Understanding the Environmental Transmission Electron Microscope

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Acknowledgements:

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Jörg R. Jinschek, FEI Europe, Eindhoven, The Netherlands

DTU Cen
Center for Electron Nanoscopy
Towards Understanding the Environmental Transmission Electron Microscope

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DTU Cen
Center for Electron Nanoscopy
Where are We?
DTU Center for Electron Nanoscopy

- Realized by a generous donation from the A.P. Møller og Hustru Chastine McKinney Møller’s Fond til Almene Formaal
- DKK 100,000,000 ~ €14,000,000
- Grant announced in January 2006
- “Establish a World Class Facility with a unique suite of advanced electron microscopes, in a purpose-built building”
- Inaugurated in December 2007

- Hosting 7 electron microscopes
  - 2 high-end TEMs (1 ETEM)
  - 1 work horse TEM
  - 2 dual beam SEM/FIB
  - 2 SEM
What is *In Situ* Microscopy

- ...depends on who you ask...
- “The class of experiments allowing observations of materials’ dynamic response to an externally applied stimulus as it happens inside the microscope”
- The *in situ* observations may be accompanied by simultaneous measurements of the materials’ properties to directly establish structure-functionality relationships
In Situ Microscopy
- Many flavors

STM

Conductivity

Nano-indentation

Light

ETEM

Heating/annealing

FEBID

...probably many more...
What are We Trying to Achieve?

- Obtain high-resolution information
- Dynamic responses of materials as they are exposed to reactive gases at elevated temperatures
- Surface structure of materials in various environments
- Morphology of materials in different surroundings

A Look Inside the Catalytic Reactor

Reactants

Reactants

T: RT-1000° C+
P: $10^2$bar

Catalyst pellets

10mm

Supported metal particles

100nm

Active surfaces

2nm

Products
Why do We Want to do *In Situ* Microscopy? Equilibrium shapes versus gas composition

**H₂/H₂O**
- Cu(111), d=0.21nm
- ZnO(012), d=0.19nm

**H₂**
- Cu(200), d=0.18nm
- Cu(111), d=0.21nm
- ZnO(011), d=0.25nm

**H₂/CO**
- Cu(111)
- ZnO(011)

1.5mbar, H₂/H₂O=3/1, 220°C
1.5mbar, 220°C
1.5mbar, H₂/CO=95/5, 220°C

Why do We Want to do *In Situ* Microscopy? ...continued

- Conventional electron microscopy does not always tell the full story
  - Samples are (usually) not in their operational environment
- Materials respond dynamically to changes in environment
  - Surface reconstruction due to gas adsorption
  - Phase transitions
  - Growth
- Lack of temporal resolution
- Essential for establishing structure-activity correlations

$b_5$ sites on the (105) surface of Ru. These sites were proposed to be the active sites for N$_2$ splitting (van Hardeveld and von Montfoort Surf. Sci. 4 (1966) 396. Figure from T.W. Hansen *et al.* *Catal Lett.* **84**, 7 (2002).
In Situ Techniques

- **In situ XRD**
  - Phase determination
  - Good for large areas

- **In situ EXAFS, FTIR**
  - Coordination
  - Chemical bonding

- **Average values**
  - No local information

- **In situ TEM**
  - Gives local information

- Etc...

Evolution of activity of industrial HDS catalysts,
B.M. Moyse, World Refining Jan/Feb (2001) 28
Imaging in the fog of gas

Can we get a clear view...?
Windowed Design

J. F. Creemer et al., Ultramicroscopy 108, 993 (2008)

N. de Jong et al., Nano Letters 10, 1028 (2010)
Differentially pumped Column

• FEI Titan 80-300
  – Highly stable platform
  – Variable high tension 80, 200, 300kV
  – Field emission electron source (XFEG)
  – Monochromator
  – Objective lens aberration corrector
  – De-contaminator (plasma cleaner)
• Differential pumping system
  – Gas is leaked in
  – Two sets of diffusion limiting apertures
  – Turbo molecular pump (TMP)
  – Ion getter pump (IGP)

The Environmental Cell
- not really a cell...

- Main purpose: to confine the gas to the vicinity of the sample thus making the gas path length along the direction of the electrons as short as possible

![Diagram of the Environmental Cell]

- Reactive gas
- Resistive heating
- e\(^{-}\) beam
- Pumping
- Capillary for residual gas analysis via QMS
- Resistive heating
- 7mm
Quantitative ETEM !?

• Obtain high-resolution information
• Dynamic responses of materials as they are exposed to reactive gases at elevated temperatures
• Surface structure of materials in various environments
• Morphology of materials in different surroundings
• Adsorbed molecules

D. S. Su et al., Angew. Chem. 47, 5005 (2008)

Loss of Intensity

- Main effect of imaging in gas is loss of intensity
- Intensity measured on a bottom mounted camera as a function of argon pressure in the sample region
- At high Ar pressure, >1400Pa, the intensity passing through the objective lens has decreased by more than a factor of 2 at 300kV
- Increasing pressure leads to loss of temporal resolution
Loss of Intensity

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- Intensity measured on a bottom mounted camera as a function of argon pressure in the sample region
- At high Ar pressure, >1400Pa, the intensity passing through the objective lens has decreased by more than a factor of 2 at 300kV
- As high a primary energy is desired due to a longer mean free path in the gas phase
- Increasing pressure leads to loss of temporal resolution
Apparent Mean Cross Sections and Mean Free Paths

• Intensities fitted to:

\[
\frac{I}{I_0} = e^{-x/\lambda}
\]

• Mean free path:

\[
\lambda = \frac{1}{\sigma n}
\]

• Assuming ideal gas:

\[
pV = NRT \Rightarrow n = \frac{N}{V} = \frac{P}{RT} \Rightarrow \lambda = \frac{RT}{\sigma P}
\]

