Catalytic properties at the nanoscale probed by surface x-ray diffraction and coherent diffraction imaging

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Outline

Introduction

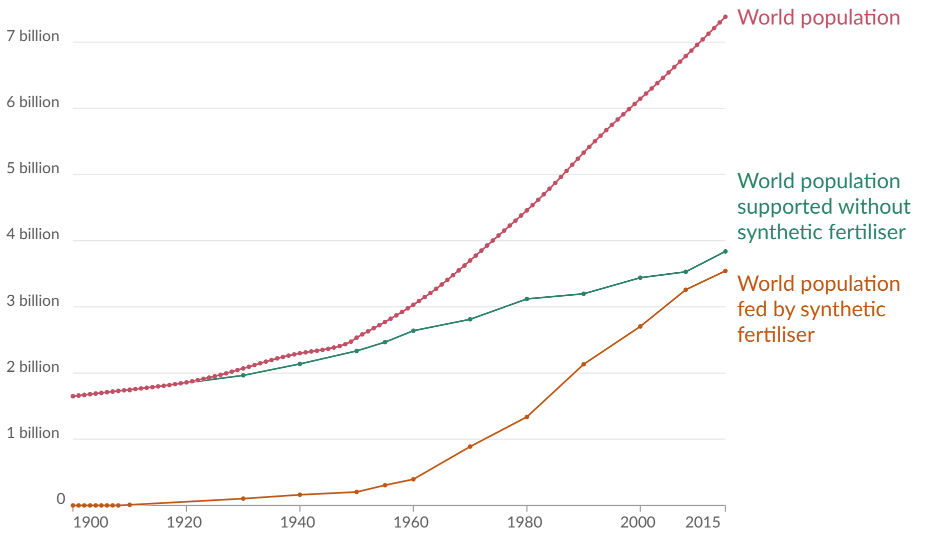
I. Probing the average structure with surface x-ray diffraction

II. Single particle structural study with Bragg coherent diffraction imaging

III. Pt single crystals during ammonia oxidation

Conclusions and Perspectives

World population with and without synthetic nitrogen fertilizers



Data source: Erisman et al. (2008); Smil (2002); Stewart (2005)

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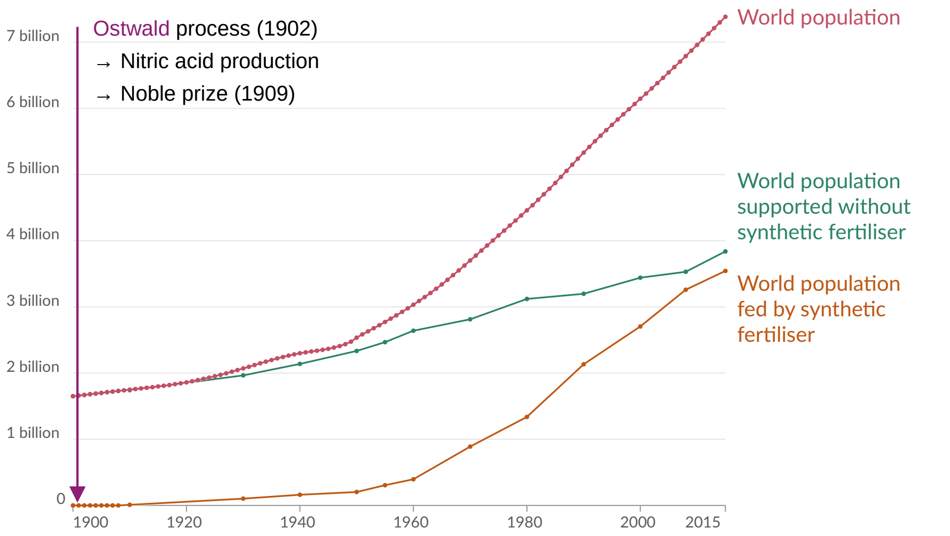

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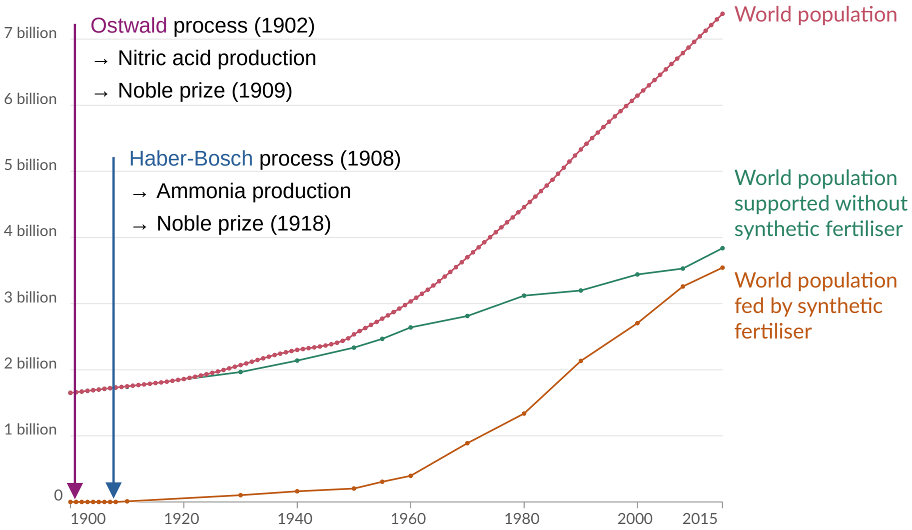

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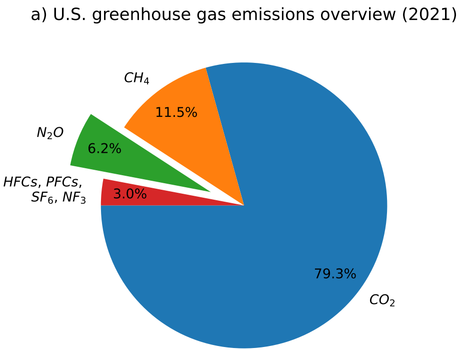
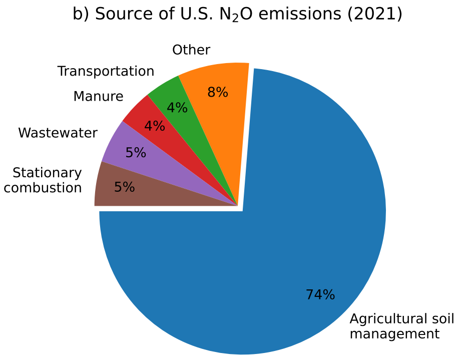
Environmental impact: N_2O





Adapted from Environmental Protection Agency (2023).

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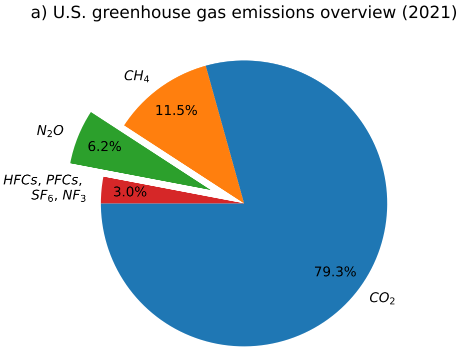

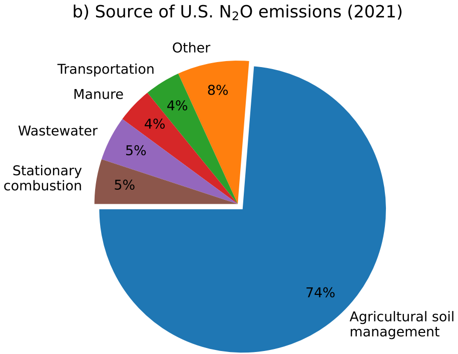

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- Nitrogen fertiliser use expected to keep increasing in the southern hemisphere.

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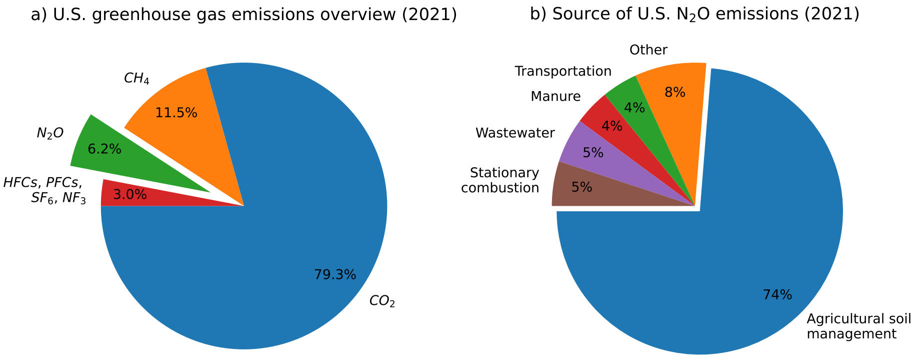

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- Nitrogen fertiliser use expected to keep increasing in the southern hemisphere.
- N_2O emissions come also directly from nitric acid manufacture.

Ostwald process and ammonia oxidation

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$$4\ NH_3 + 3\ O_2 \rightarrow 6\ H_2O\ + 2\ N_2$$
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1. Producing NO from NH_3 (ammonia oxidation).

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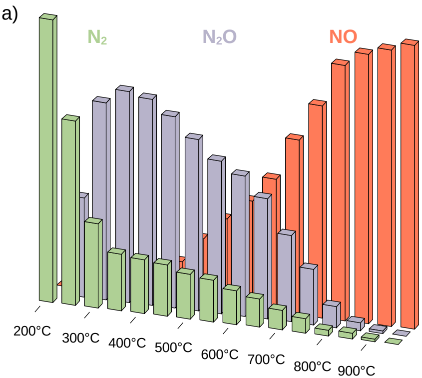
Selectivity → temperature, pressure, reactant ratio, type of catalyst.

Ostwald process: industrial conditions



Figures adapted from literature review[1].

NO selectivity increases with temperature,

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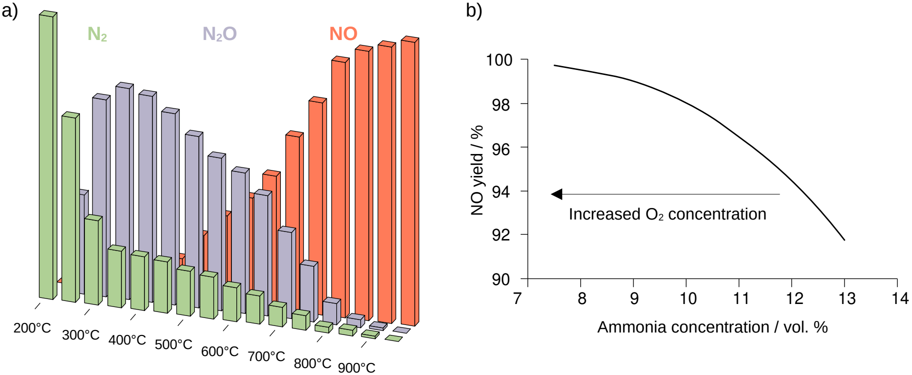

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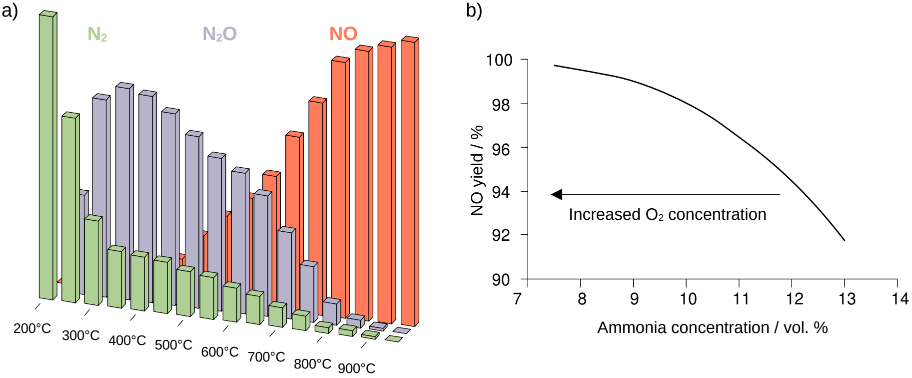

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NO selectivity increases with temperature, and O_2 / NH_3 partial pressure ratio.

→ navigate between conditions to understand the production of NO or N_2.

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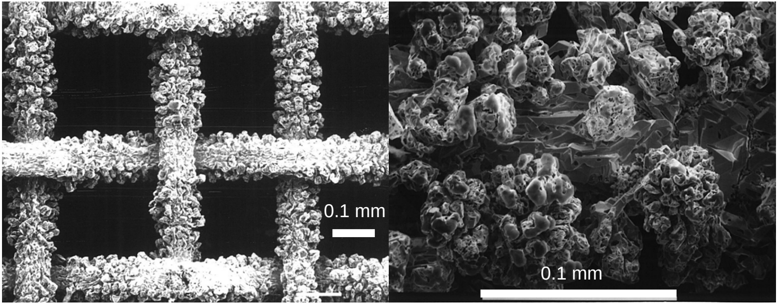

SEM images of Pt-Rh reconstructed gauzes with *cauliflower* patterns after use in industry[2].

