Angstrom analysis with dynamic in-situ aberration corrected electron microscopy

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Abstract. Following the pioneering development of atomic resolution in-situ environmental TEM (ETEM) for direct probing of gas-solid reactions, recent developments are presented of dynamic real time in-situ studies at the Angstrom level in an aberration corrected electron microscope. The in-situ data from Pt-Pd nanoparticles on carbon with the corresponding FFT/optical diffractogram (OD) illustrate an achieved resolution of < 0.11 nm at 500 °C and higher, in a double aberration corrected JEOL 2200 FS TEM/STEM employing a wider gap objective pole piece and gas tolerant TMP column pumping system. Direct observations of dynamic biofuel catalysts under controlled calcinations conditions and quantified with catalytic reactivity and physico-chemical studies show the benefits in-situ aberration correction in unveiling the evolution of surface active sites necessary for the development efficient heterogeneous catalysts. The new results open up opportunities for dynamic studies of materials in an aberration corrected environment and direct future development activities.

1. Introduction

Many technological processes are carried out in dynamic reaction environments. Therefore, for a full understanding, dynamic in-situ data related to the real world are needed under controlled conditions of vacuum/gas/vapour/liquid environment and temperature. The direct observation of the sequence of nanostructural evolution under dynamic reaction conditions is a powerful structural tool in the chemical and materials sciences. Dynamic in-situ experiments access metastable states and the mechanisms of reactions, phase transformations and nanostructure development, as well as contributing key information to synthesis, processing and stability studies. They have proved particularly informative in heterogeneous catalysis and solid state defect phenomena in controlled atmospheres [1-4], semiconductor studies in high vacuum [5] and metallurgy [6]. To be useful they need to be conducted under controlled conditions of temperature, and where appropriate environment, and of course always with a minimal, mechanistically non-invasive influence of the electron beam. This means the microscope must be able to accept a hot stage, if heating is the driving force for change being investigated, and with all other conditions held constant. In-situ E(S)TEM under controlled reaction conditions provides dynamic information on processes and performance critical defect structures which cannot be obtained so directly and readily by other techniques.

Recently, atomic resolution-ETEM has been pioneered by Gai and Boyes for probing of gas-solid reactions directly at the atomic level under controlled atmosphere conditions [3,4]. Temperature, time
and pressure resolved studies with high precision are possible. Briefly, the whole EM column in a high resolution 300 kV CM30T high resolution (S)TEM has been extensively modified with the introduction of a fully integrated and permanently mounted ECELL system for atomic resolution studies of dynamic gas-solid reactions and for in-situ nanosynthesis [4,7]. Highlights of this development include a novel ETEM design with objective lens pole-pieces incorporating radial holes for the first stage of differential pumping; in addition, the controlled environment ECELL volume is the regular sample chamber of the ETEM and is thus integral to the ETEM [4]. ‘Blank’ calibration experiments (without the beam and the beam switched on only to record the final reaction end point and compared to in-situ data) are used to ensure that there are no deleterious effects of the electron beam [1]. The novel design of the in-situ atomic resolution-ETEM [4] has been adopted by TEM manufacturers FEI for commercial production and later versions of this in-situ ETEM instrument (including the CM 200-300 series, Tecnai and Titan (including the aberration corrected versions) have been installed in other laboratories around the world (ref: American Chemical Society’s Chemical and Engineering News and Materials Research Society (MRS) Bulletins) [8-10]. 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 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 [11,12]. Both the in-situ development and its applications to nanoparticles and biofuels are described below.

