In situ and operando hard X-ray tomography from micro- to nanoscale: opportunities and applications in catalysis and materials science

Thomas Sheppard - X-ray Microscopy Group
The XRM Group at KIT

- Located in Karlsruhe – the (2nd or maybe 3rd) sunniest city in Germany!

Expertise in the XRM group:
- Hard X-ray microscopy and tomography
- Design of in situ cells
- Experiments under in situ / operando conditions
- Image processing and chemical understanding
- Mainly a heterogeneous catalysis group

We are not a high pressure group – but there are overlaps between HP research and XRM/tomography applied to catalysis!
Contents

- Introduction – hard X-ray microscopy and tomography
- Case studies - catalysis and materials science
- Design & Development - *in situ* cells and sample environments
- Perspective – tomography in high pressure research
- Outlook - potential of the EBS upgrade

--- Question time! ---
Introduction to hard X-ray microscopy

- XRM – collecting spatially-resolved imaging data from a sample
- Not a single instrument – but need source, optics, sample environment, detector

Excellent review article!
XRM is not one technique/instrument – but an ‘umbrella’
Provides data rich in information

Key point: almost any X-ray method can be applied using XRM in 2D/3D

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Microscopy (2D) vs Tomography (3D)

- What is X-ray tomography?
  - Non-invasive 3D spatially-resolved imaging
  - A series of 2D projections (x,y) at different angles (θ)
  - Reconstructed to provide 3D spatial resolution

- How does it work?

  ![Diagram showing the process of tomography](image)

  - Translate sample (x)
  - Rotate sample (θ)
  - Repeat over 180°
  - Translate (z) + repeat

  - SLICE
  - STACK

- What is the potential in chemistry/materials research?
  - Non-invasive
  - Various contrast methods
  - Chemical information
  - ‘Realistic’ sample conditions

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In situ and operando hard X-ray tomography from micro- to nanoscale

ESRF – EBS Workshop Series
High Pressure Techniques
17-21st June, Grenoble, FR
How does tomography work?

- **Data collection**
  - Projections (1D line or 2D area) → sinograms (x, θ) 0-180° or 0-360°

- **Data reconstruction**
  - Many tools/algorithms available – FBP, MLEM, (S)ART, tomopy, tomoJ, Astra

- **Data analysis**
  - Sample dependent – what do you want to learn?

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What information can we get?

- In general – 3 types of studies appear in literature:

  **Spatial resolution**

    - Focus – high resolution imaging
      - e.g. Porosity, structural components
      - Methods - ptychography, STXM

  ![Image of spatial resolution]

  **Time resolution**

    - Focus – rapid imaging
      - e.g. Samples in motion, dynamic processes
      - Methods – full field microscopy, holography

  ![Image of time resolution]

  **Chemical resolution**

    - Focus – chemically meaningful data
      - e.g. Crystalline phases, fluorescent species
      - Spectromicroscopy, multimodal imaging

  ![Image of chemical resolution]
Very short introduction to catalysis research

- Catalysts improve **efficiency, selectivity & productivity** of chemical processes
- **>90% industrial processes** and **>60% chemical products** involve a catalyst

**Size / Length Scale**

**Model Catalysts**
- e.g. clusters, DFT models

**Structured Catalysts**
- e.g. powders, particles on support

**‘Real’ Catalysts**
- e.g. pellets, monoliths

**Complexity**

- Co-silica core@shells
- Pd/Zn surface model
- Pd/Ga nanoparticles
- CuZnAl₂O₃ powder
- Mesoporous SiO₂ spheres
- Automotive catalytic converter

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In situ and operando hard X-ray tomography from micro- to nanoscale
Why in situ / operando?

- Two examples of ‘post mortem’ analysis (before/after reaction)
- We see **what** happens – e.g. change in porosity, or attenuation/composition

![Schematic Diagram]

- But catalysts and functional materials are dynamic
- **In situ/operando** tells us **why, how, when, how fast, if**, etc...

**Structure-activity relationships**

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![Schematic Diagram]

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**In situ and operando hard X-ray tomography from micro- to nanoscale**
Case Study – Energy-Dispersive XAS Tomography

- Customised setup at beamline ID24 - ESRF
  - aRCTIC – rotating capillary for tomographic in situ catalysis


- Gas flow / temperature in closed environment
- Free rotation allows for tomography
- ED-XAS uses polychromatic beam
- 1 XANES spectrum in a single shot
- Time resolution on order of ms
Sample of Cu-chabazite exhaust gas monolith catalyst

Tested for NO\textsubscript{x} reduction: \(4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}\)

- One tomographic slice acquired per energy
- Each pixel contains complete XANES
- Oxidation state changes depending on position
- Apparent gradient observed in catalyst bed
Case Study – XAS/XRF/XRD Tomography

Setup at beamline I18 – Diamond Light Source

- Sample: CuZn/Al₂O₃ methanol synthesis catalyst

- Bifunctional core@shell catalyst
  - Core: Methanol catalyst
    - CuO/ZnO/Al₂O₃
  - Shell: Solid acid catalyst
    - MFI-type zeolite ZSM-5

- Reaction:
  1. CO + 2H₂ ⇌ CH₃OH
  2. 2CH₃OH ⇌ CH₃OCH₃ + H₂O

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Simultaneous acquisition

- XRD: CMOS detector
- XRF: Vortex ME-4 SDD
- STXM: Ion chamber

Setup similar to aRCTIC

- Conventional XAS much slower
- But can acquire XRF/XRD at the same time
Multimodal tomography (XAS/XRF/XRD) is also possible *in situ*

