

## Atomic Resolution *In situ* Environmental-TEM (ETEM) Studies of Novel Nanostructures for Hydrogenation and Hydrogen Energy Economy

Pratibha L. Gai <sup>\*,\*\*</sup>, Leland Hanna <sup>\*</sup> and Edward D. Boyes <sup>\*</sup>

<sup>\*</sup> Central Research and Development Laboratories, DuPont, Wilmington, DE 19880-0356.

<sup>\*\*</sup> Department of Materials Science and Engineering, University of Delaware, Newark DE.

Global challenges in the 21<sup>st</sup> century include environmentally clean chemical processes for polymerization, sustainable energy sources and novel routes to nanomaterials for energy storage, through catalysis on the surface of essentially nanoscopic reactive materials. For many of these applications, data transfer through air and analysis in high vacuum environments at room temperature are not very useful. Atomic resolution *in situ* environmental transmission electron microscopy (ETEM) [1-3], provides facilities for dynamic *in situ* experiments at the atomic scale under controlled gas/vapor environments (figure 1). Pressures up to 50 mbar (usually rather less for atomic resolution) and at selected and accurately known temperatures from -170 °C to 1100 °C and in a few cases up to 2000 °C. The basic concept of atomic resolution-ETEM is straightforward. Many dynamic processes do not occur in nature or industry in a typical TEM high vacuum environment. In addition, these processes occur at the atomic level. Dynamic surface and microstructural data related to the real world often need to be obtained under controlled conditions of environment and temperature. It is also essential to ensure with calibration experiments [2] that the effect of the electron beam is not invasive.

The modification of nanostructures allows the production of a superior and faster products [4]. In this paper, we present studies of novel nanoparticles on nanosupports for hydrogenation and polymerization reactions to manufacture linear polyamides and modified nanotube structures for potential applications in the hydrogen economy. We have carried out ETEM studies of the heterogeneous hydrogenation of complex nitriles in a liquid phase over mesoporous cobalt promoted and noble metal promoted ruthenium nanoparticles on reducible titania nanosupports using a liquid stage [5,6]. The desorbed organic products are imaged *in situ*. The experiments have shown that the nanocomposite systems demonstrate high hydrogenation activity in the presence of atomic scale anion vacancy defects on the substrate surface and an electronic and synergistic contribution to the promoter mechanism [7]. The nanoparticle catalysts were found to be very stable during the reactions at operating temperatures of up to ~ 100 °C.

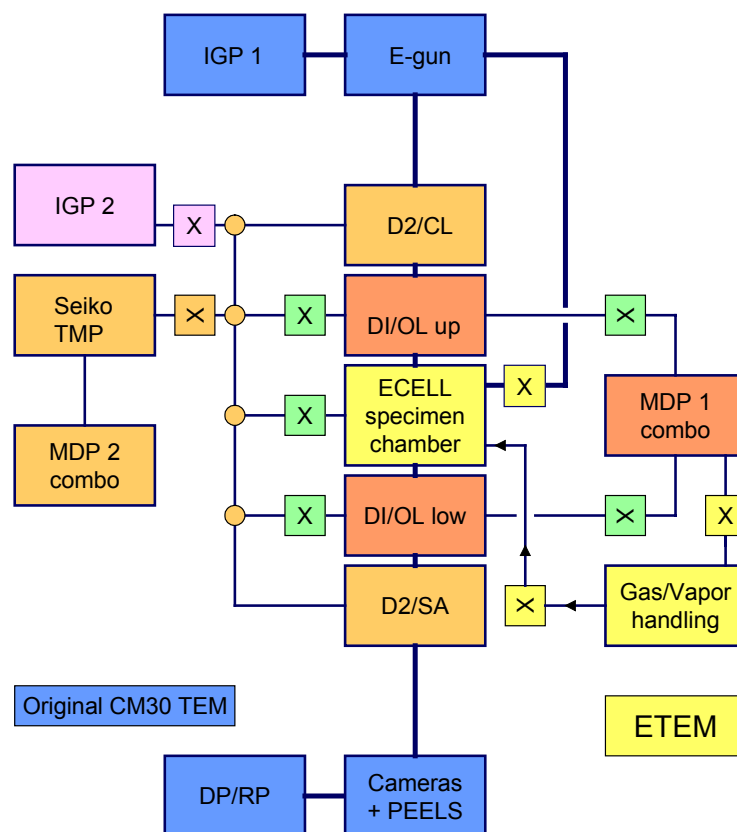
We believe that the stability of the nanoparticles on nanosupports in the liquid and gas environments is due to surface energy effects. Under equilibrium conditions, relationships between surface energies in these environments can be expressed as:

$$\gamma_{slg} - \gamma_{ms} = \gamma_{mlg} \cos \theta$$

where,  $\gamma$  are surface energies between nanoparticles (m), substrate (s), liquid (l) and gas (g) and  $\theta$  is the wetting angle between the nanoparticle and the nanosubstrate.

The results demonstrate the important role of ETEM in the design of novel green heterogeneous routes for hydrogenation and polymerization.

Aberration corrected-ETEM (AC-ETEM) with aberration correction on the TEM side, is expected to offer superior (sub-atomic level) resolution under dynamic reaction conditions [8,9,3,4] which would be particularly beneficial for supported nanocatalysts, e.g. for fuel cell nanotechnologies.



## References

- [1] P.L. Gai et al., *Science* 267 (1995) 661.
- [2] E.D. Boyes and P.L. Gai, *Ultramicroscopy* 67 (1997) 219.
- [3] P.L. Gai and E.D. Boyes, *El. Microscopy in Het. Catal.* IOPP, Bristol, 2003.
- [4] J.M. Thomas and P.L. Gai, *Adv. Catalysis* 48 (2004) 171.
- [5] P.L. Gai, *Inst. Phys. Conf. Ser.* (London, U.K.) 168 (2002) 401.
- [6] P.L. Gai, *Microsc. Microanal.* 8 (2002) 21.
- [7] P.L. Gai et al., *Catal. Lett.* (in press), 2005.
- [8] P.L. Gai, *MSA Pre-Meeting Proceedings*, Savannah, Ga., Aug. 2004.
- [9] P.L. Gai, *Frontiers in Electron Microscopy Conf.* Berkeley, CA 2003.