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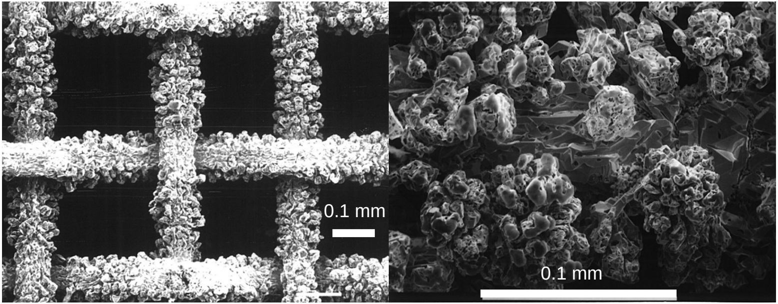

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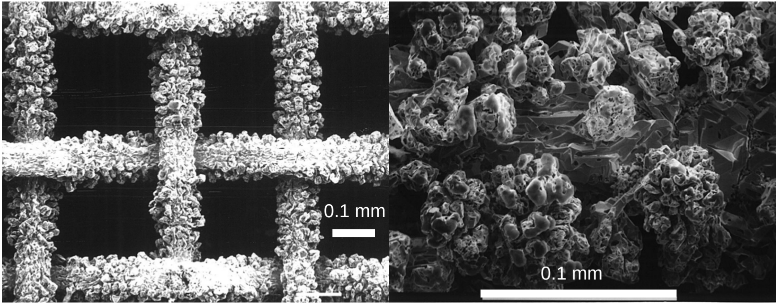

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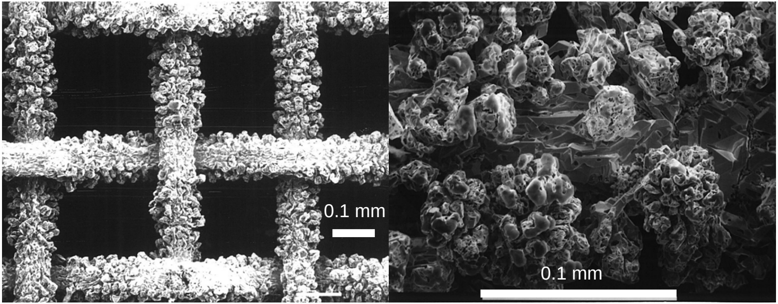

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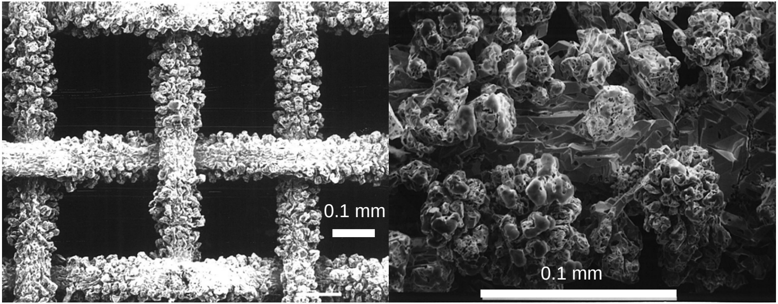

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- Final deactivation process linked to oxides reported.
- Rhodium increases NO selectivity, and limits the loss of platinum.

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The material and pressure gap

> "A long standing conundrum in the catalysis community emerged at the interface between surface science and heterogeneous catalysis, better known as the pressure and material gap."
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> *Nature Catalysis editorial, 2018.*

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	Pressure	Material	Temperature
Industrial conditions	1 bar to 12 bar	Knitted Pt-Rh gauzes (wires, diameter ≈80 μm)	750 °C to 900 °C

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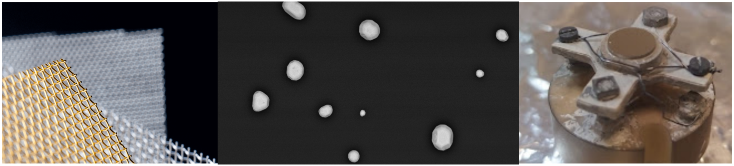
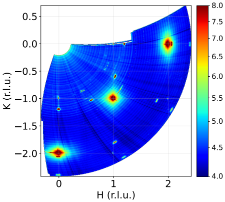
∅ ≈ 80 μm | ∅ ≈ 1 μm | ∅ ≈ 1 cm



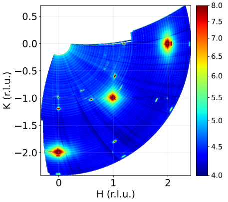
Near-ambient pressure synchrotron techniques

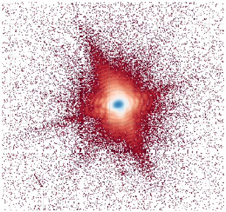
Technique	Surface X-ray Diffraction (SXRD)		
Sample	Pt(111) and Pt(100) single crystals and Pt particles		
Information	Surface structure, roughness, relaxation & crystallographic phases		
Beamline	SixS (SOLEIL)		



Near-ambient pressure synchrotron techniques

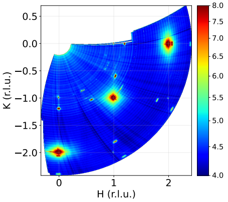
Technique	Surface X-ray Diffraction (SXRD)	Bragg Coherent Diffraction Imaging (BCDI)	
Sample	Pt(111) and Pt(100) single crystals and Pt particles	Isolated Pt particles	
Information	Surface structure, roughness, relaxation & crystallographic phases	Shape, 3D displacement and strain arrays of unique object	
Beamline	SixS (SOLEIL)	SixS (SOLEIL)	

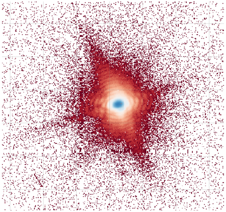


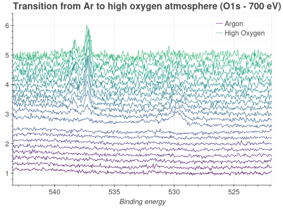


Near-ambient pressure synchrotron techniques

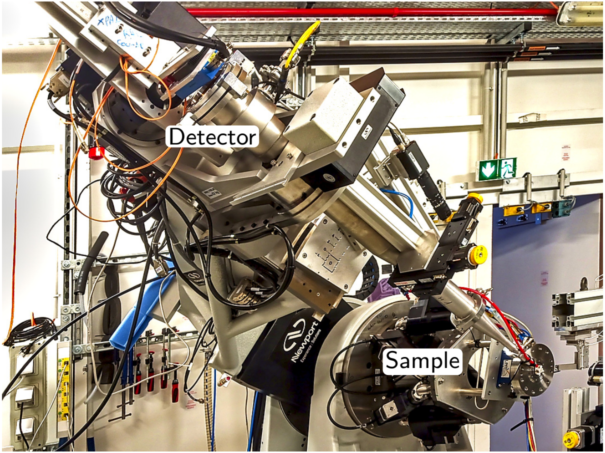
Technique	Surface X-ray Diffraction (SXRD)	Bragg Coherent Diffraction Imaging (BCDI)	X-ray Photoelectron Spectroscopy (XPS)
Sample	Pt(111) and Pt(100) single crystals and Pt particles	Isolated Pt particles	Pt(111) and Pt(100) single crystals
Information	Surface structure, roughness, relaxation & crystallographic phases	Shape, 3D displacement and strain arrays of unique object	Surface species presence, quantity & oxidation state
Beamline	SixS (SOLEIL)	SixS (SOLEIL)	B-07 (Diamond Light Source)







Sample environment at SixS



Multi Environment Diffractometer (MED), experimental end station at SixS (hard x-ray).

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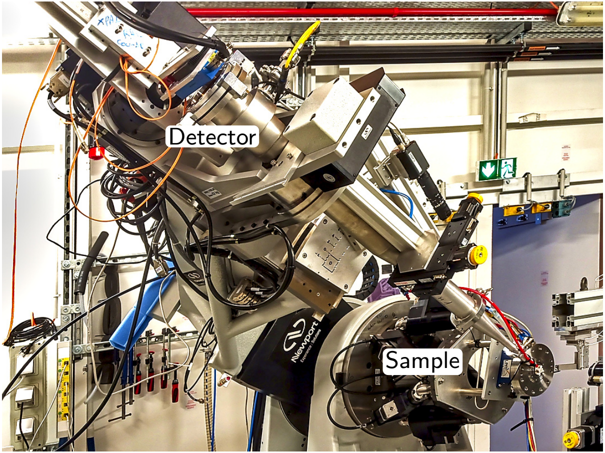

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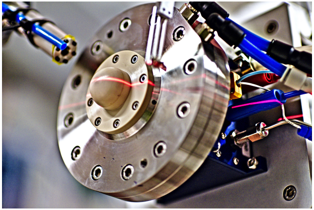

XCAT reactor cell and dome for NAP experiments.

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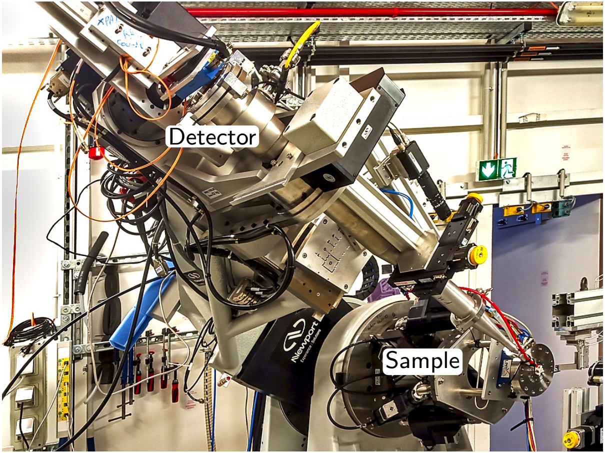

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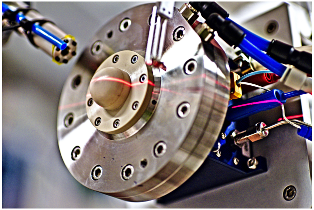

XCAT reactor cell and dome for NAP experiments.

- Gas panel with mass flow controllers (Argon, NH_3 , O_2 , . . .).

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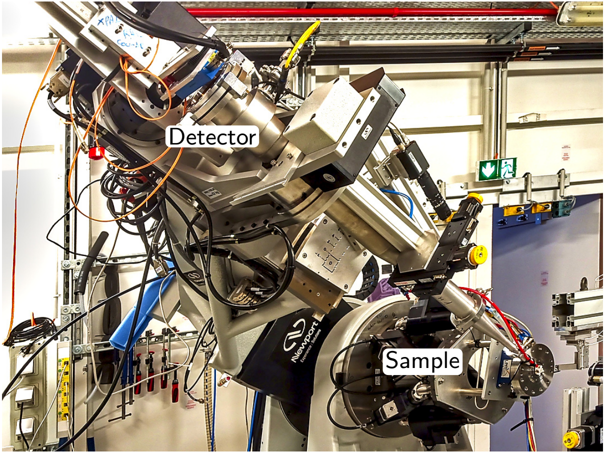

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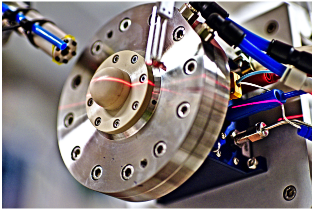

XCAT reactor cell and dome for NAP experiments.

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- Sample heater (up to 600 °C at 1 bar).

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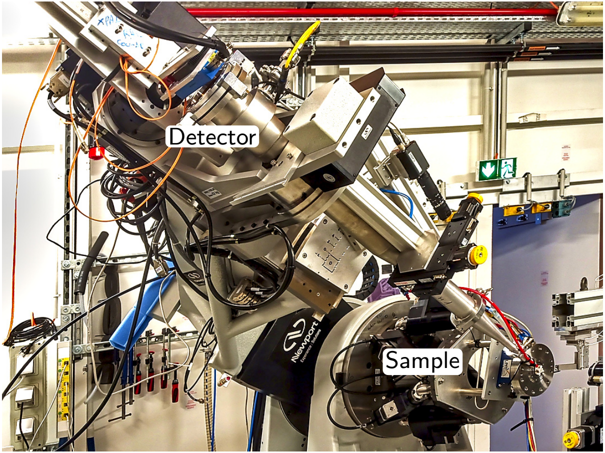

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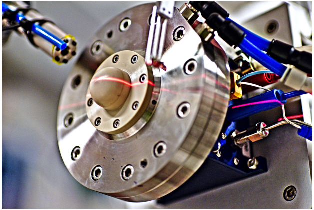

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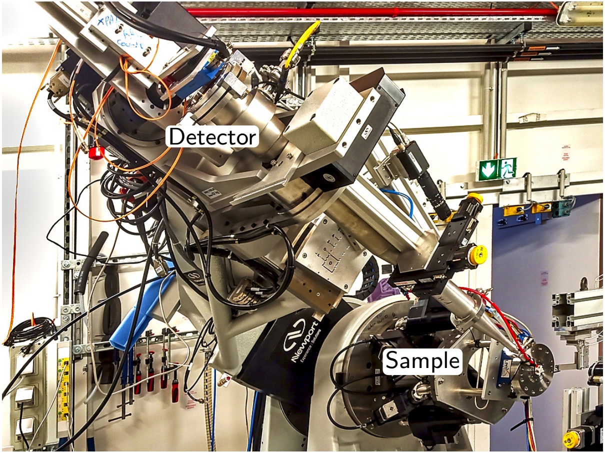

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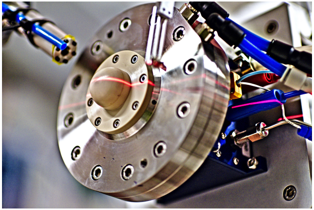
→ Study ammonia oxidation.