Nanoparticles of Pt, Pd and Au, only a few nanometres (nm) in size, are important in technological chemical processes and sintering impacts their performance. Bimetallic systems such as Pt-Pd offer better performance compared to monometallic systems in technological applications such as energy conversion, catalysis, nanoelectronics, chemical and biological sensing and photonics [13]. Biofuels are promising renewable energy sources and vegetable oils have been proposed as feed stocks [14]. Biodiesel is one such clean and renewable biofuel. Solid catalysts (e.g. alkaline earth oxides) offer advantages, especially pertaining to biodiesel separation and the opportunity for continuous process operation. Although solid catalysts have great promise in plant oil triglyceride transesterification to biodiesel, the identification of active sites and operating surface nanostructures during processing is required for the development of energy efficient heterogeneous catalysts for biofuel synthesis [14].

2. Experimental Procedures

2.1.1. We sputtered Pt-Pd nanoparticles (at various ratios including at 80-20 wt%) on carbon, which are of interest in catalysis and fuel cell technology, to an average thickness of 2.5nm with particle sizes of ≤ 1 to 2 nms on carbon, following methods similar to those reported [15]. We prepared high quality nanocrystalline-MgO (nano-MgO) practical powder catalysts using magnesium hydroxide methoxide precursor (Mg(OH) (OCH₃)) at 300°C [14].

2.1.2. To observe changes in the nanostructure as a function of operating temperature under controlled in-situ conditions in an aberration corrected environment, we employed the following procedures. The need to accommodate special specimen holders in an aberration corrected machine has been one of the more important criteria driving the specification of the JEOL 2200FS double aberration corrected (2AC) FEG TEM/STEM operating at 200 kV in the new Nanocentre at the University of York. 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 was also desired. Both these conditions benefit from the larger gap (HRP/Midi) objective lens polepiece [11,12], shown in the
The Cs (C3) aberration correctors [16] on both the STEM probe forming and TEM images sides of the instrument were used to provide the desired expanded specimen geometry with minimal effect on the 1Å imaging performance of the system. The effect of the increased polepiece gap on Cs in this range is much more evident (x2) than on Cc (x1.2); and of course Cs is now corrected (Cs~0).

| 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                  |

The advantages of the configuration we have adopted, include promoting a 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 (<2nm) nanoparticles and clusters on supports, using high resolution TEM as well as HR STEM; facilitating HAADF STEM and extending HAADF STEM resolution to 1Å (0.1nm) and below [17]. As well as benefiting from improved resolution at 1Å 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 1Å to 3Å. This is where atomic neighbourhoods in crystals lie in low index projections and it is especially important in studying 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 section 1).

3. Results and Discussion

We show in both theory (www.maxsidorov.com), with contrasting CTFs shown in figure 1, and in practice (figure 3), it is possible with Cs aberration correction to combine demonstrated spatial resolution around 1Å with the HRP lens polepiece with the large ~ 4.3 mm gap [11,12] needed to accommodate a standard hot stage (Gatan model 628); and with it in operation (using Gatan Digital Micrograph). This is an example of using 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 TEM and STEM experimental capabilities.

![Figure 1: Calculated contrast transfer functions (CTFs) for uncorrected (B) and aberration corrected (A) imaging conditions of the HRP version of the double aberration corrected JEOL 2200FS FEG TEM/STEM STEM at the University of York (UK).](image-url)
The system is in practice stability limited (CTF envelope terms) and some of the practical steps necessary to deliver this powerful combination of capabilities will be covered elsewhere with further examples of the new tool in action. These considerations quickly set a limit to how far the lens gap can be stretched without beginning to compromise performance too seriously; taking into consideration realistically attainable stabilities in internal electronics and mechanics, and in key external environmental factors.

Our instrument is further configured with 3 turbomolecular pumps (TMPs) as the main column vacuum system to be tolerant to out-gassing hot samples, and as a key foundation for controlled gas environment experiments [11, 12]. The ‘stretched’ instrument configuration is considered to be a pre-requisite for further in-situ developments adding additional facilities and capabilities [4,3,9] to the exciting and still relatively new generation of aberration corrected TEM and STEM machines. In our case both capabilities are combined on the remotely controlled JEOL 2200 FS platform (figure 2).

Figure 2. A schematic of the 2200FS conversion at the York Nanocentre. The instrument is configured with turbo-molecular pumps as shown.