- Complementary techniques can reveal useful info on the sample

<table>
<thead>
<tr>
<th>Region of Interest</th>
<th>XRF-CT</th>
<th>XRD-CT</th>
<th>STXM-CT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu Kα (8 keV)</td>
<td>Cux, Cu+, Cu0, Zn2+, Zn0, ZSM-5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn Kβ (9.5 keV)</td>
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<table>
<thead>
<tr>
<th>Observable</th>
<th>In situ and operando hard X-ray tomography from micro- to nanoscale</th>
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</thead>
</table>
| Cu, Zn in core    | Crystalline phases
| Elemental distribution | Zeolite shell |
| Relative beam     | --- |
| attenuation, absorption |

| Not Observable    | Zeolite shell (Si/Al)
|-------------------| Metal oxidation state
| Amorphous phases  | --- |
Case Study – Ptychographic Tomography

- Sample: monolithic nanoporous gold
- Hierarchical pores from <1nm to ~100’s nm
- High surface area – ‘pure’ catalyst active sites

- Ptychography / scanning coherent diffraction imaging
- Extremely high resolution imaging technique!
- Firstly ex situ results – from SLS cSAXS beamline

Nanoporous gold and subvolume imaged with ~16 nm spatial resolution

Extending ptychography to \textit{in situ} techniques

Nanoscale imaging under temperature and gas flow

Customised setup installed at DESY P06

- Sample – CoMn$_2$O$_4$ ‘hollowsphere‘ with alumina shell
- Multiple tomograms acquired from 20-720 °C
- However – limited viewing angle +/-35°
- Data reconstruction is challenging, still in progress
Design and development of in situ cells

- Several examples of *in situ* cells shown for different XRM techniques
  - ED-XAS, XRF/XRD, ptychography

- Lessons learned:
  - In situ studies are very informative – should be done where possible/needed
  - High spatial resolution, fast time resolution, chemical info – you can’t have all 3!
  - Tomography provides high quality info – which can’t be obtained in other ways
  - Correlative or multimodal techniques give complementary data on same sample

- There are parallels between cell design / measurement requirements for catalysis and high pressure research
Design and development of in situ cells

Thought process

- Imagine the “perfect” cell
- Start to compromise
- Design prototype, test, validate

Tomography under extreme conditions
Spatial resolution <10 nm
Free rotation 0-180°
Low ‘Z’ windows, perfect X-ray transmission
Can do XAS, XRD, XRF, and more
Makes coffee, free WiFi...

Define requirements:
Which materials will be studied?
Which spatial resolution do we need?
Do we need free rotation 0-180°?
Which detection modes are needed?
...etc...

e.g. Start with a standard Diamond Anvil Cell

Realistic approach

Idealistic approach
Perspective – tomography in HP research

- Consider the DAC, how to expand tomography applications?
- Direct tomography has already been demonstrated

Essential components of the cell
- Pressure generator, anvils, gasket, pressure medium

Other important considerations
- X-ray must pass through the gasket – with rotation in plane of the sample
- X-ray path length should be as short as possible – only measure the sample
- Rotation angle should be as big as possible (up to 180°) – better reconstruction
- Entire setup must be able translate/rotate with (sub)-µm precision

Carbon is low Z

Pressure generator, anvils, gasket, pressure medium

X-ray must pass through the gasket
X-ray path length should be as short as possible

gasket thickness/diameter, ambient air

Mount DAC in vacuum chamber

How thin do we need / can we go?

Also important to relax angular requirements / Crowther criterion

Minor challenges

Major challenges

Rotation in plane of the sample – up to 180°

Difficult because of screws/support frame for pressure system
How big an angle is feasible – how thin can the frame be?

Entire setup must translate/rotate with (sub)-µm precision

Maintaining lateral and centre of rotation position is critical
Mechanical vibrations must be minimised

Geometric limitations can be dealt with through reconstruction
- e.g. electron tomography
- e.g. deep learning algorithms

Macroporous zeolite imaged by ptychography and reconstructed tomo data.

Translational/rotational stability must be designed from the ground up
- Ultrastable base / platform
- Low vibration / zero motor recoil
- Sample / position tracking

Strongly depends on desired resolution

Beamline P06 - ‘PtyNAMi’
- Nanofocusing 30*30 nm²
- Ultrastable sample stage
- Inteferometric positioning

Schroer et al, SPIE 2017, 103890E
Outlook – the EBS upgrade

Why is the EBS so important for X-ray microscopy and tomography?

- Increased flux and brilliance.
  - Lower emissivity / smaller beams / easier focusing
  - Increased coherence (for certain applications)

3 out of 4 new EBS beamlines are designed for XRM applications:

- Hard X-ray diffraction microscope
- Coherent X-ray dynamics and imaging
- High throughput large-field phase contrast tomography

Outlook – the EBS upgrade

- More photons in = more photons out
  - Good for ‘photon hungry’ techniques
  - Allows for longer transmission path, relaxes *in situ* cell requirements
  - Also good for small / dilute samples such as in DAC

- Less divergent / more focused beam
  - Higher spatial resolution (scanning tomography techniques)

- Increased coherence
  - Excellent for ptychography, CDI, Bragg ptychography, etc.

Key point: improved experimental capabilities should be matched by available sample environments!

Further reading:
Outlook – the EBS upgrade

Spatial-resolution
- Ptychography
- STXM
- Resolution <10nm
- More coherence
- Smaller focus

Time-resolution
- High-throughput
- Dynamics

Chemical Imaging
- Combined exps.
- More photons + more detectors = more data

What are some of the challenges for XRM and tomography?

- H-U-G-E volumes of data - Petabytes/week just from new tomo beamline!
- Analysis software – user friendly data collection, data treatment
- Sample environments – pressure, temperature, in situ, operando
- Staff and students – phys/chem/bio/engineers/data scientists
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