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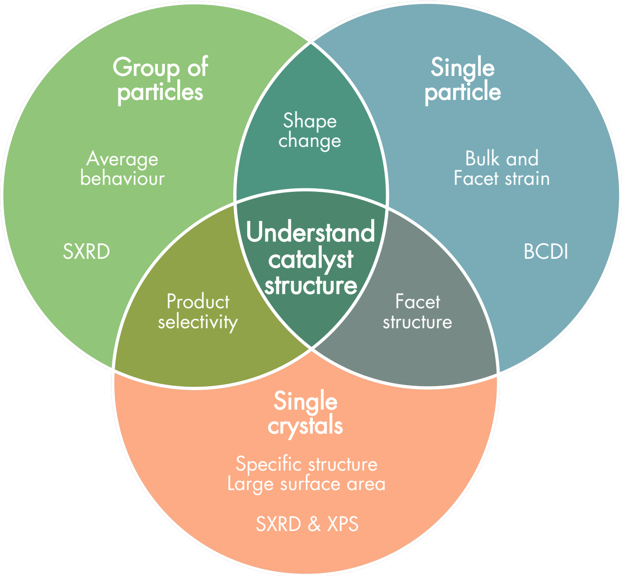
Group of particles
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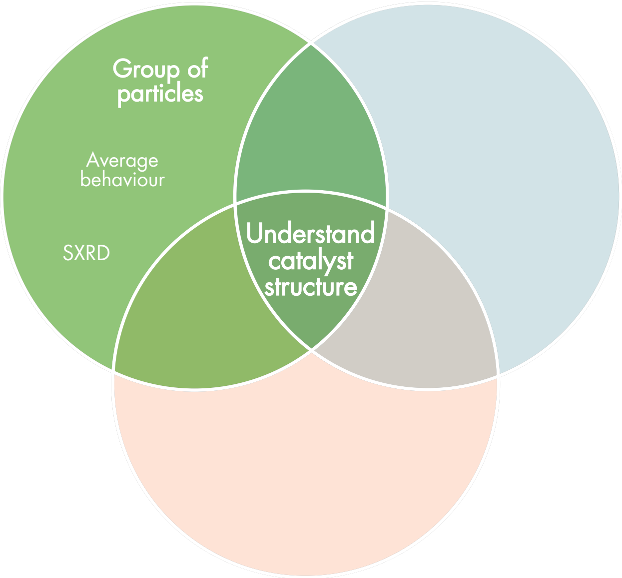
SXRD
Single particle
Bulk and Facet strain
BCDI
Shape change
Understand catalyst structure
Product selectivity
Facet structure
Single crystals
Specific structure
Large surface area
SXRD & XPS


Group of
particles
Average
behaviour
SXRD
Understand
catalyst
structure

Conditions

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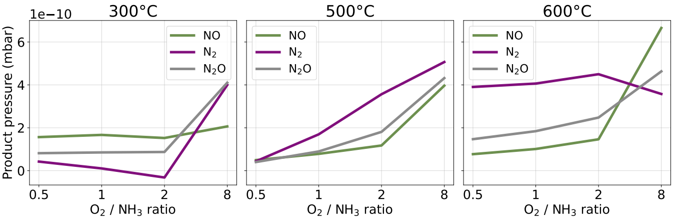

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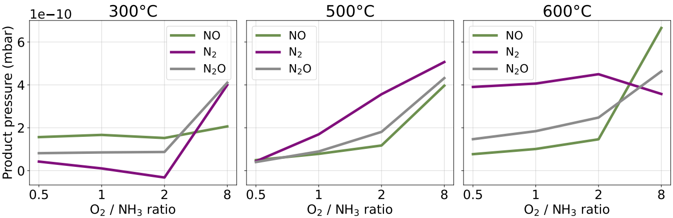
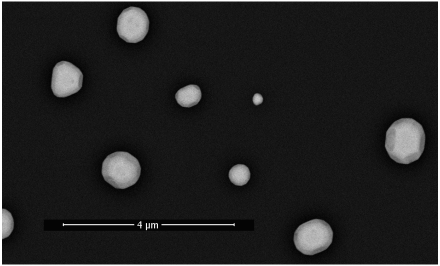


Product pressure evolution similar to reported literature behaviour!

Heterogeneous catalysis is a surface process



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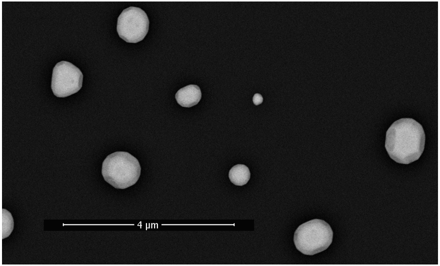

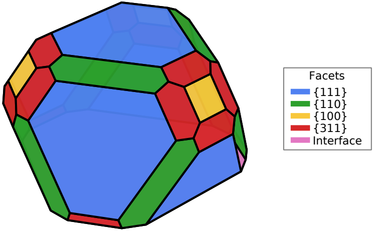

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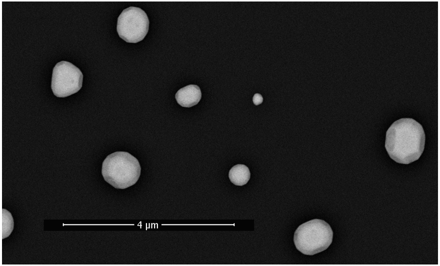

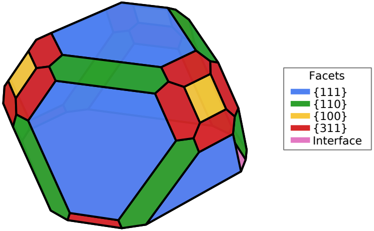

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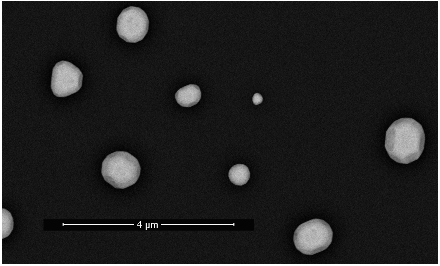

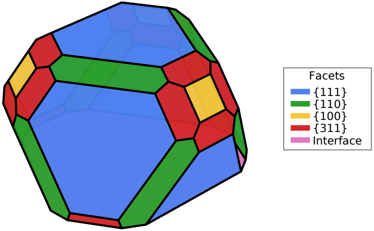

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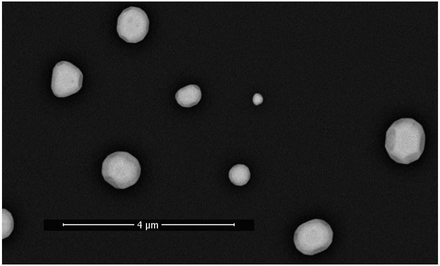

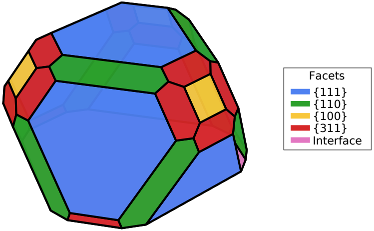

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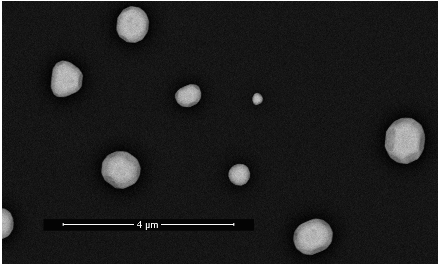

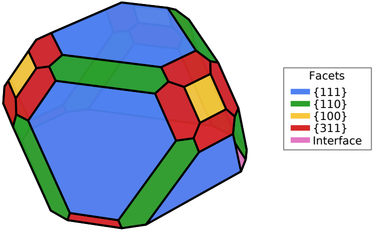

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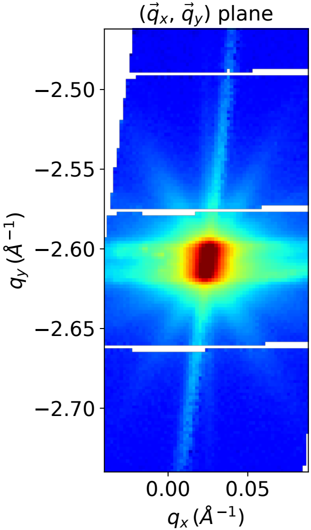
→ Property of diffraction: important signal perpendicular to those facets!

Collective behaviour of Pt particles



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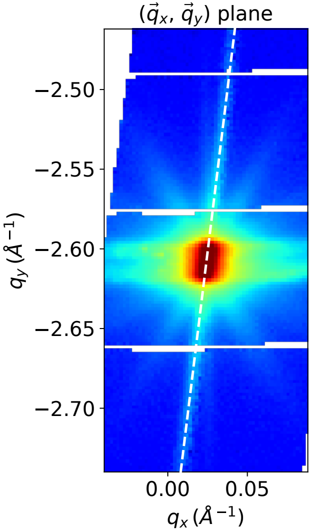

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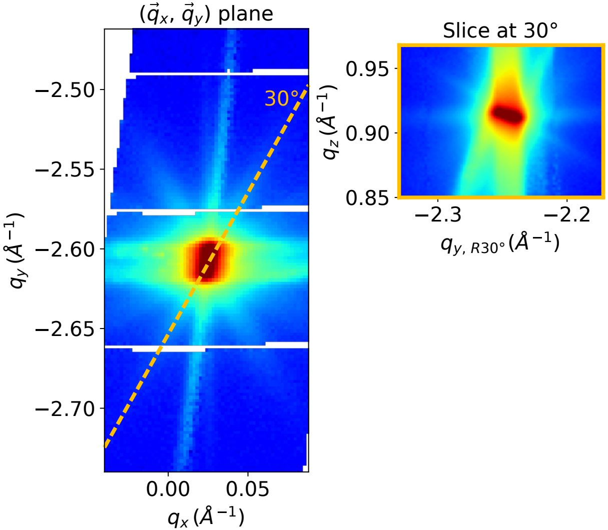

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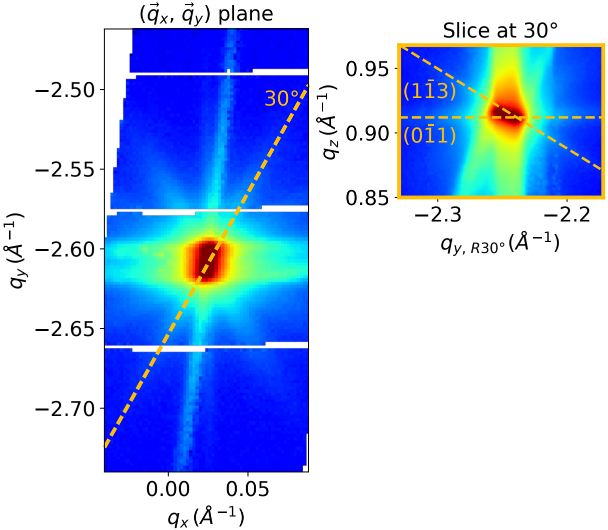

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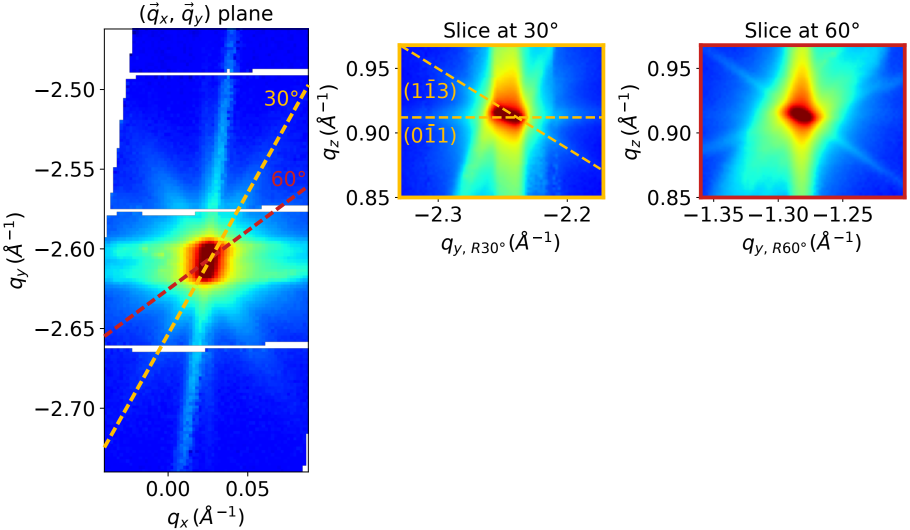

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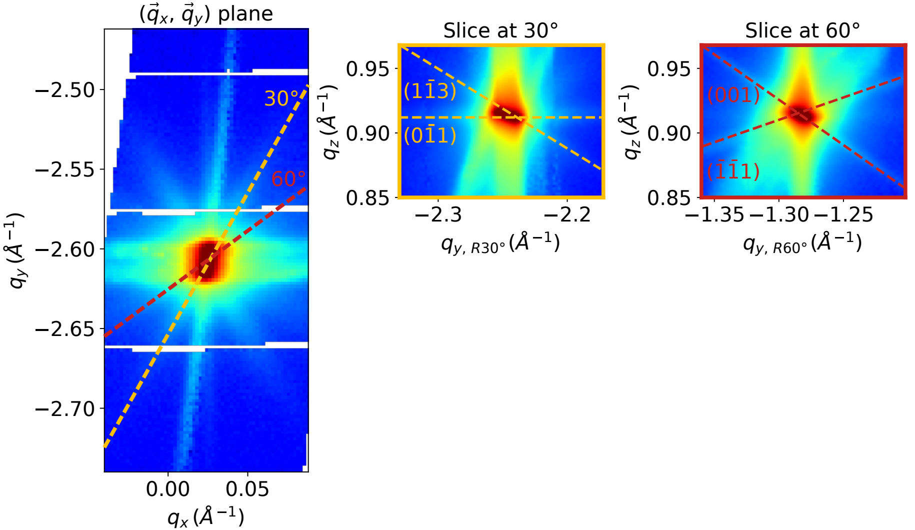

