Karlsruhe Institute of Technology

ESRF – EBS Workshop Series
High Pressure Techniques
17-21st June, Grenoble, FR

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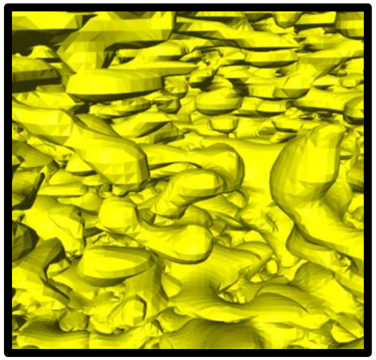
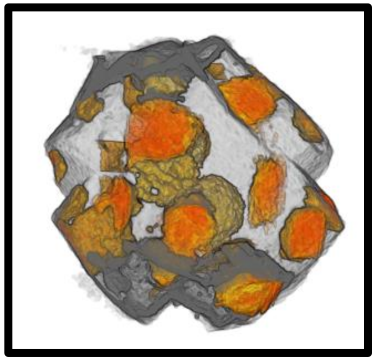
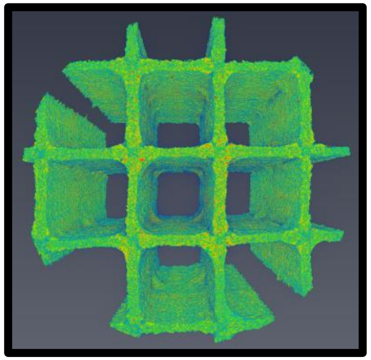
# *In situ* and *operando* hard X-ray tomography from micro- to nanoscale: opportunities and applications in catalysis and materials science


**Thomas Sheppard - X-ray Microscopy Group**

Institute of Catalysis Research and Technology
Institute for Chemical Technology and Polymer Chemistry

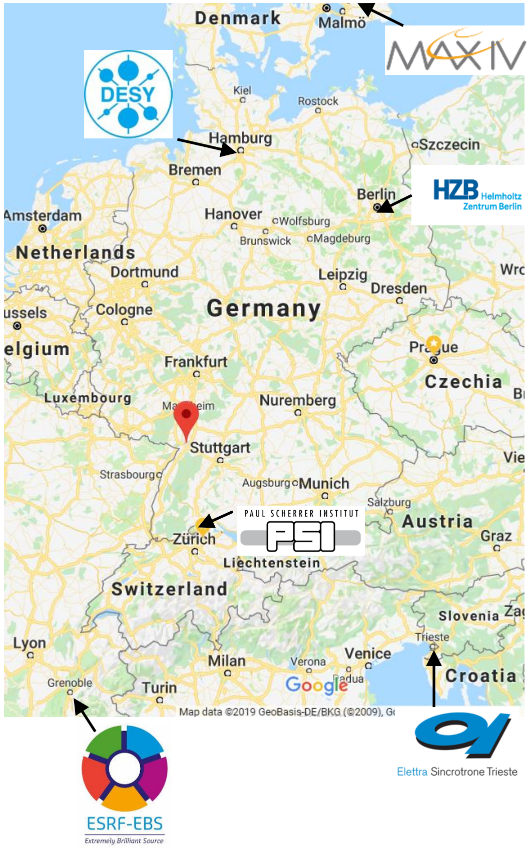







# The XRM Group at KIT

- 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!