TEM correction montage procedures (Zemlin tableaux) and image resolution to 1Å have been maintained with the hot stage, including with power connected and the samples held at elevated temperatures; so far to ~ 900°C. Figure 3(a) shows an in-situ AC-TEM image of Pt-Pd nanoparticles on carbon support at room temperature (RT) and (b) shows the corresponding FFT/optical diffractogram (OD). The particles are in the size range of ≤ 1nm to 2 nm, with the carbon support contributing strongly to the diffraction. Figure 3(c) and (d) show in-situ hot stage images of a selected Pt-Pd nanoparticle on carbon at 500 °C, and the corresponding FFT/optical diffractogram with < 0.11 nm resolution, respectively. In-situ AC HAADF-STEM studies showed this is possible (with some difficulty).
Figure 3. Left: (a) Pt-Pd nanoparticles on carbon at room temperature (RT); (b) the corresponding FFT/optical diffractogram (OD). The particles are in the size range ≤ 1nm to 2 nm with the carbon support contributing strongly to the diffraction; right: (c) In-situ hot stage image of a selected Pt-Pd nanoparticle on carbon at 500 °C; (d) the corresponding FFT/OD in with < 0.11 nm resolution.

**In-situ studies of nanocatalysts for biofuels:**
MgO is a commercially important alkaline earth oxide, and a strong candidate for use in solid base catalysed triglyceride transesterification. It adopts a cubic structure with a = 0.4212 nm. Our as-prepared nano-MgO showed randomly orientated, overlapping single crystallites of only 3-4 nm mean

Figure 4: Real time dynamic in-situ AC TEM studies: (a) single and overlapping nanocrystals of only about 3 to 5 nms (arrowed) are observed at room temperature (RT); (b) nucleation of defects at 500 °C in calcinations in surface profile imaging. The defects are at or near the surface (e.g. indicated by arrows). They are viewed in (110) projection and are along <111> directions; (c) profile image (at the same magnification as in (b)) at 700 °C shows the defects have increased in concentrations and have grown along their length extending into the bulk (some are indicated by arrows).
width, embedded within an amorphous medium, with crystallites primarily in (110) and (001) type orientations. We have carried out systematic direct observations of dynamic nano-MgO catalysts in these orientations under controlled calcination conditions using in-situ AC-TEM at the 0.1 nm level and quantified with parallel reactivity (catalytic turn over frequency) and chemical studies [14]. Figure 4 shows real time in-situ, dynamic AC-TEM studies of the calcination of (110) nano-MgO: (a) at room temperature (RT); (b) extended defects are observed at the catalyst surface at 500 °C; (c) the growth of the defects is observed at 700 °C. We have used high resolution and diffraction contrast imaging under dynamic conditions to determine the displacement vector of the defects. The analyses have indicated that they are partial screw dislocations formed by crystal glide shear mechanism along <111> and the shear or the displacement vector $\mathbf{R}$ of the type, $\pm a/2 <111>$ lies in the plane of shear (figure 5). The correlation between the atomic scale glide shear defects with the catalytic activity implicate coplanar anion vacancies in active sites in the transesterification of triglycerides to biodiesel.

![Figure 5. Structure modification to account for the defects along <111> in in-situ AC-TEM implicates coplanar anion vacancies (indicated at V) between Mg atoms. Inset: A possible glide shear model along <111> (arrowed) for the defect mechanism is shown in part in the inset, consistent with the experimental observations: projection of one layer in an idealised magnesium oxide onto (110) indicating the defect boundary.](image)

4. Conclusions
Dynamic in-situ studies of Pt-Pd nanoparticles and MgO nanocatalysts for biofuels within an aberration corrected-TEM modified with a wide gap objective polepiece have been conducted at high temperatures while maintaining 0.1 nm resolution. Preliminary experiments suggest that dynamic in-situ AC experiments are more readily performed with TEM than STEM.

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