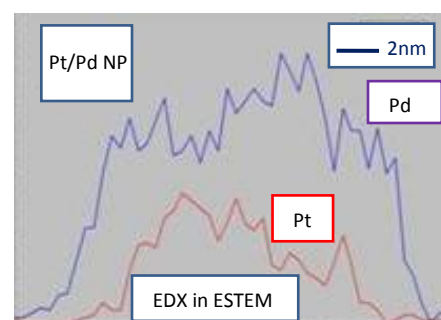
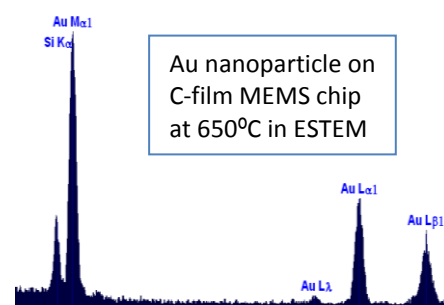


Fig.2: Au nanoparticle EDX at 650°C
Fig.3: EDX data [14] recorded in the ESTEM from a core-shell nanoparticle

References

- [1] P L Gai et al, *Science* (1995) 267, p661
- [2] E D Boyes and P L Gai, *Ultramicroscopy* (1997) 67, p219
- [3] P L Gai and E D Boyes, *Microscopy Research and Technique* (2009) 72, p153
- [4] E D Boyes, M R Ward, L Lari and P L Gai, *Annalen der Physik*, (2013) 525, p432
- [5] P L Gai, L Lari, M R Ward and E D Boyes, *Chem. Phys. Letts.* (2014) 592, p335
- [6] H Hashimoto, T Naikui, T Etoh and K Fujiwara, *Jap. J. Appl. Phys.*, (1968) 7, p946
- [7] P R Swann and N Tighe, *Jernkont. Ann.*, (1971) 155, p497
- [8] P R Swann and N Tighe, *Metall. Trans. B Process Metallurgy*, (1977) 8, p479
- [9] P L Gai, B C Smith and G Owen, *Nature*, (1990) 348, p430
- [10] P L Gai, *J Sol State Chem*, (1983) 49, p25
- [11] P L Gai and K Kourtakis, *Science*, (1995) 267, p661
- [12] G Somorjai, R L York, D Butcher and J Y Park, *Phys. Chem. Chem. Phys.*, (2007) 9, p3501
- [13] J Sagar, L Fleet, M Walsh, L Lari, E D Boyes, O Whear, T Huminiuc and A Hirohata, *Appl. Phys. Letts.*, (2014) 105, p032401
- [14] M R Ward, T Hyde, E D Boyes and P L Gai, *Chem. Cat. Chem.*, (2012) 4, p1622

Support from the University of York and the UK Engineering and Physical Sciences Research Council (EPSRC) through Critical Mass Grant EP/J018058/1 and other funding is gratefully acknowledged.