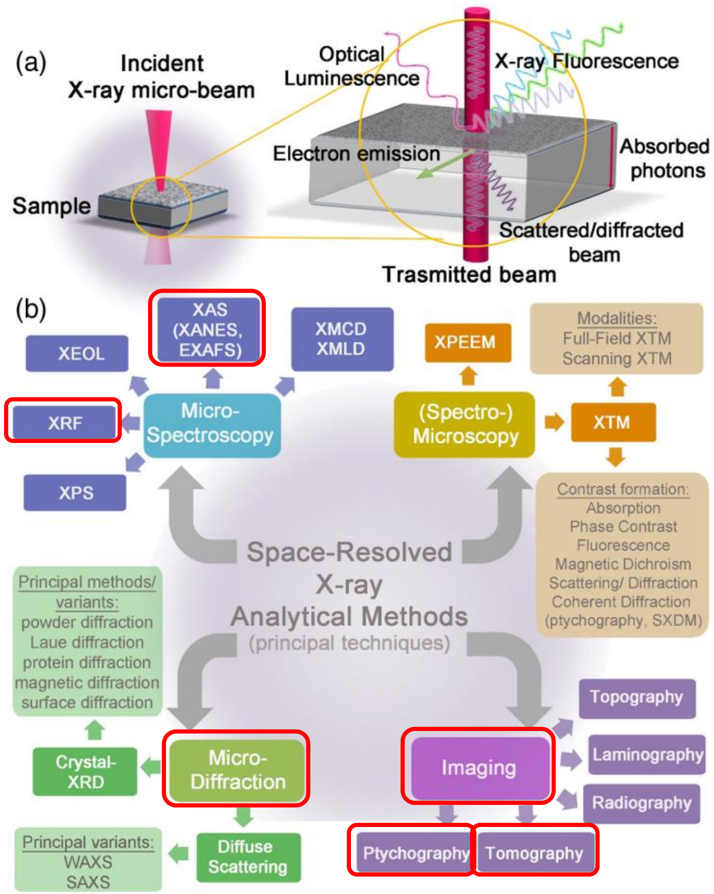
# Contents

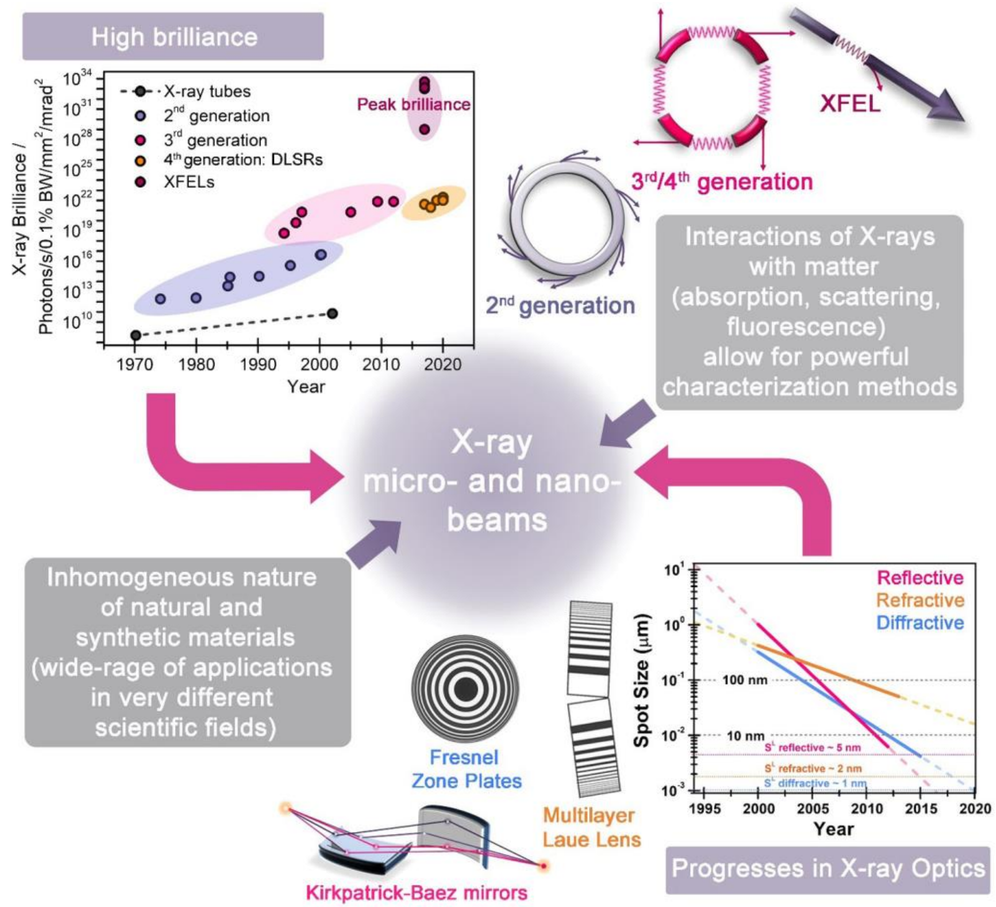


--- Question time! ---

# 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



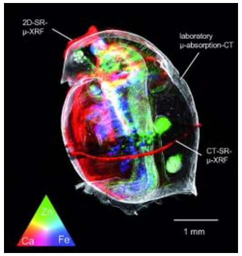




Mino, L., Borfecchia, E., Segura-Ruiz, J., Giannini, C., Martinez-Criado, G. and Lamberti, C., 2018. Reviews of Modern Physics, 90(2), p.025007 ← Excellent review article!

- XRM is not one technique/instrument – but an ‘umbrella‘
- Provides data rich in information

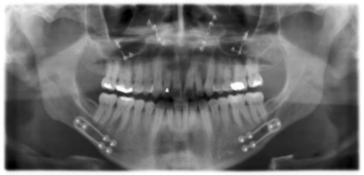
XRM

fluorescence



De Samber et al., J Anal At Spectrom, 23, 829-839 (2008)

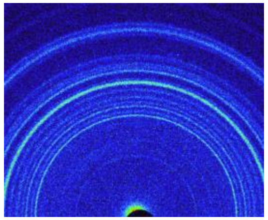
absorption



XAS / XANES

Identification / concentration of metals
Oxidation state / coordination sphere

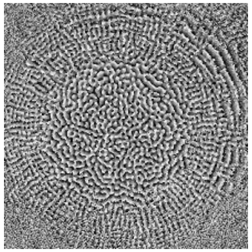
diffraction



XRD

Crystalline structure / phase info

phase



Ptychography / CDI

Electron density maps
Amorphous structure
Low ‘Z‘ materials

- Key point: almost any X-ray method can be applied using XRM in 2D/3D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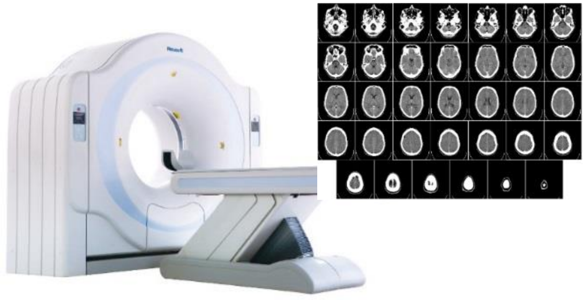
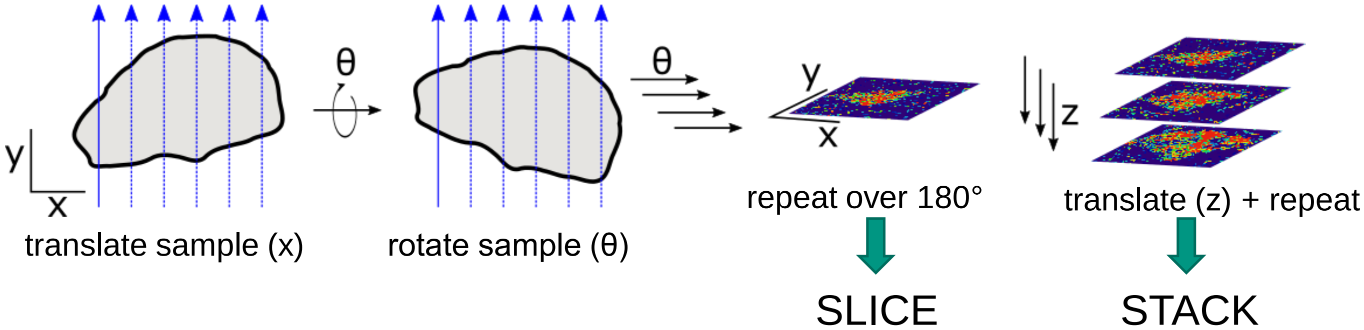
# Microscopy (2D) vs Tomography (3D)

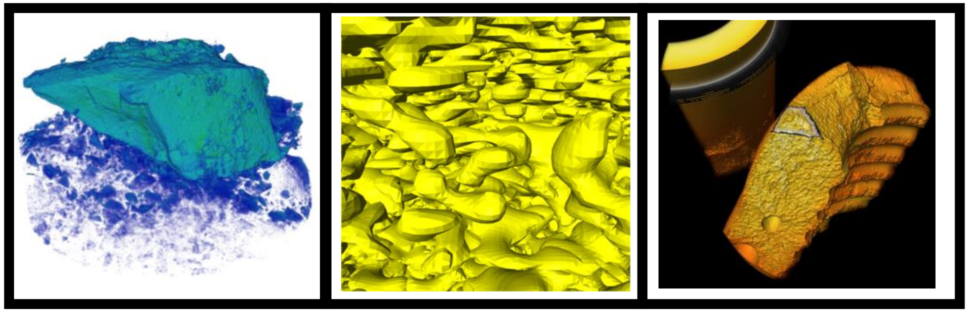
- What is X-ray tomography?
  - Non-invasive 3D spatially-resolved imaging
  - A series of 2D projections (x,y) at different angles (θ)
  - Reconstructed to provide 3D spatial resolution



- How does it work?