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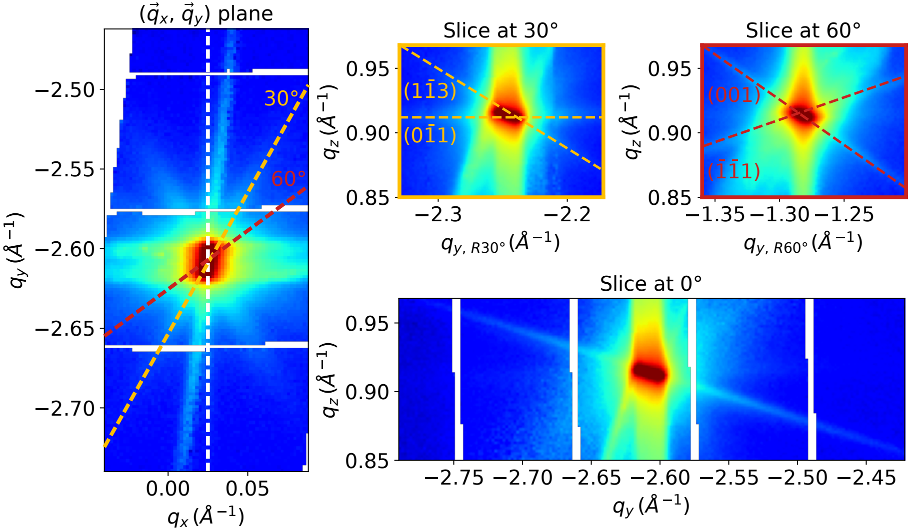

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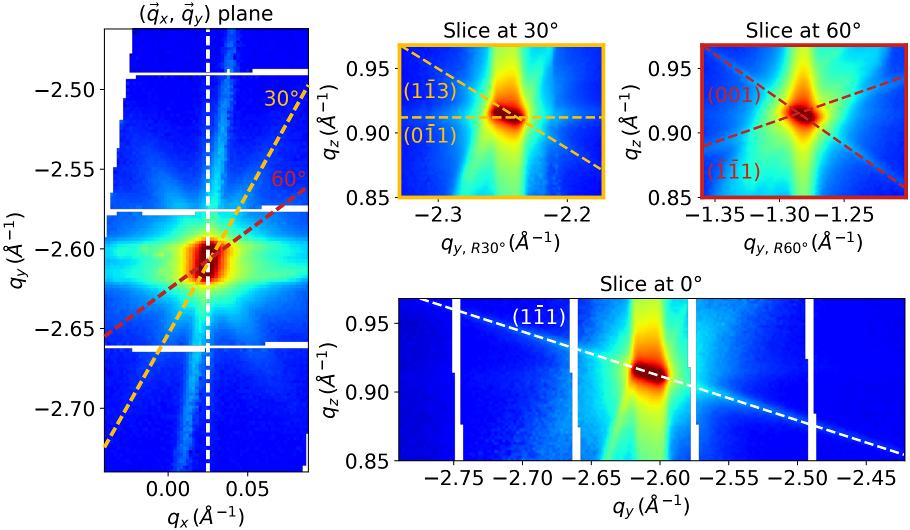

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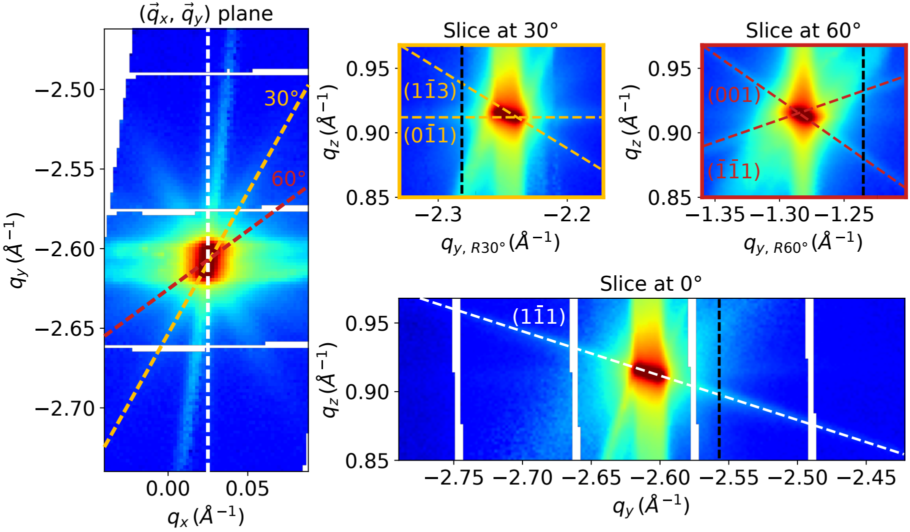

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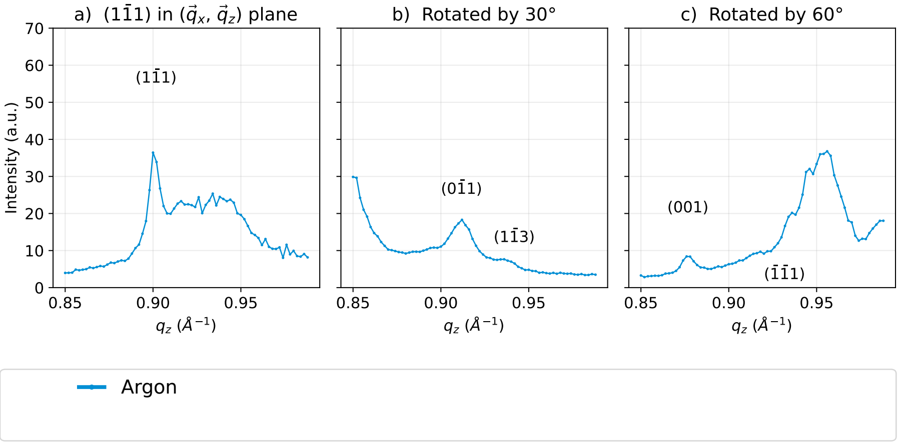

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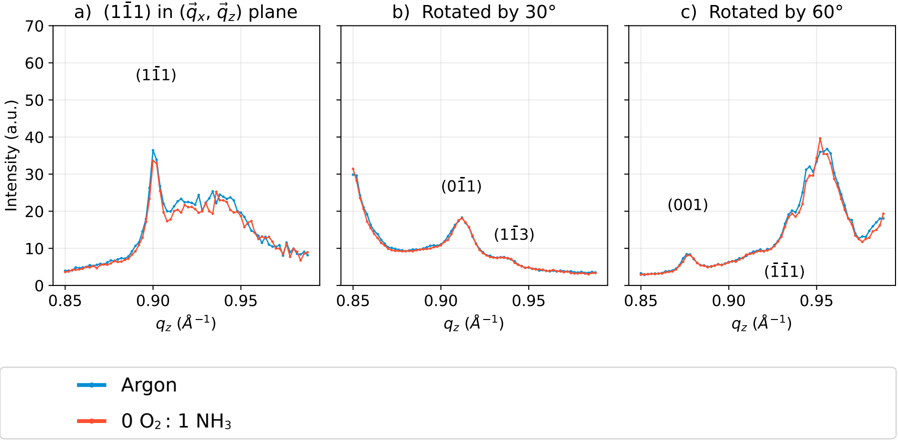

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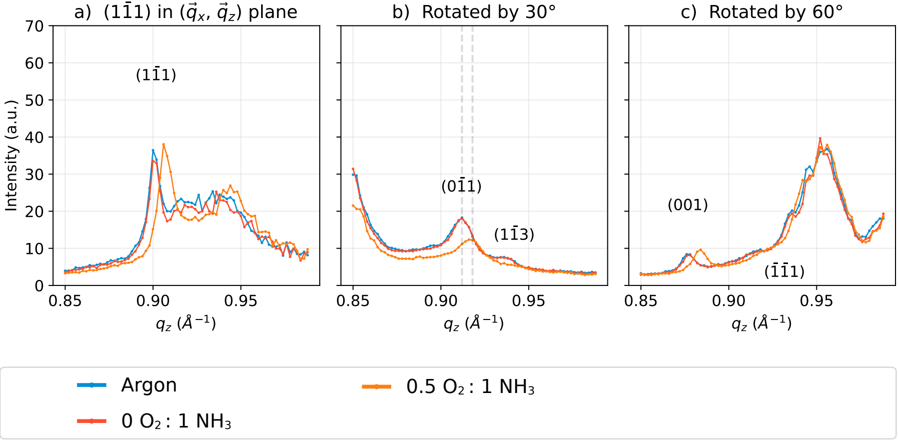

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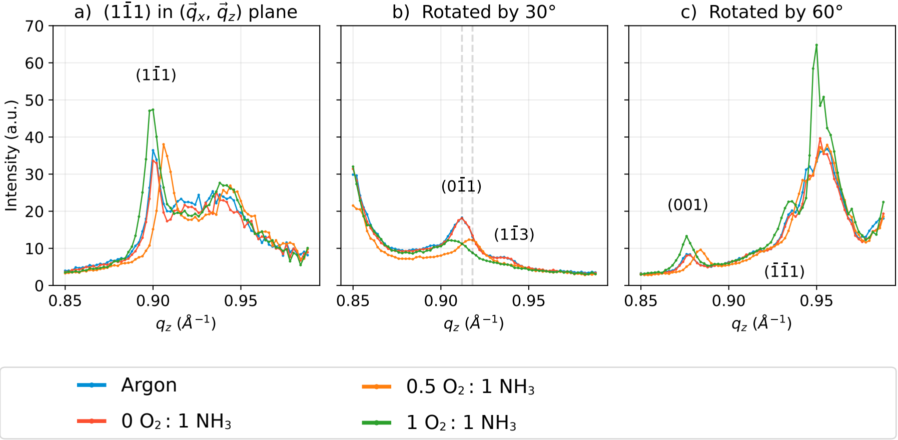

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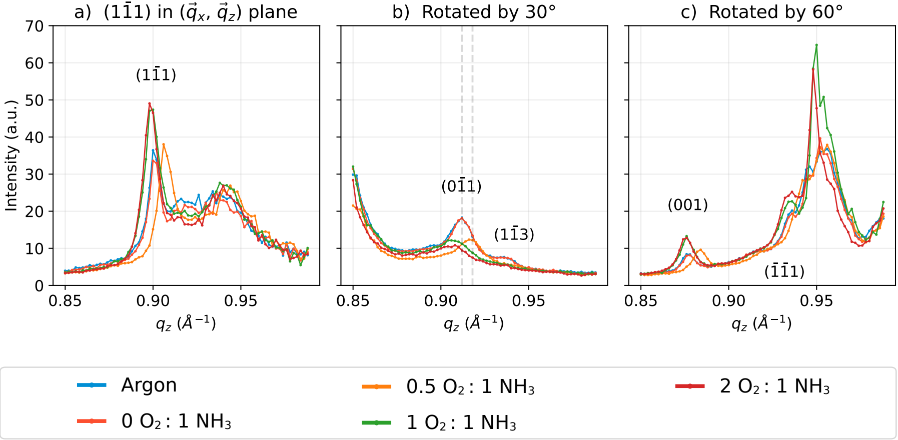

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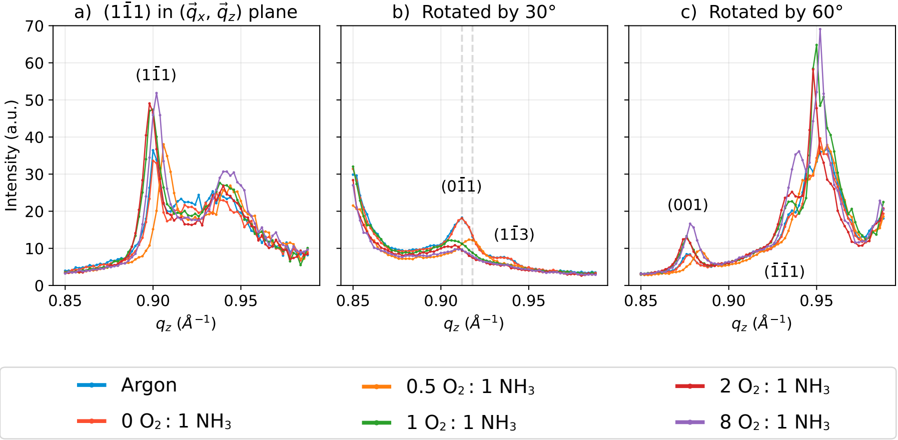

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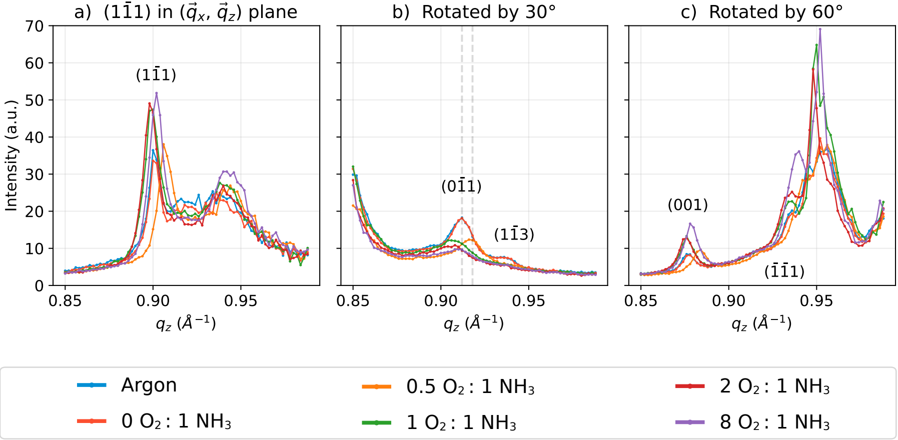

Reshaping associated to increasing O_2 / NH_3 ratio, linked to NO production?