• Fit function becomes:

\[
\frac{I}{I_0} = e^{-\sigma P \times 7.5 \times 10^{-3} m}
\]

<table>
<thead>
<tr>
<th>Voltage</th>
<th>Gas</th>
<th>(\sigma [m^2])</th>
<th>(\lambda (500 Pa) [10^{-3} m])</th>
</tr>
</thead>
<tbody>
<tr>
<td>80kV, H(_2)</td>
<td>1.8E-22</td>
<td>46</td>
<td></td>
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<tr>
<td>80kV, He</td>
<td>9.7E-23</td>
<td>85</td>
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<tr>
<td>80kV, N(_2)</td>
<td>8.9E-22</td>
<td>9</td>
<td></td>
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<tr>
<td>80kV, O(_2)</td>
<td>9.1E-22</td>
<td>9</td>
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<tr>
<td>80kV, Ar</td>
<td>1.3E-21</td>
<td>7</td>
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<tr>
<td>200kV, N(_2)</td>
<td>4.1E-22</td>
<td>20</td>
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</tr>
<tr>
<td>200kV, O(_2)</td>
<td>4.1E-22</td>
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<tr>
<td>200kV, Ar</td>
<td>6.0E-22</td>
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<td>300kV, N(_2)</td>
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<tr>
<td>300kV, O(_2)</td>
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<tr>
<td>300kV, Ar</td>
<td>4.5E-22</td>
<td>19</td>
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</tr>
</tbody>
</table>
Contrast and Loss of intensity (Bright field imaging)

- How does the contrast of BF images change with gas pressure?
- 2.7mrad objective aperture (semiangle)
- Illumination conditions kept constant
Contrast and Loss of intensity (Bright field imaging)

- How does the contrast of BF images change with gas pressure?
- 2.7mrad objective aperture (semiangle)
- Illumination conditions kept constant

![Graph showing relative intensity vs. position with different gas pressures: Vacuum, 460Pa Ar, 980Pa Ar, 1240Pa Ar. The graph displays a decrease in relative intensity with increasing gas pressure.]
Contrast and Loss of intensity (Bright field imaging)

- Carbon Film
- Compared to $N_2$ gas
- 1000 Pa $N_2$ between pole pieces corresponds to approx. 10nm thick solid

- Very little dependence on the objective aperture for the gas related intensity loss
- The ‘contrast’ from the gas scattering appears higher than for corresponding area density of solid
Geometry of scattering

- Scattering takes place over several millimeters.
- Back focal plane and image plane not well-defined for gas scattering.
Resolution and contrast in the presence of gas (Phase contrast)

- Effects of imaging in gas can be observed from the power spectrum of amorphous carbon film

![Image of carbon film with resolution scale and power spectrum graph]
CTF in the Presence of Ar (300kV)

- In high vacuum (red), the power spectrum is almost identical to that calculated from ctfExplorer (purple).
- At low pressures, the effect is not observable (green).
- With increasing pressure, the damping becomes increasingly visible (blue and cyan).
- With lighter gas molecules, this effect is significantly lower.
- An image was acquired in vacuum after the series (red) to ensure that the aC was not significantly damaged.
Fitting of Damping of FFTs in Ar (300kV)

- The step height in the power spectrum is plotted as a function of k.
- Each plot is fitted to an exponential decay.
- At increased pressure, the step height decreases considerably faster.
Gas composition and pressure by EELS

- Pressure (Low-loss EELS)
- Gas composition (Core-loss EELS)
- CO – EELS acquired in image mode
- IMFP is collection angle dependent

900Pa CO (300kV)
Gas composition and pressure by EELS

- CO – EELS acquired in image mode
- The collection angle is measured in the eucentric height

![Graph showing C K-edge and O K-edge](image1.png)

![Graph showing C/O quantification vs. Collection angle (mrad)](image2.png)

Legend:
- Diffraction mode (Obj. lens on)
- Image mode (Obj. lens on)
- Diffraction mode (Obj. lens off - Lorentz)
Apparent / mean collection angle (300kV)

- The measured collection angle makes little sense as the scattering occurs all over the pressurized volume.

- The atomic ratio between carbon and oxygen calculated from the acquired spectra fits the theoretical value for small (~1 mrad) collection angles.

- Consistent with the small ‘scattered contribution’ of gas to the image intensity – ‘high contrast of gas’.
Angle resolved EELS

- Angle resolved EELS are acquired in Lorentz mode (objective lens off) to simplify scattering geometry

Broadening of scattering is usually less than 5%
Spectrum imaging (300kV) - Argon

- 1100Pa of Argon – no specimen
- Spectrum imaging with 0.3eV energy-selecting slit width
- Rotationally averaged
Beam Effects

• Electrons can ionize gas molecules making them more reactive
• Surfaces can be etched by reactive gas atoms, ions and molecules
• Local heating in the electron beam
• Knock-on damage altering atomic structure
• Sample ionization
• Sample charging and de-charging
  – Removal of charge from sample as in ESEM
Is aberration correction needed / useful in Environmental TEM?

• Yes, as interface regions (including surface regions) are not disturbed by delocalisation

• Au on graphene, $P_{H_2} = 430$Pa, RT

• Dynamics at interface / surface
Outlook and Challenges (Wish list)

• More to be done to understand the gas-electron interaction in the imaging process
• Detector efficiency
• Sample heating holders
  – Drift-free environment
  – Investigations while ON the heating ramp
  – Interference with electron beam
• Sealing technology
• Complementary *in situ* techniques
  – Light (Visible, IR, UV)
  – XRD (Transfer system)
• Sample heating and local temperature
  – The local temperature is a multi-parameter problem involving multiple sources and sinks