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

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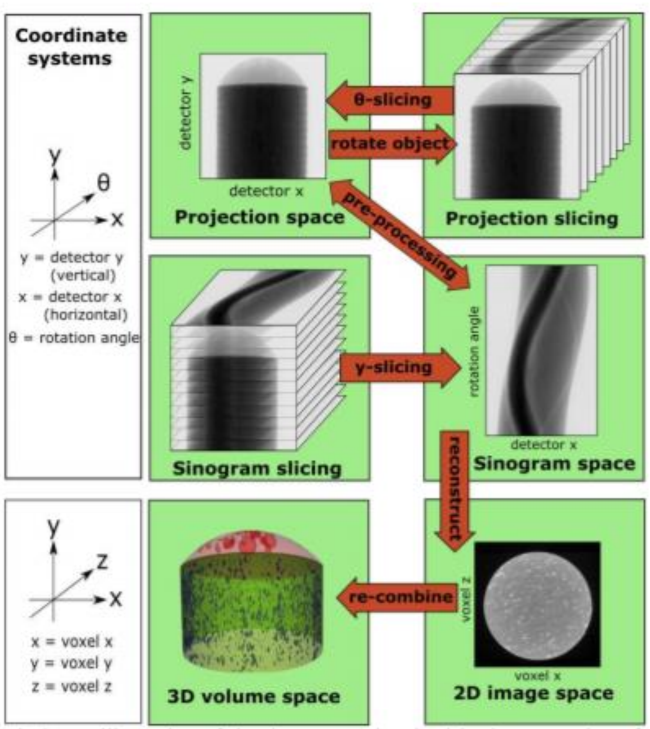
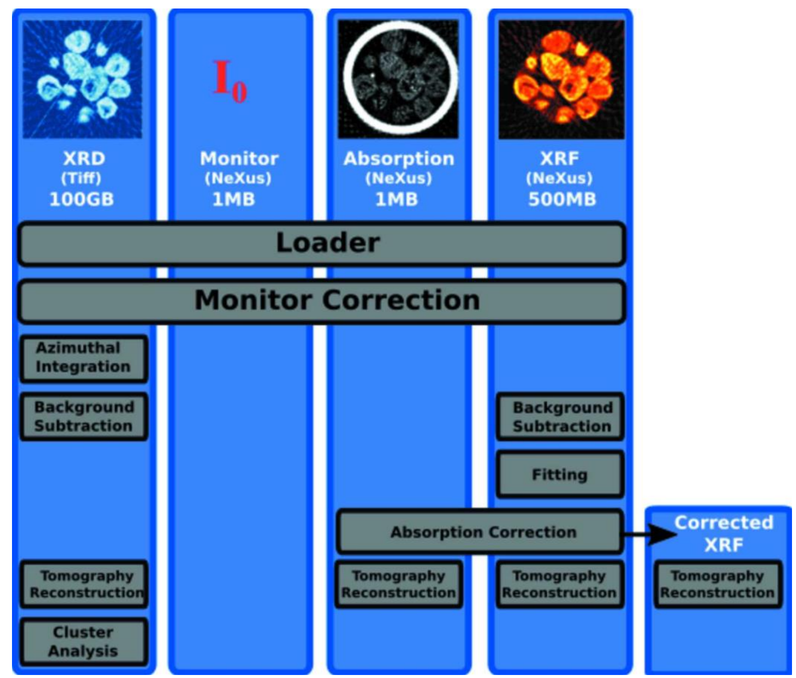
# How does tomography work?

- 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?




Wadeson, N. and Basham, M., 2016. *arXiv:1610.08015*.

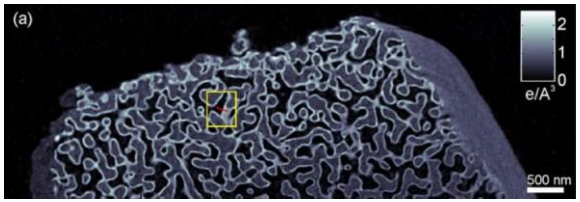



Parsons, A.D., Price, S.W., Wadeson, N., Basham, M., Beale, A.M., Ashton, A.W., Mosselmans, J.F.W. and Quinn, P.D., 2017. *Journal of synchrotron radiation*, *24*(1), pp.248-256.

# What information can we get?

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

**Spatial resolution**




Holler M. Et al, 2014. *Sci. Rep.,4, 3857*.

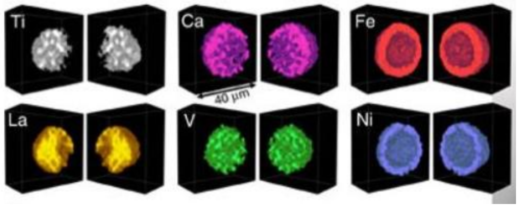
- Focus – high resolution imaging
  - e.g. Porosity, structural components
  - Methods - ptychography, STXM

**Time resolution**


Mokso R. et al, 2015. *Sci. Rep.,5, 8727*.

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

**Chemical resolution**




Liu Y. et al, 2016. *Nat. Commun., 7, 12634*.

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



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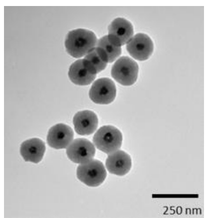
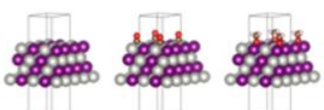
# Very short introduction to catalysis research

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

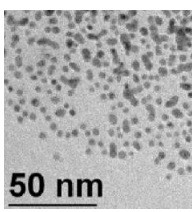
## Size / Length Scale




Co-silica core@shells

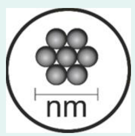


Pd/Zn surface model




Pd/Ga nanoparticles

**Model Catalysts**

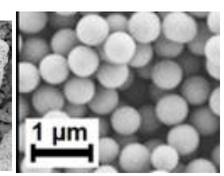



***e.g. clusters, DFT models***

**Structured Catalysts**

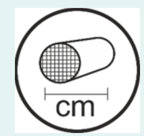

***e.g. powders, particles on support***

$CuZnAl_2O_3$ powder



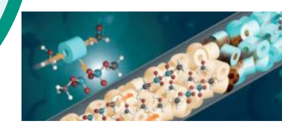

Mesoporous $SiO_2$ spheres

**'Real' Catalysts**




***e.g. pellets, monoliths***

Anacortes Refinery, USA



HDS catalyst (Jensen et al, *Chem. Eng. J.* 2019, 361, p. 1285)

Automotive catalytic converter

## Complexity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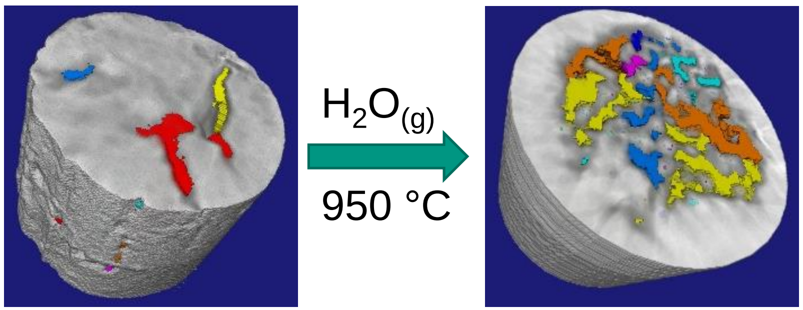
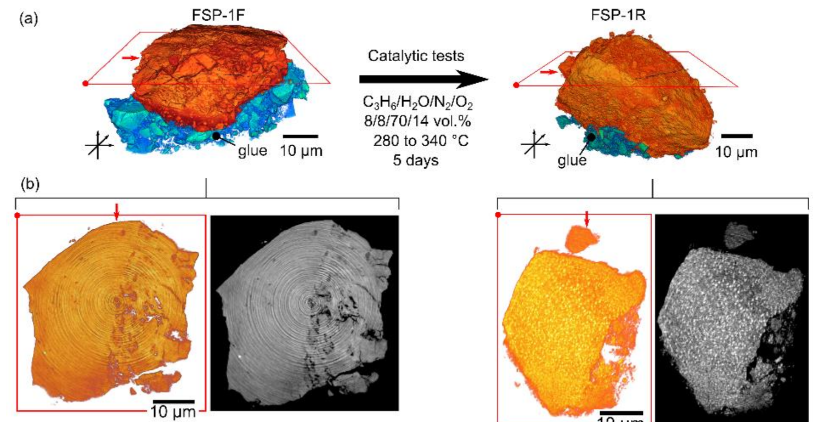
# Why in situ / operando?