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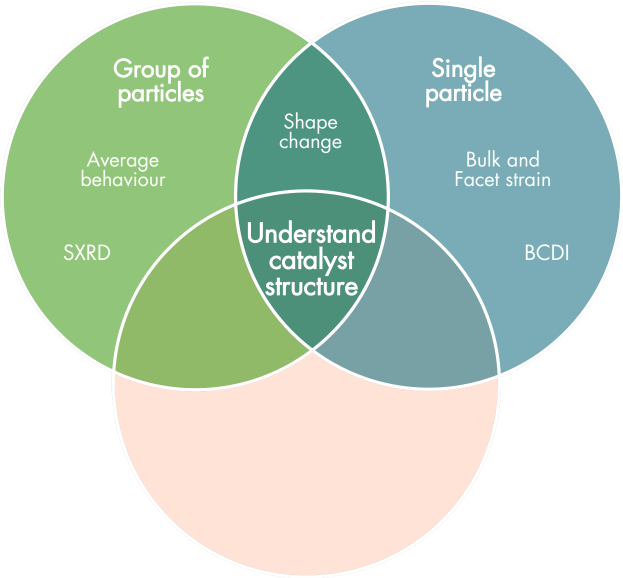
How to obtain more detailed information about single particles?


Group of particles
Average behaviour
SXRD
Shape change
Single particle
Bulk and Facet strain
BCDI
Understand catalyst structure

BCDI at SixS

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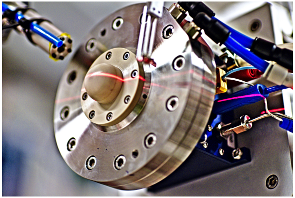

Reactor cell and dome.

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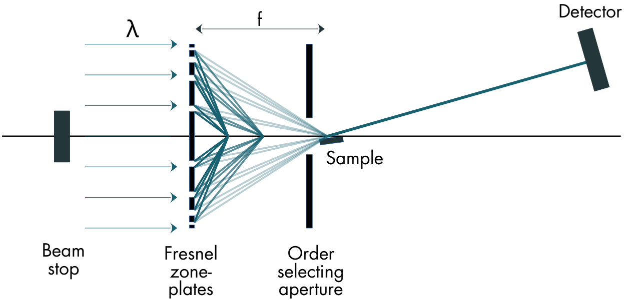
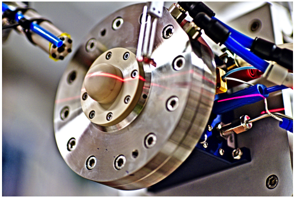


Coherence optical elements used at SixS (8.5 keV).



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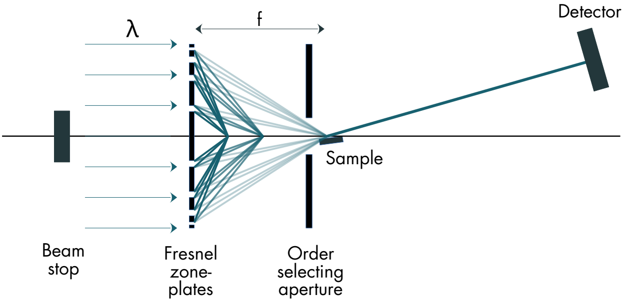

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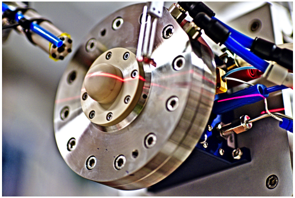
	Beam stop	FZP	OSA	Beam
Diameter	80 μm	300 μm	70 μm	$\approx 1\ \mu m$



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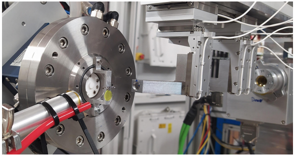

Optical elements.

Patterned sample used for BCDI

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- (111)-oriented particles.
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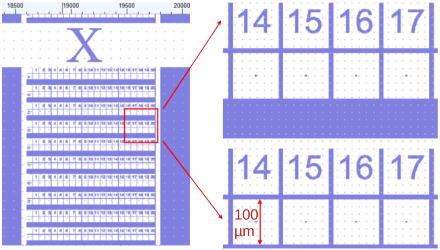

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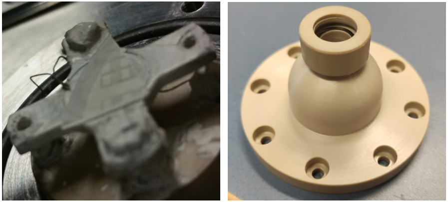
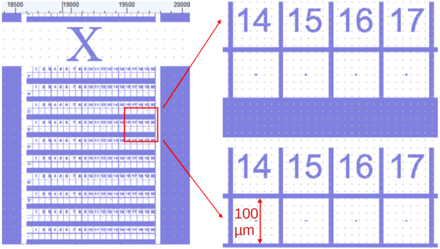


Sample holder (left) and dome (right).



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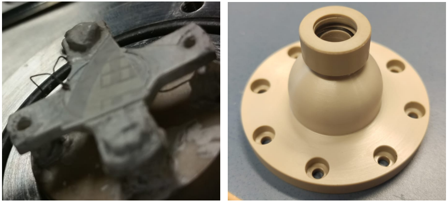
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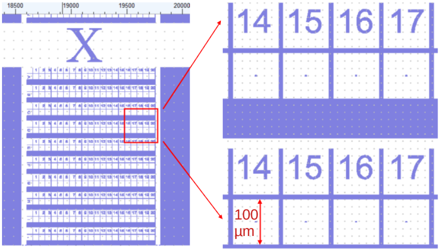

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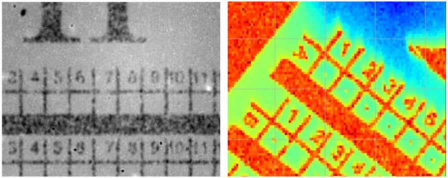
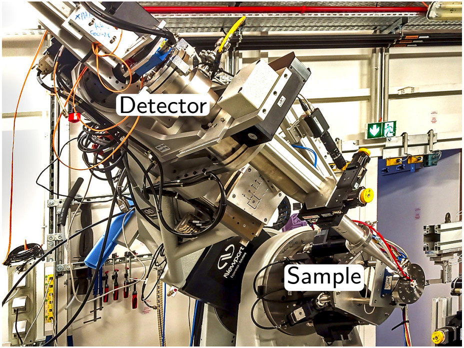

Microscope image (left).
Sample map performed in Bragg condition in ≈5 min (right).

BCDI data collection



Multi Environment Diffractometer (MED), experimental end station at SixS.

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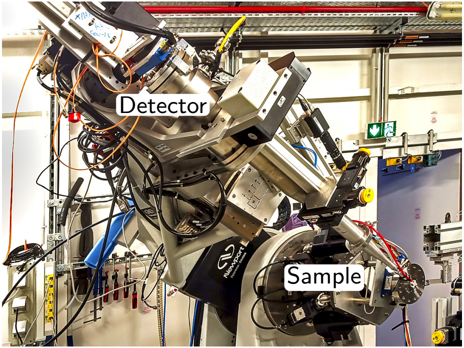

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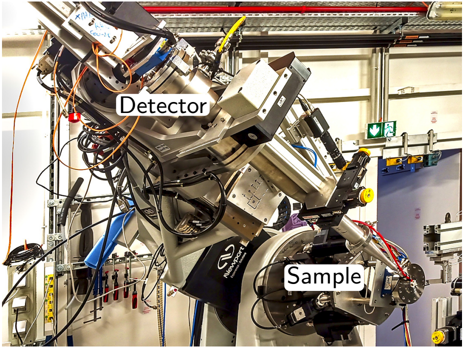
Measuring 3D diffraction patterns at SixS



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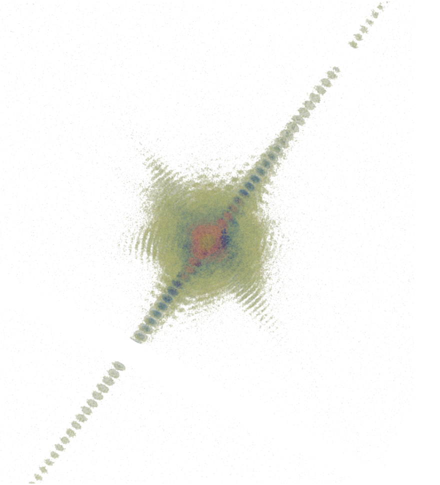
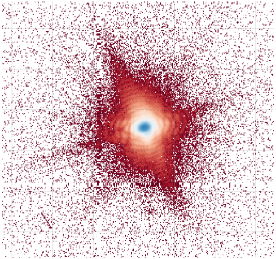
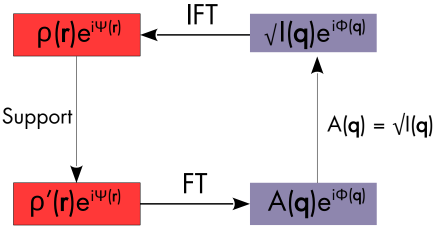


Coherent fringes visible in multiple directions in 3D diffraction pattern.

Phase retrieval



Coherent Bragg peak.



Phase retrieval with PyNX using iterative algorithms[3].

[3]Favre-Nicolin *et al.* Fast computation of scattering maps of nanostructures using graphical processing units, JAC, 2011

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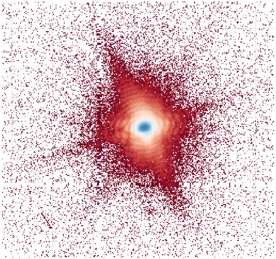

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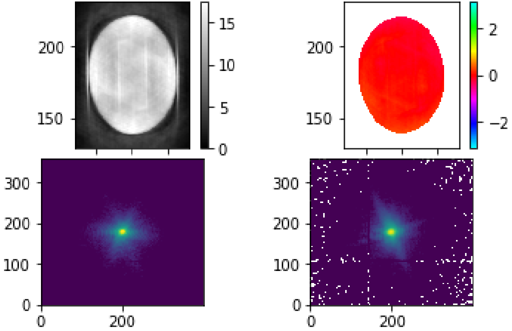

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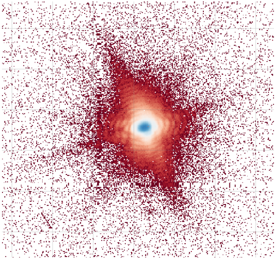

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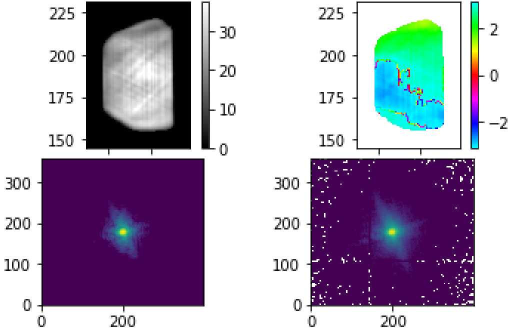

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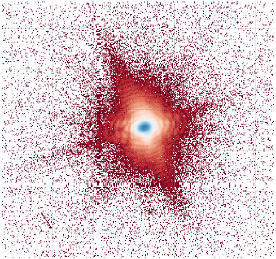
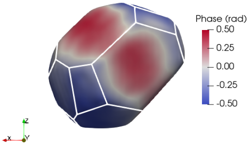
[3] Favre-Nicolin *et al.* Fast computation of scattering maps of nanostructures using graphical processing units, JAC, 2011

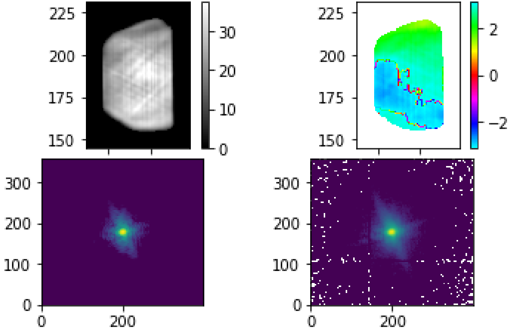
Phase retrieval



Coherent Bragg peak.



Reconstructed particle.

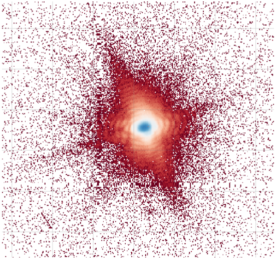


Phase retrieval with PyNX using iterative algorithms[3].

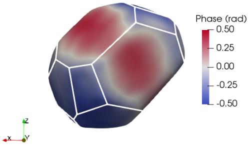
Complex object: $\rho(\vec{r})e^{i\vec{G}_{hkl}.\vec{u}(\vec{r})}$

[3]Favre-Nicolin *et al.* Fast computation of scattering maps of nanostructures using graphical processing units, JAC, 2011

Phase retrieval



Coherent Bragg peak.



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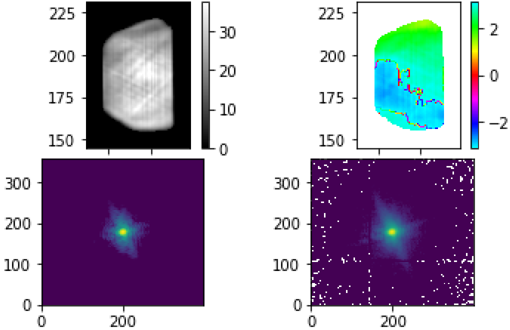


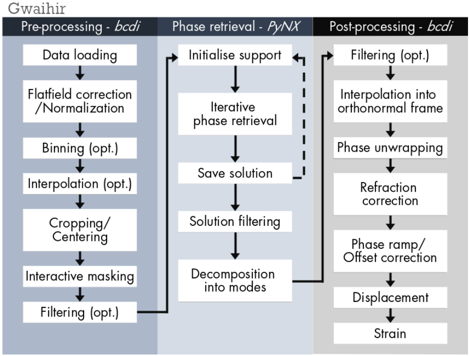
Phase retrieval with PyNX using iterative algorithms[3].