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

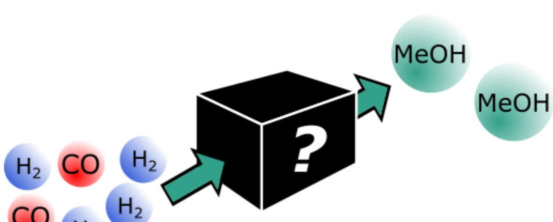



Hydrothermal ageing of exhaust gas catalyst



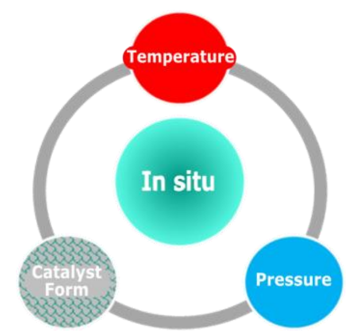

Sprenger, P. et al, *Catalysts* 2018, 8, 356

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



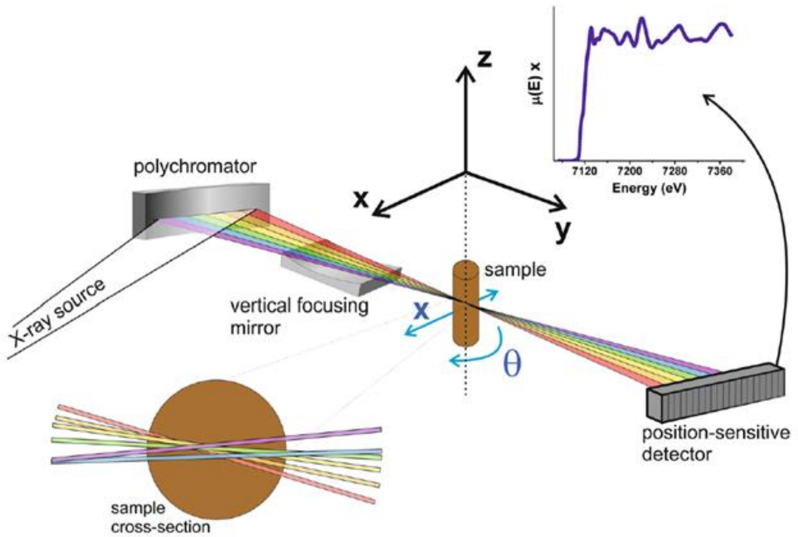

‘black box‘ caricature

**Structure-activity relationships**

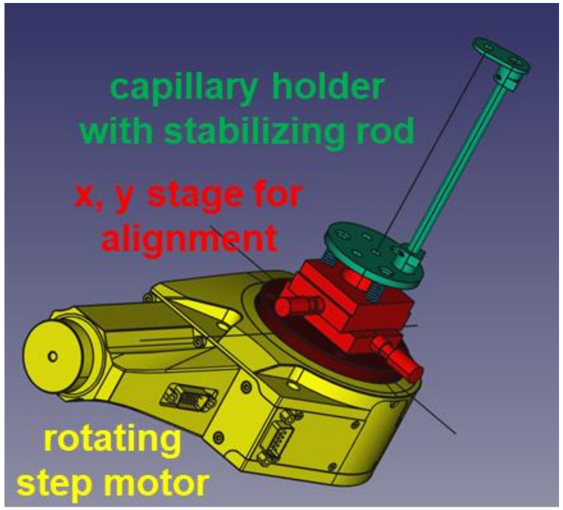


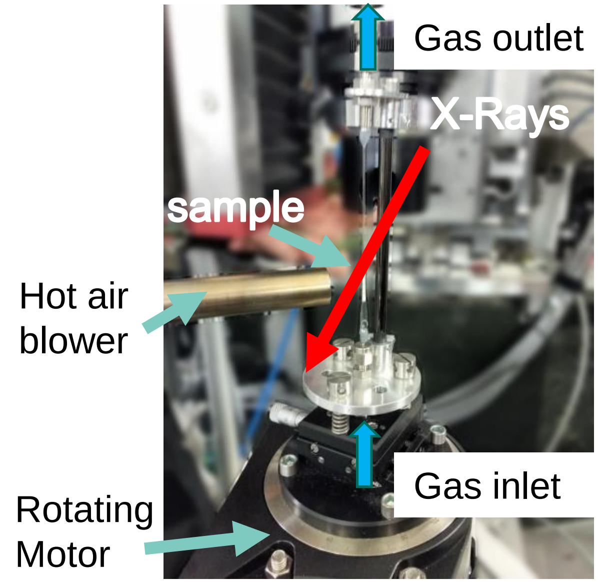
# Case Study – Energy-Dispersive XAS Tomography

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



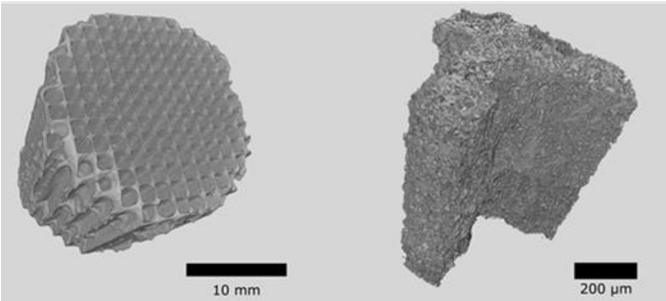

Sanchez, D. F., et al. (2017). Scientific Reports **7(1): 16453.**



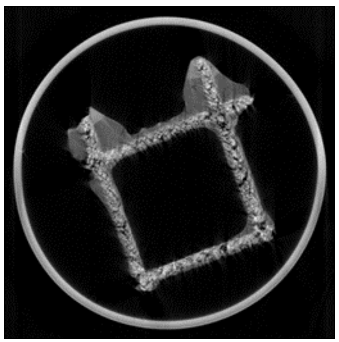




- Gas flow / temperature in closed environment
- Free rotation allows for tomography
- ED-XAS uses polychromatic beam
- 1 XANES spectrum in a single shot
- Time resolution on order of ms

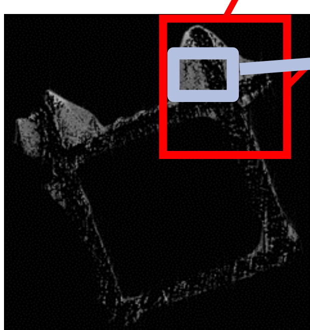
- Sample of Cu-chabazite exhaust gas monolith catalyst
- Tested for $NO_x$ reduction: $4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$