Complex object: $\rho(\vec{r})e^{i\vec{G}_{hkl}.\vec{u}(\vec{r})}$

Phase $\propto$ projection of displacement field!

[3]Favre-Nicolin *et al.* Fast computation of scattering maps of nanostructures using graphical processing units, JAC, 2011

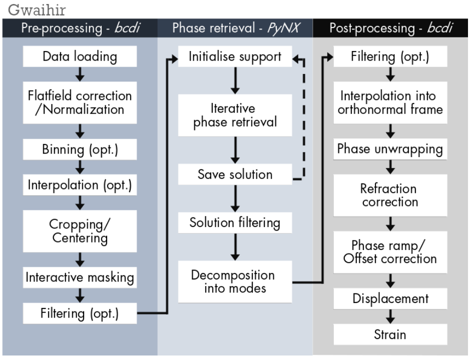
BCDI data analysis workflow



Flow chart of the main steps in the BCDI data analysis workflow.

[4]Simonne *et al.* Gwaihir: Jupyter Notebook graphical user interface for Bragg coherent diffraction imaging, JAC, 2022

BCDI data analysis workflow



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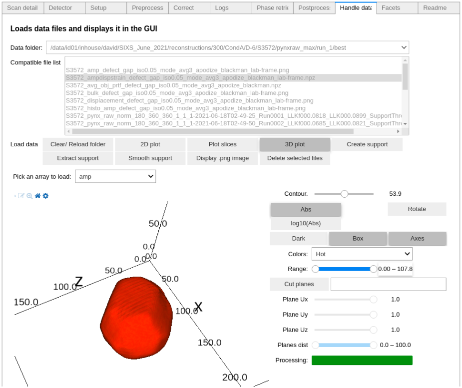
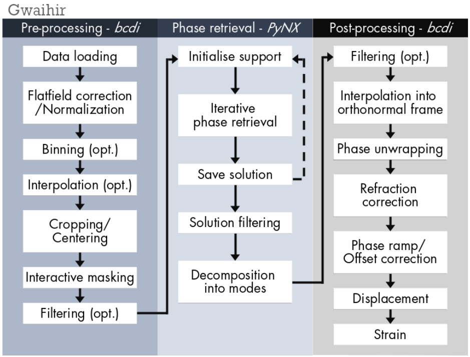


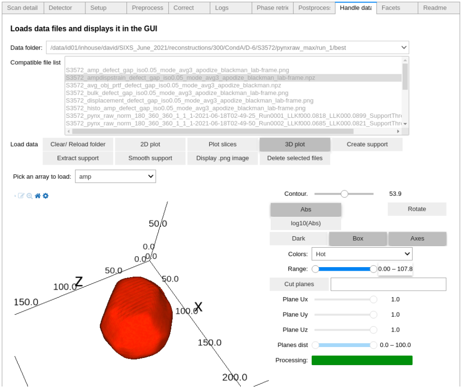
Interactive widgets for data analysis.

[4]Simonne *et al.* Gwaihir: Jupyter Notebook graphical user interface for Bragg coherent diffraction imaging, JAC, 2022

BCDI data analysis workflow



Flow chart of the main steps in the BCDI data analysis workflow.



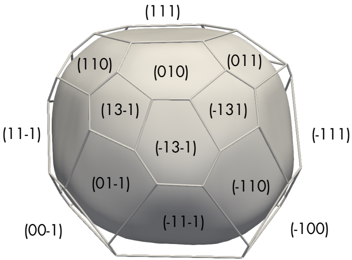
Interactive widgets for data analysis.

Open access[4]: GitHub.com/DSimonne/Gwaihir#welcome

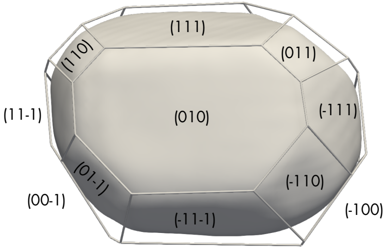
[4]Simonne *et al.* Gwaihir: Jupyter Notebook graphical user interface for Bragg coherent diffraction imaging, JAC, 2022

Facets on Pt particles

Small particle: $\varnothing \approx 350\,\text{nm}$.



Large particle: $\varnothing \approx 800\,\text{nm}$.



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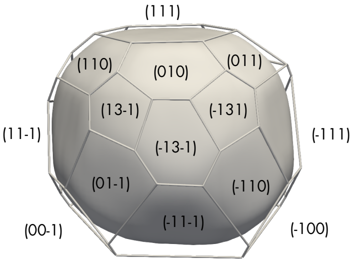

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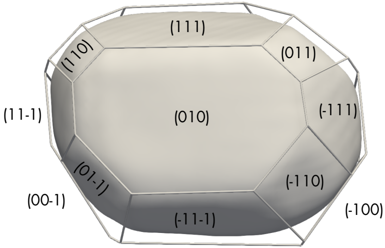

- Difference in size, shape, and in the type of facets exhibited.

Facets on Pt particles

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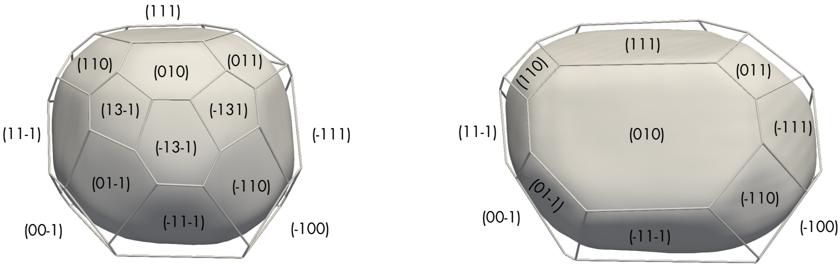

- Difference in size, shape, and in the type of facets exhibited.
- Most of the facets have low Miller indices, $\{100\}$, $\{110\}$, $\{111\}$.

Facets on Pt particles

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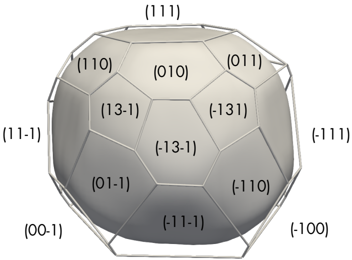

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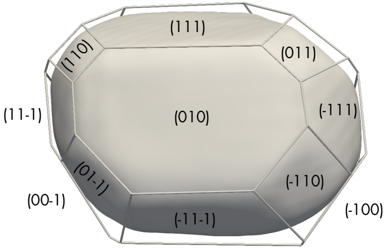
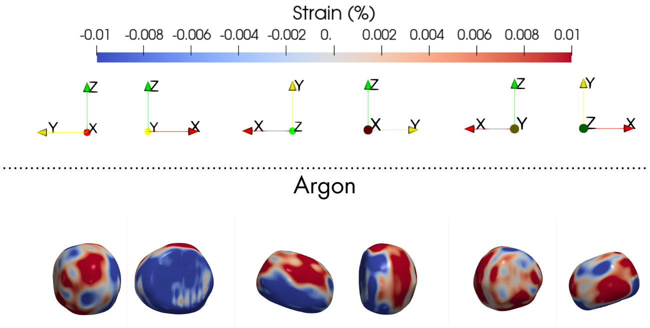


- Difference in size, shape, and in the type of facets exhibited.
- Most of the facets have low Miller indices, $\{100\}$, $\{110\}$, $\{111\}$.
- The smaller particle has more 'open' facets, such as $\{113\}$.

Operando BCDI: small particle (350 nm), 300 °C



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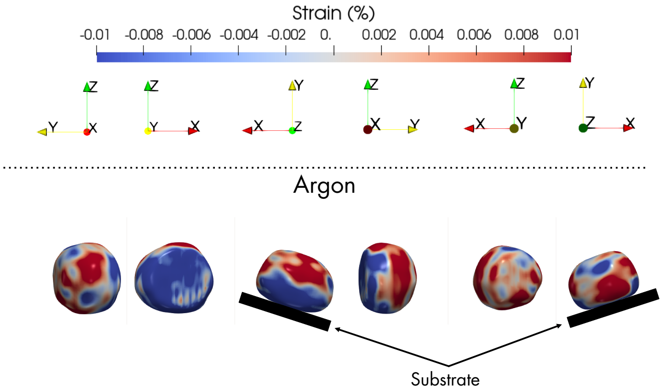

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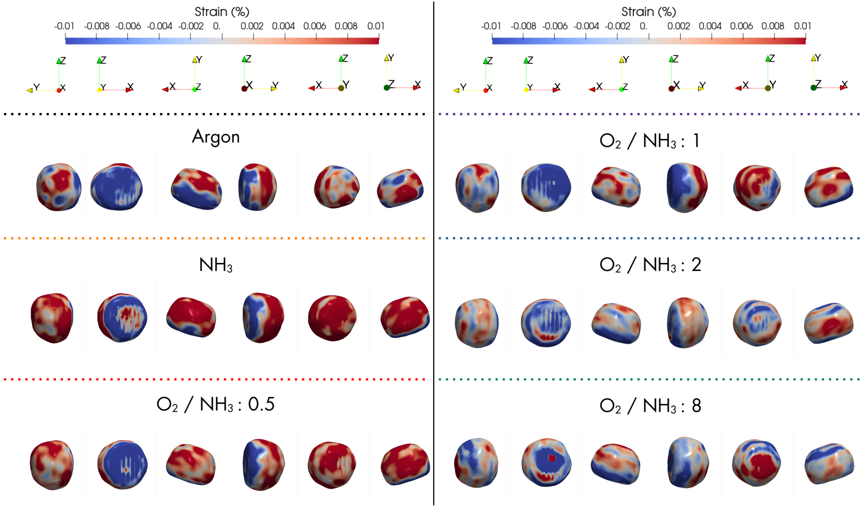
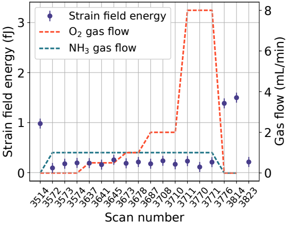


Strain field energy

Large particle, ∅ = 800 nm

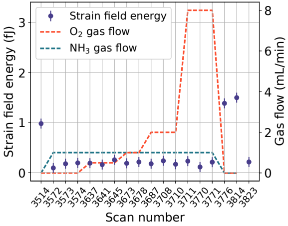
300°C



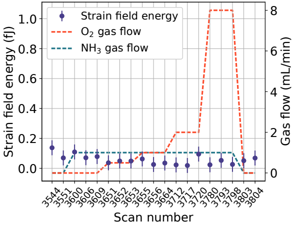
$$E = \frac{A}{V} \int \epsilon_{zz}^2 dV$$

300°C

Large particle, ∅ = 800 nm



Small particle, ∅ = 350 nm



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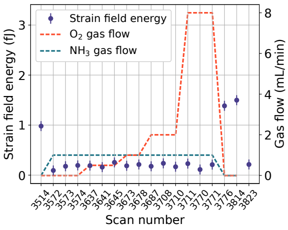
Strain field energy

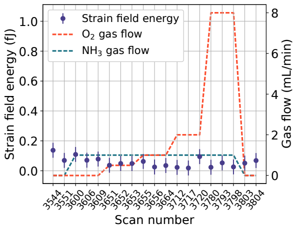
Large particle, ∅ = 800 nm

Small particle, ∅ = 350 nm

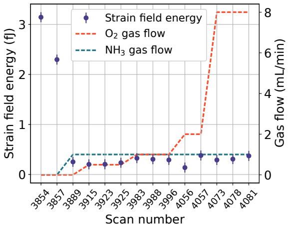
$$E = \frac{A}{V} \int \epsilon_{zz}^{2} dV$$

300°C

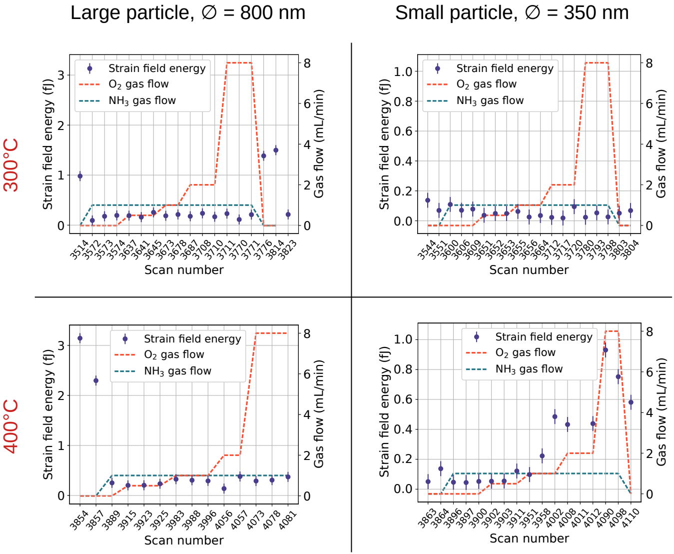




400°C



Strain field energy

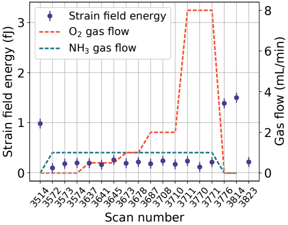


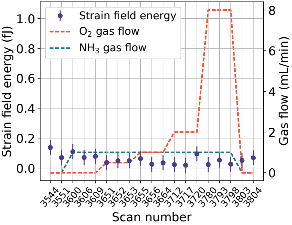
$$E = \frac{A}{V} \int \epsilon_{zz}^2 dV$$