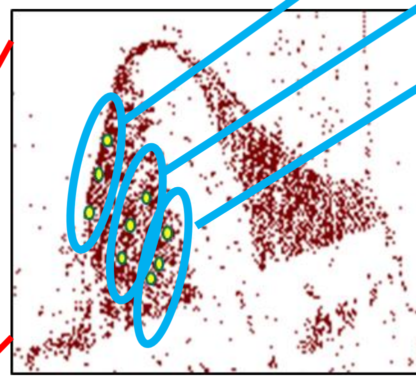

microtomo

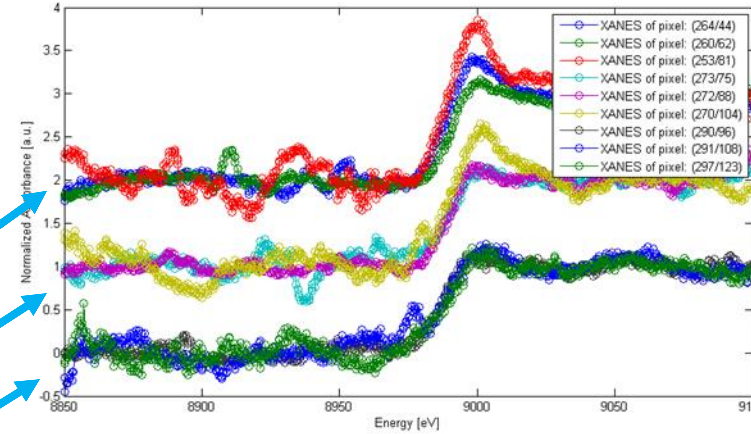


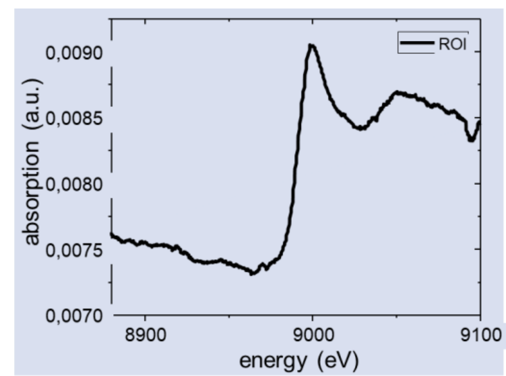
1-slice ED-XAS tomo



Difference map
(Cu K edge – pre-edge)






- One tomographic slice acquired per energy
- Each pixel contains complete XANES
- Oxidation state changes depending on position
- Apparent gradient observed in catalyst bed



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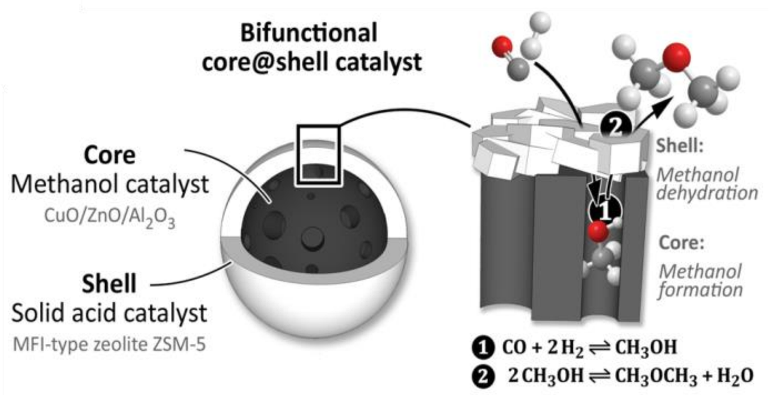
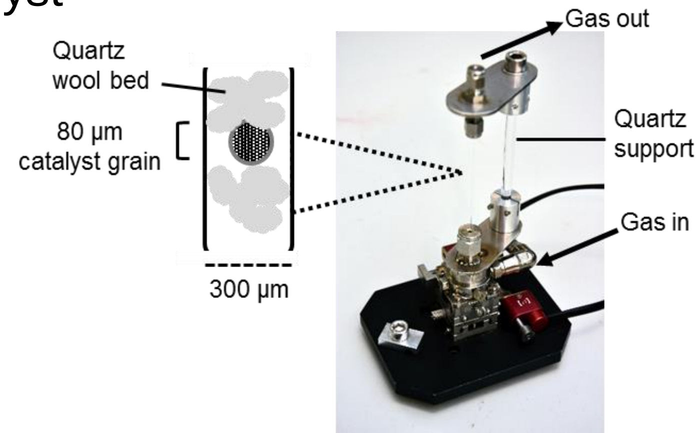
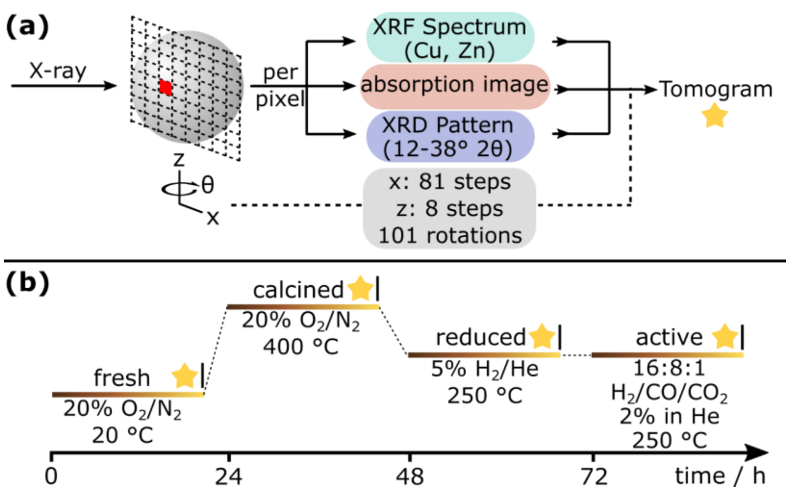
# Case Study – XAS/XRF/XRD Tomography

- Setup at beamline I18 – Diamond Light Source
  - Sample: $CuZn/Al_2O_3$ methanol synthesis catalyst



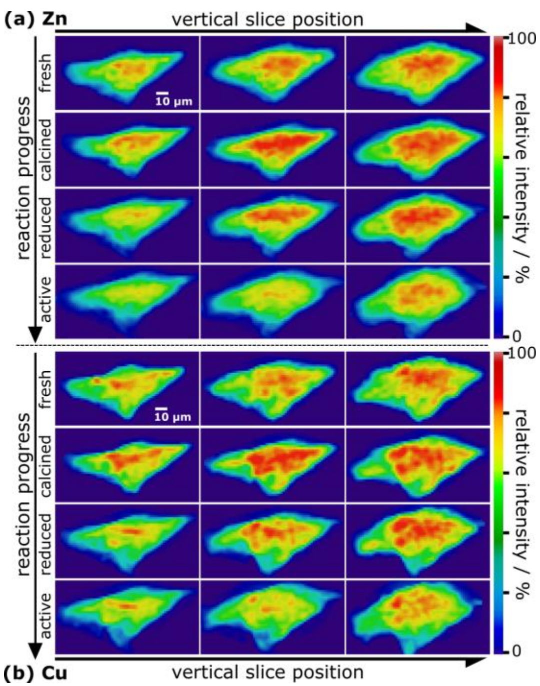



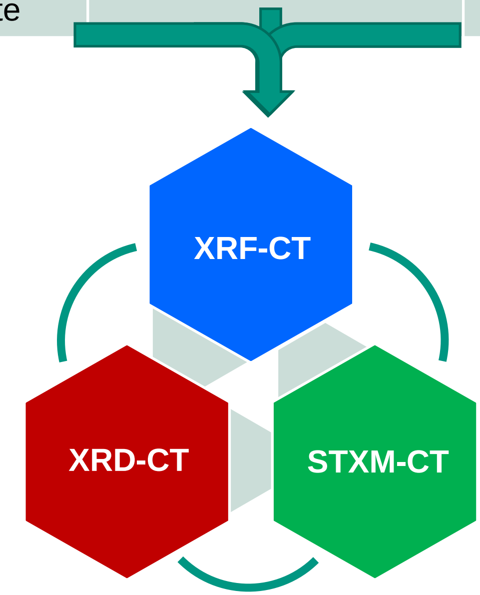

Simultaneous acquisition

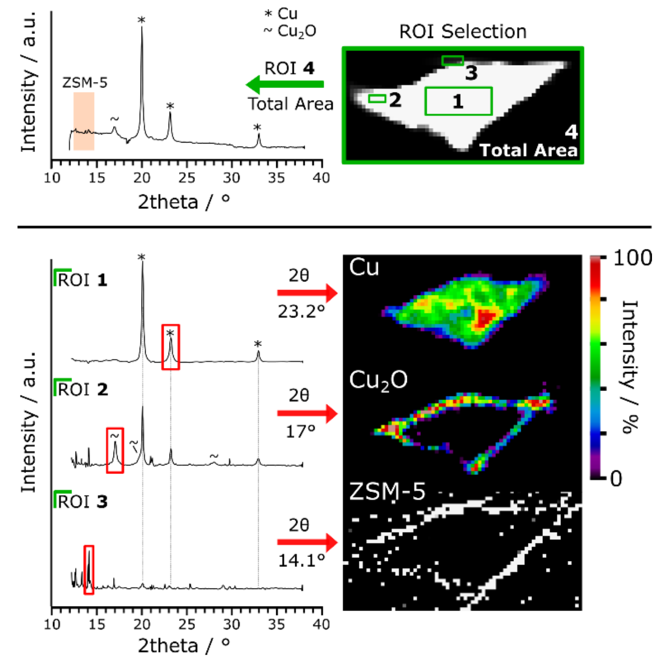
- XRD: CMOS detector
- XRF: Vortex ME-4 SDD
- STXM: Ion chamber

- Setup similar to aRCTIC
- Conventional XAS much slower
- But can acquire XRF/XRD at the same time

| | XRF-CT | XRD-CT | STXM-CT |
|---|---|---|---|
| **Region of Interest** | Cu $K_\alpha$ (8 keV)<br>Zn $K_\beta$ (9.5 keV) | $Cu^{2+}$, $Cu^{+}$, $Cu^{0}$, $Zn^{2+}$, $Zn^{0}$, ZSM-5 | --- |
| **Observable** | Cu, Zn in core<br>Elemental distribution | Crystalline phases<br>Zeolite shell | Relative beam attenuation, absorption |
| **Not Observable** | Zeolite shell (Si/Al)<br>Metal oxidation state | Amorphous phases | --- |



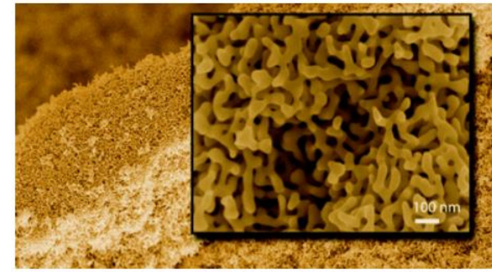




- Multimodal tomography (XAS/XRF/XRD) is also possible *in situ*
- Complementary techniques can reveal useful info on the sample

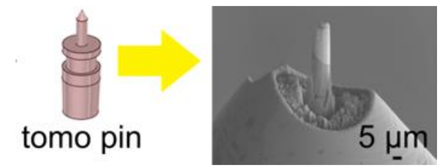
# Case Study – Ptychographic Tomography

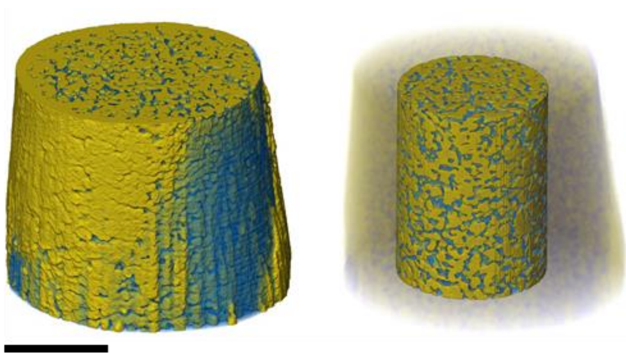
- Sample: monolithic nanoporous gold
- Hierchical pores from <1nm to ~100‘s nm
- High surface area – ‘pure‘ catalyst active sites




Wittstock *et al.*, *Phys. Chem. Chem. Phys.* 2010, 12,12919.

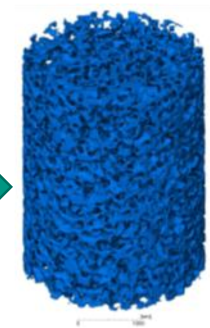
- Ptychography / scanning coherent diffraction imaging
- Extremely high resolution imaging technique!
- Firstly ex situ results – from SLS cSAXS beamline