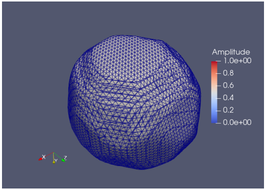
Strain field energy

Large particle, ∅ = 800 nm | **Small particle, ∅ = 350 nm**

300°C







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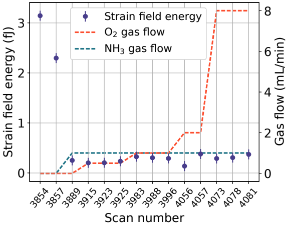
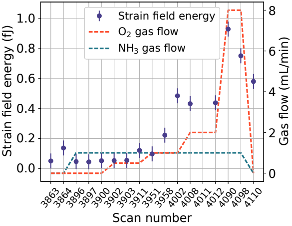


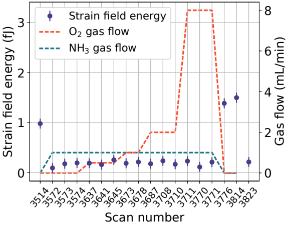


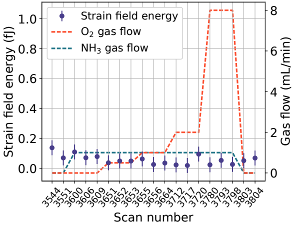
Strain field energy

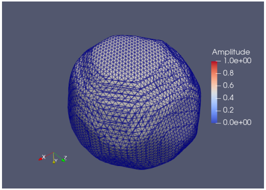
Large particle, ∅ = 800 nm

Small particle, ∅ = 350 nm

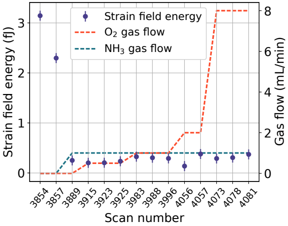
300°C

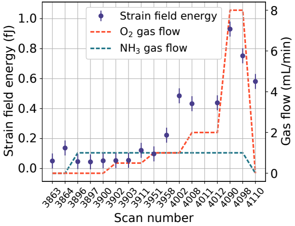


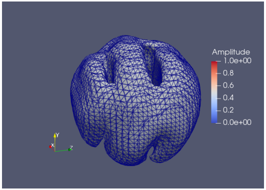




400°C







Pt particles: summary

How to obtain information about single particles? $\rightarrow$ Use BCDI!

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- Different evolution for particles of different size, shape, and initial strain state.

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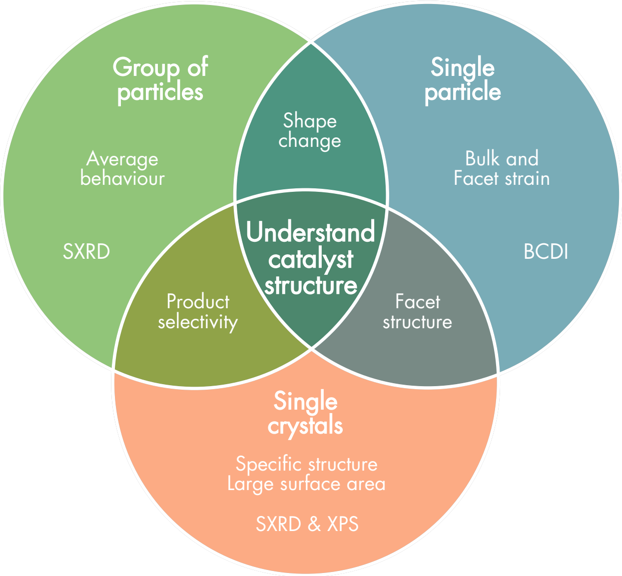
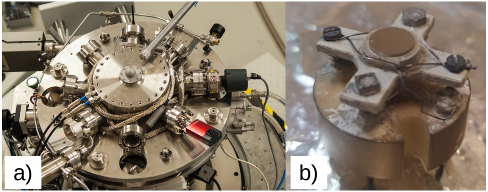
How to obtain information about specific facets?


Group of particles
Average behaviour
SXRD
Single particle
Bulk and Facet strain
BCDI
Shape change
Understand catalyst structure
Product selectivity
Facet structure
Single crystals
Specific structure
Large surface area
SXRD & XPS

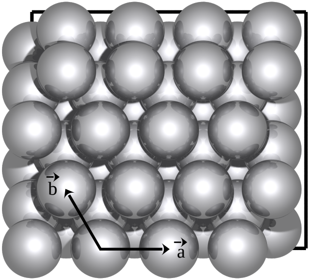
Conditions

Atmosphere (450 °C)	Interest
Argon (inert gas)	Catalyst state without reactants (unactive).
High O_2 pressure	Surface oxidation
8 O_2 + 1 NH_3 0.5 O_2 + 1 NH_3	Influence of (O_2 / NH_3) partial pressure ratio
NH_3	Ammonia adsorption
Argon (inert gas)	Probing cycle reproducibility
Low O_2 pressure	Surface oxidation



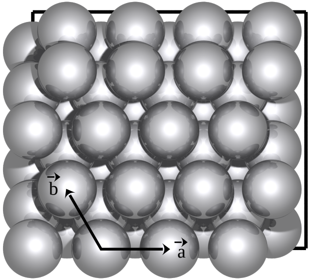
Large reactor used at SixS (a), and single crystal sample (b).

Pt(111)

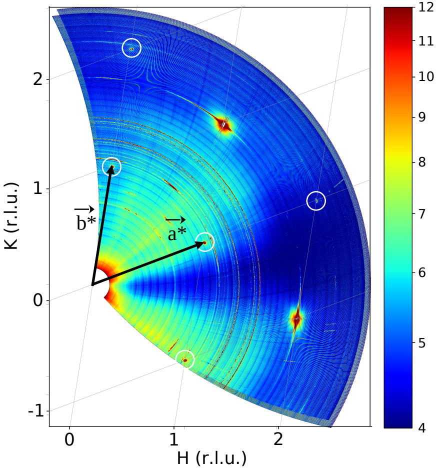


Pt(111) surface.

Pt(111)



Pt(111) surface.

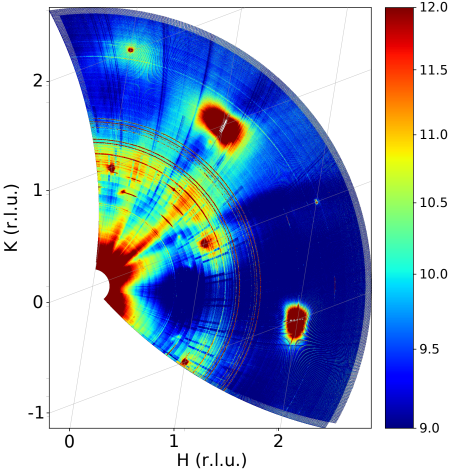


Pt(111) bulk-terminated structure reciprocal space in-plane map (Argon).

Pt(111): structures appear under 80 mbar of O_2

Argon (mbar)	NH_3 (mbar)	O_2 (mbar)
500	0	0
420	0	80
410	10	80
485	10	5
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.



Reciprocal space map under 80 mbar of oxygen.

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490	10	0
500	0	0
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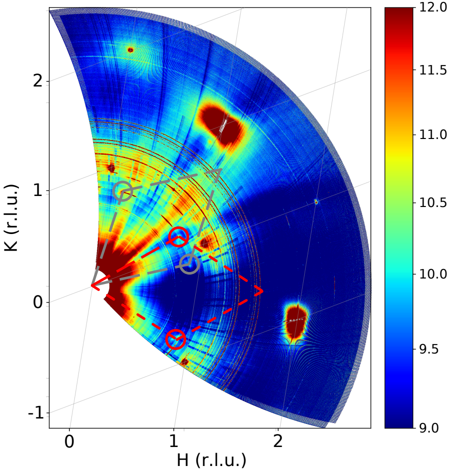
Partial pressures during reaction cycle.
In experimental order.

Rotated lattices: red and gray diamonds.



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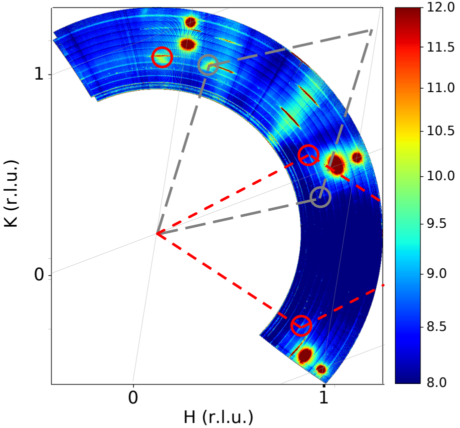

Reciprocal space map under 80 mbar of oxygen.
9h30 after oxygen exposure.

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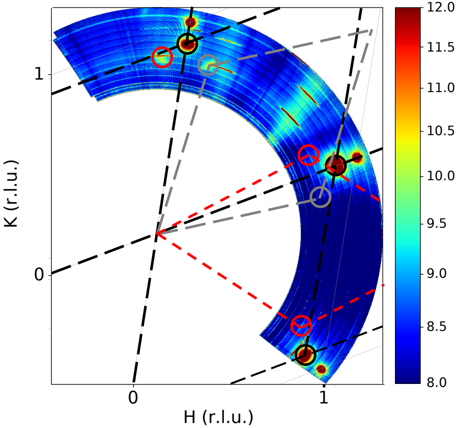
Argon (mbar)	NH_3 (mbar)	O_2 (mbar)
500	0	0
420	0	80
410	10	80
485	10	5
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.

Rotated lattices: red and gray diamonds.

Surface oxide: black diamond.



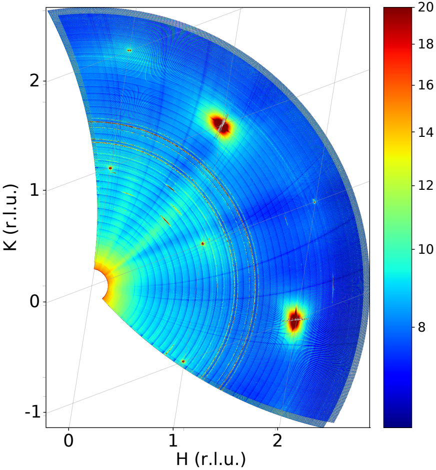
Reciprocal space map under 80 mbar of oxygen.
9h30 after oxygen exposure.

Pt(111): reaction conditions, O_2 / NH_3 : 8

Argon (mbar)	NH_3 (mbar)	O_2 (mbar)
500	0	0
420	0	80
410	10	80
485	10	5
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.

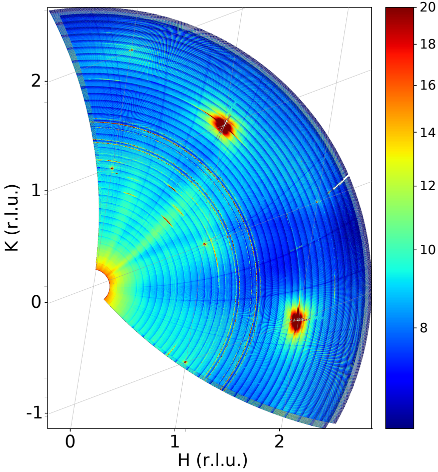
The addition of ammonia removes all the signals.



Pt(111): reaction conditions, O_2 / NH_3 : 0.5

Argon (mbar)	NH_3 (mbar)	O_2 (mbar)
500	0	0
420	0	80
410	10	80
485	10	5
490	10	0
500	0	0
495	0	5

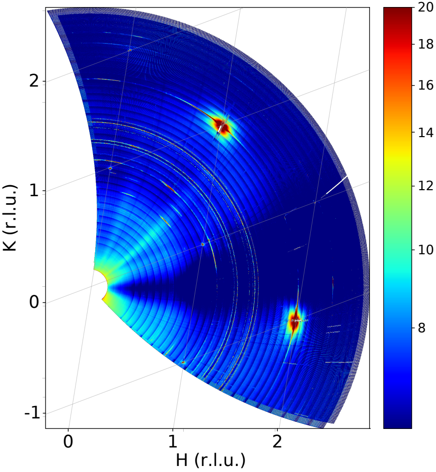
Partial pressures during reaction cycle.
In experimental order.



Pt(111): only ammonia

Argon (mbar)	NH_3 (mbar)	O_2 (mbar)
500	0	0
420	0	80
410	10	80
485	10	5
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.

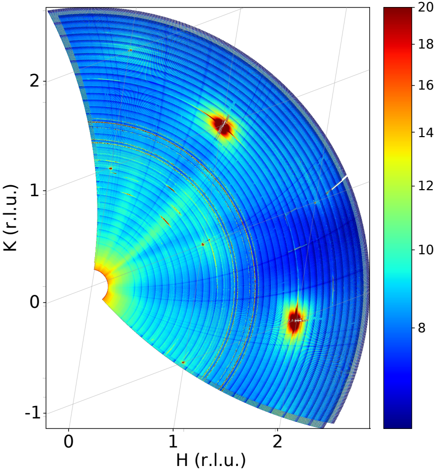


Pt(111): back to inert atmosphere

Argon (mbar)	NH_3 (mbar)	O_2 (mbar)
500	0	0
420	0	80
410	10	80
485	10	5
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.

The initial surface is reproducible.

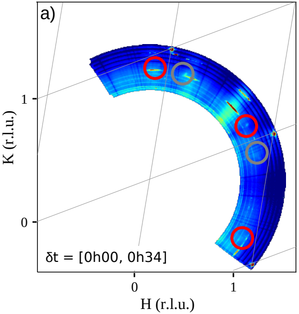


Pt(111): low oxygen pressure (5 mbar)

Argon (mbar)	NH_3 (mbar)	O_2 (mbar)
500	0	0
420	0	80
410	10	80
485	10	5
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.

→ Rotated lattices visible from the start.



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495	0	5

Partial pressures during reaction cycle.
In experimental order.