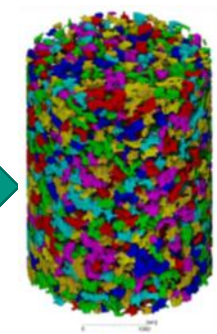




Nanoporous gold and subvolume imaged with ~16 nm spatial resolution

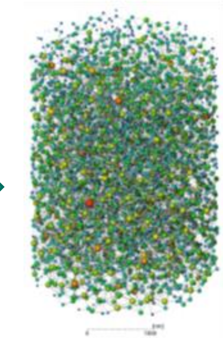
Segment pores

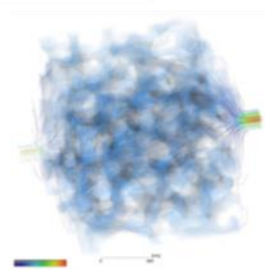


Label pores



Calculate paths





Compute fluid flow, thermal conductivity, other physical properties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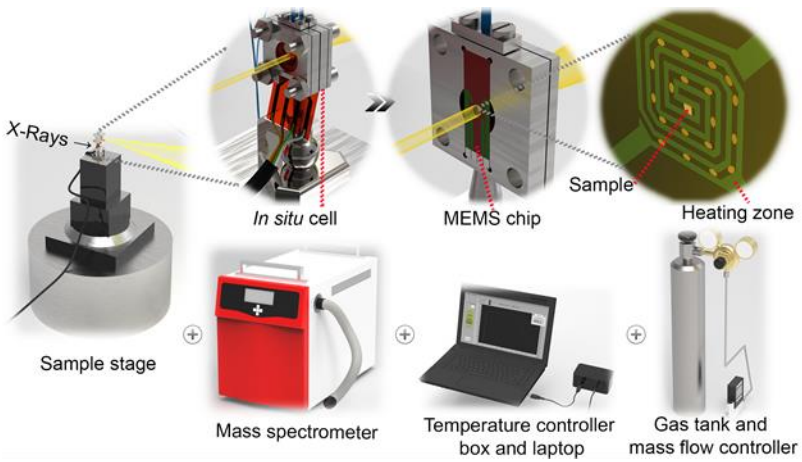
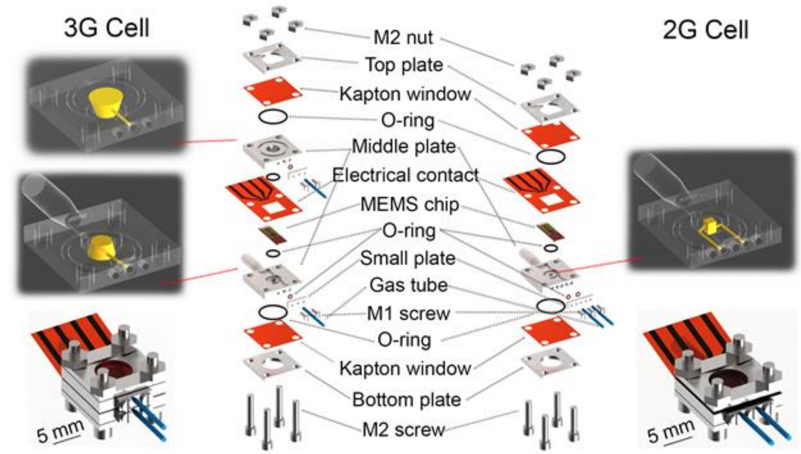
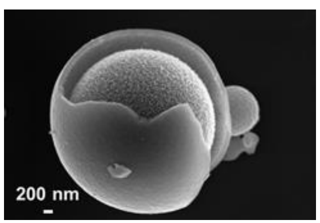
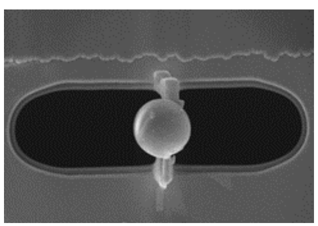
- Extending ptychography to *in situ* techniques
- Nanoscale imaging under temperature and gas flow
- Customised setup installed at DESY P06



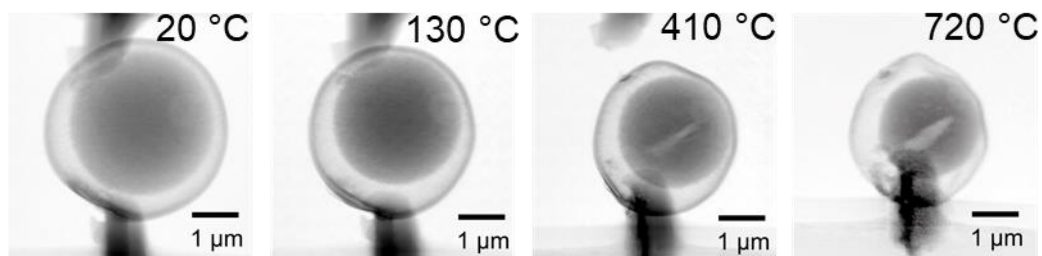



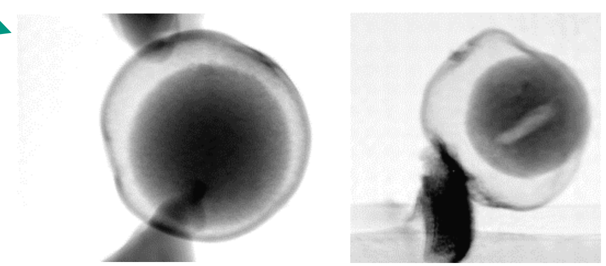




SEM image of $CoMn_2O_4$ hollowsphere



FIB preparation on MEMS chip

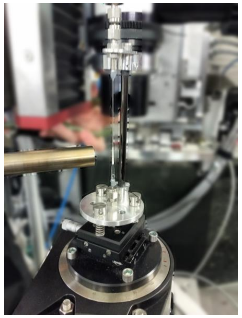


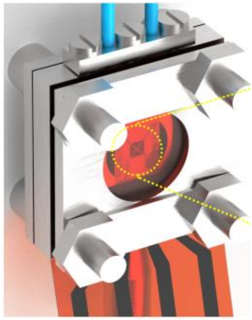



- Sample – $CoMn_2O_4$ ‘hollowsphere‘ with alumina shell
- Multiple tomograms acquired from 20-720 °C
- However – limited viewing angle +/-35°
- Data reconstruction is challenging, still in progress

# Design and development of in situ cells

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



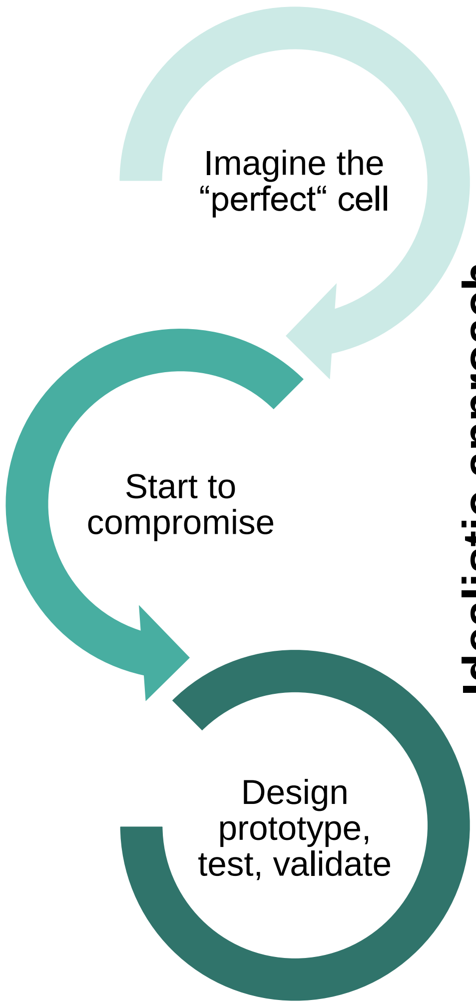


- Lessons learned:
  - In situ studies are very informative – should be done where possible/needed
  - High spatial resolution, fast time resolution, chemical info – you can't have all 3!
  - Tomography provides high quality info – which can't be obtained in other ways
  - Correlative or multimodal techniques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




Idealistic approach

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...

**Realistic approach**

e.g. Start with a standard Diamond Anvil Cell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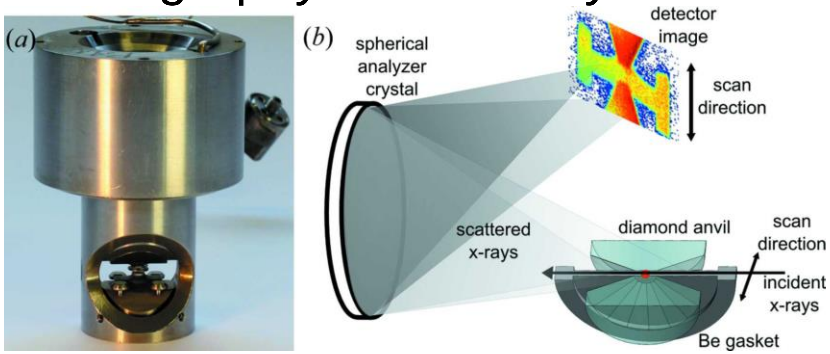
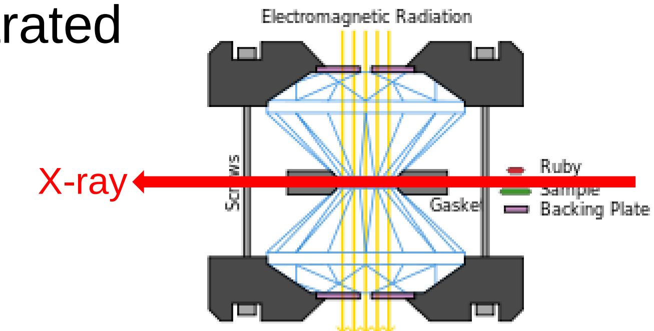
# Perspective – tomography in HP research

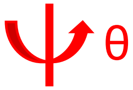
- Consider the DAC, how to expand tomography applications?
- Direct tomography has already been demonstrated




Sahle, C.J. et al. (2017). *J. Synchrotron Radiat.*, 24, 269.




DAC (Wikipedia)




- 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



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Carbon is low Z — Normally low Z

- Pressure generator, ~~anvils~~, gasket, ~~pressure medium~~

→ Al, Be, BN,...

- 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

$$N_\theta \simeq \pi D / d$$

N = number of angles
D = object diameter
d = target resolution

## Minor challenges

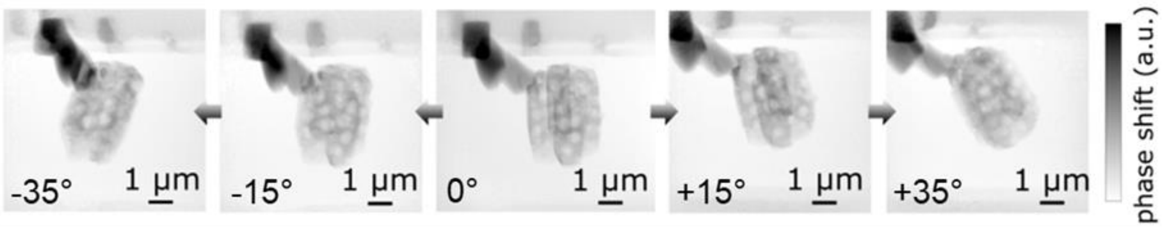
## Major challenges

- 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?

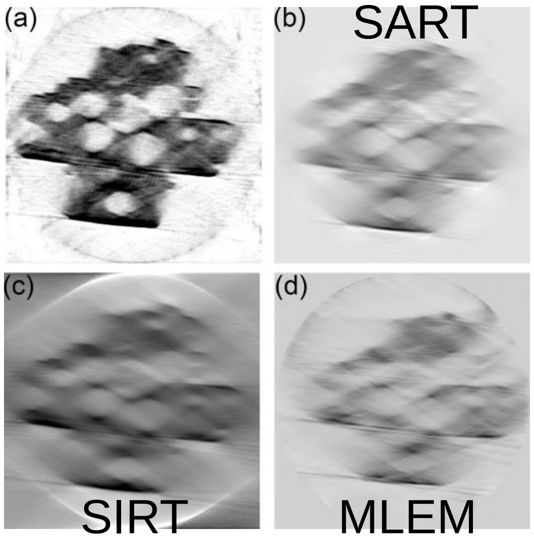
- Entire setup must translate/rotate with (sub)-µm precision
  - Maintaining lateral and centre of rotation position is critical
  - Mechanical vibrations must be minimised

W. Mao et al, *Engineering* (2019), doi - 10.1016/j.eng.2019.01.006

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



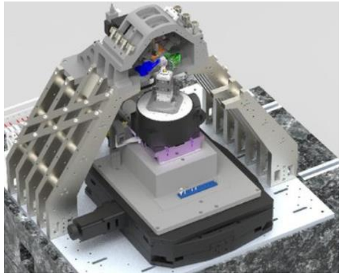

Macroporous zeolite imaged by ptychography and reconstructed tomo data.



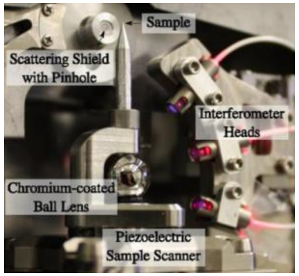

- Translational/rotational stability must be designed from the ground up
  - Ultrastable base / platform
  - Low vibration / zero motor recoil
  - Sample / position tracking
- Strongly depends on desired resolution

Beamline P06 - ‘PtyNAMi‘

- Nanofocusing 30*30 nm$^2$
- Ultrastable sample stage
- Inteferometric positioning



Schroer et al, *SPIE* 2017, 103890E



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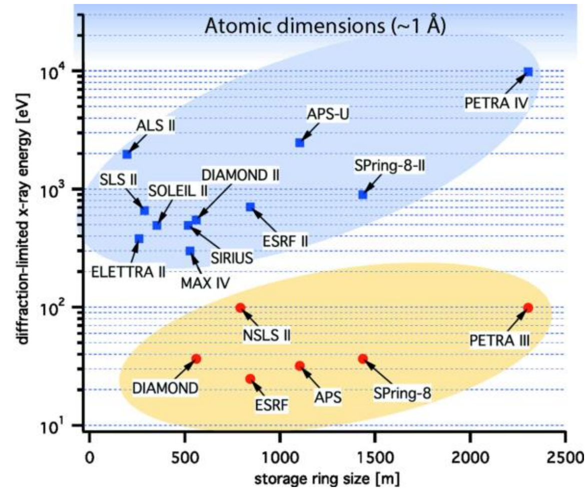
# Outlook – the EBS upgrade

Advanced Photon Source (APS) Annual Report, 2014




Schroer et al., *J. Synchotron. Rad.* 2018, 25, p.1277

## 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:

Liu et al, *Appl. Phys. Lett.* 104, 043108 (2014); https://doi.org/10.1063/1.4863229

Mao et al, *Engineering* 2019, https://doi.org/10.1016/j.eng.2019.01.006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# Outlook – the EBS upgrade

Karlsruhe Institute of Technology

**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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# Thank you for your attention!