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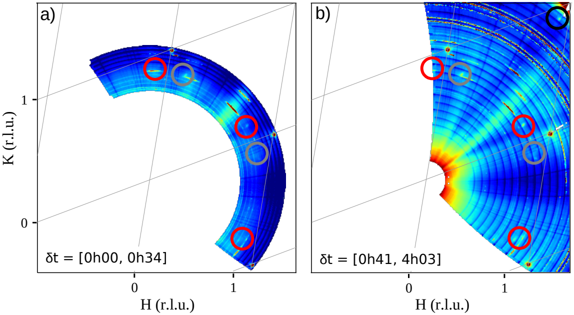

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Argon (mbar)	NH_3 (mbar)	O_2 (mbar)
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420	0	80
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485	10	5
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.

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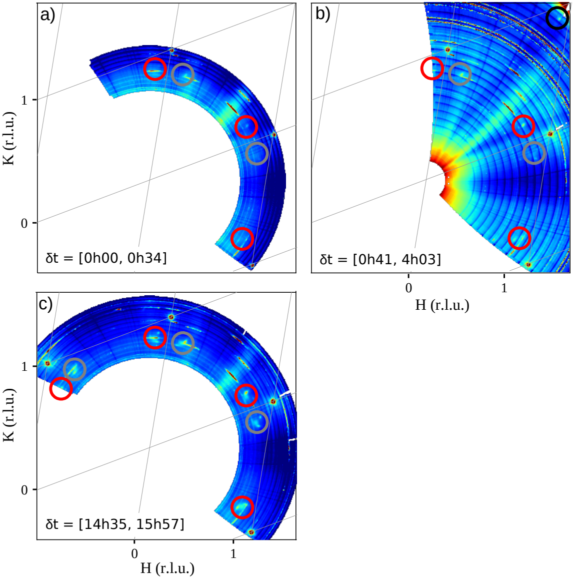

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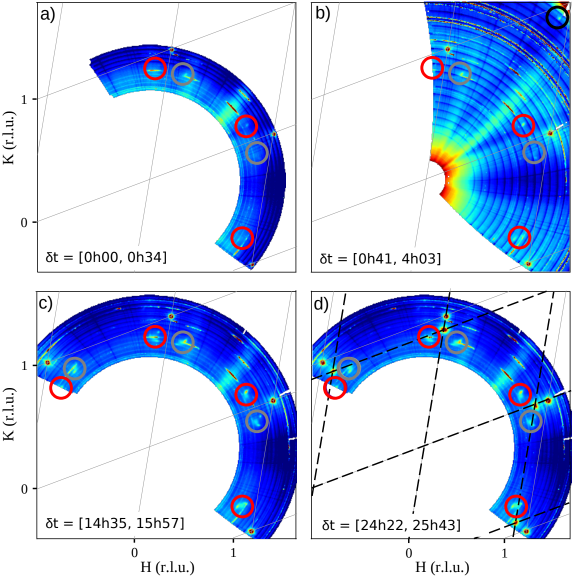
500	0	0
420	0	80
410	10	80
485	10	5
490	10	0
500	0	0
495	0	5

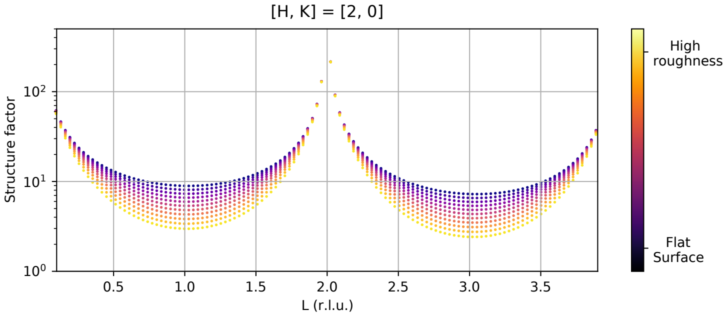
Partial pressures during reaction cycle.
In experimental order.

→ Rotated lattices visible from the start.

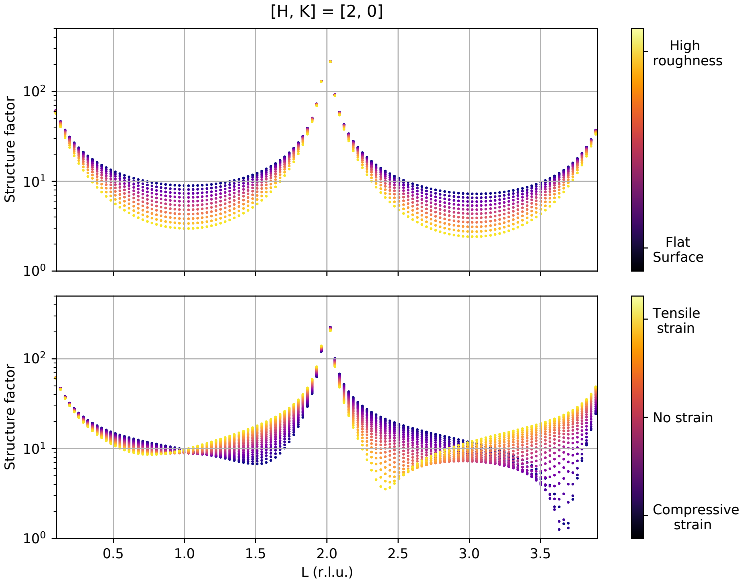
→ Surface oxides appears later under lower oxygen pressure!



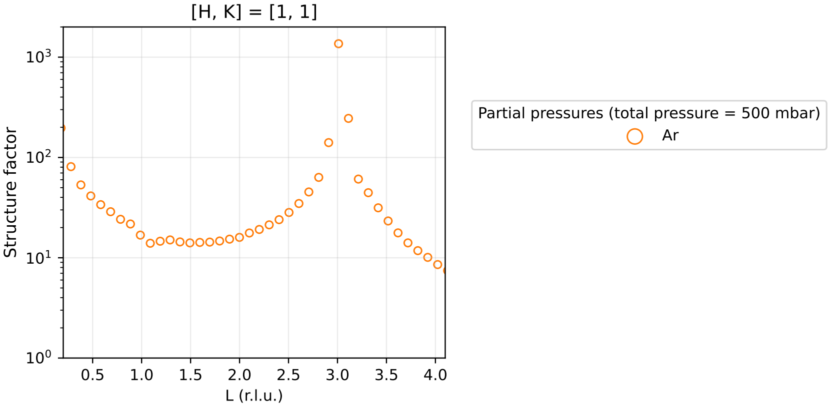
Understanding CTR intensity



Understanding CTR intensity



Pt(111): crystal truncation rods



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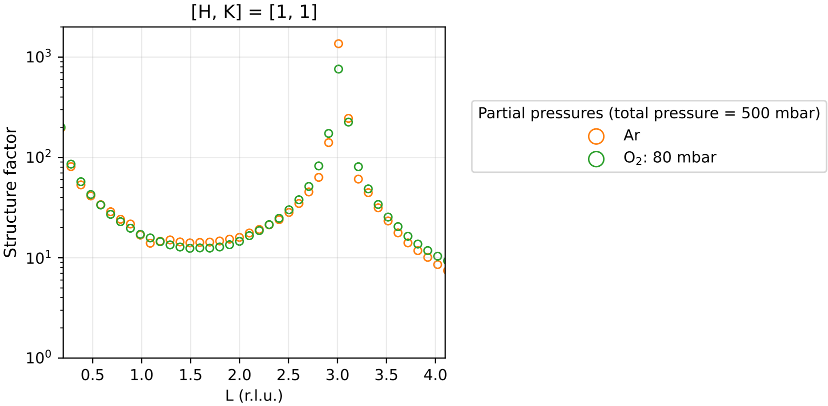
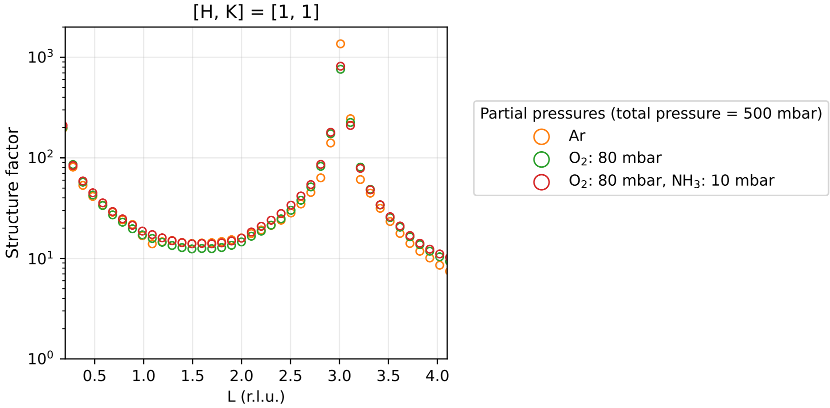
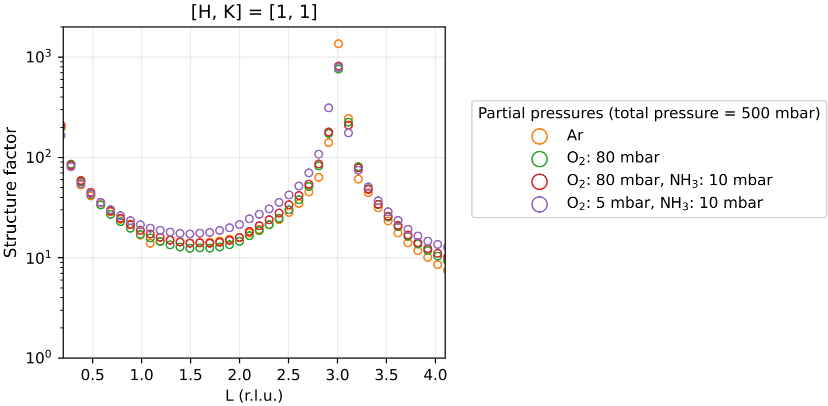


Pt(111): crystal truncation rods

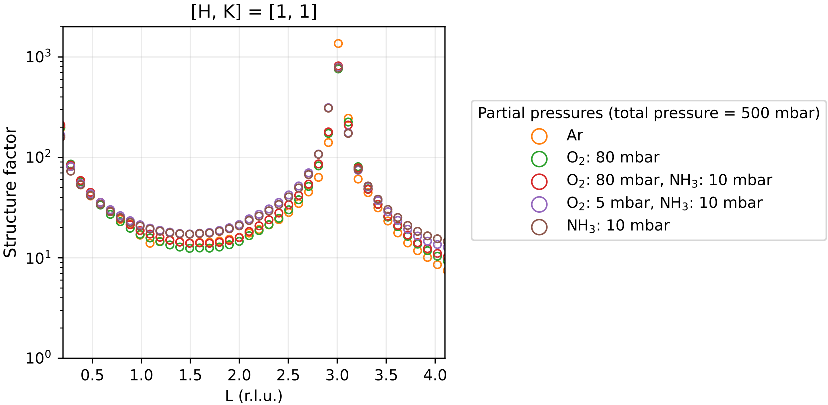


Pt(111): crystal truncation rods



→ Roughness changes linked to oxygen presence are clearly visible.

Pt(111): crystal truncation rods



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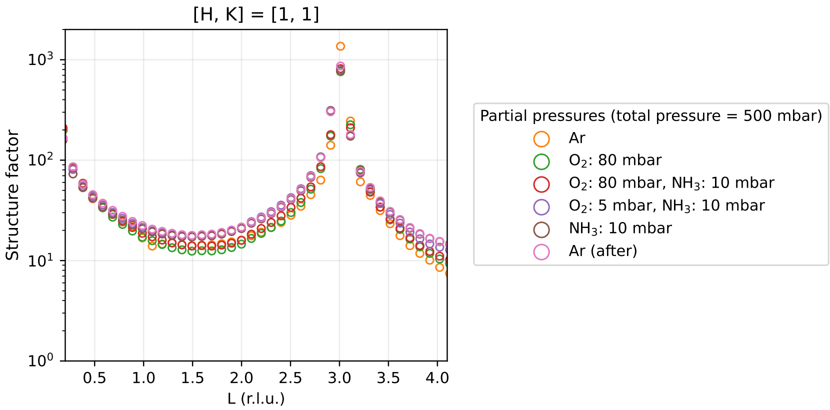
Pt(111): crystal truncation rods



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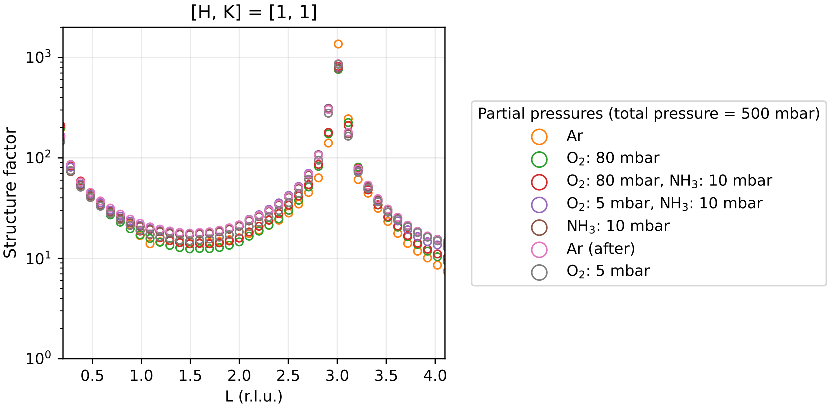
Pt(111): crystal truncation rods



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Pt(111): summary

O_2 (mbar)	NH_3 (mbar)	Pt(111)
80	0	Two rotated hexagonal lattices, Surface oxide after 9 h30 min Increased surface roughness

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5	0	Rotated lattices also visible. Surface oxide measured later.

Pt(111): summary

O_2 (mbar)	NH_3 (mbar)	Pt(111)
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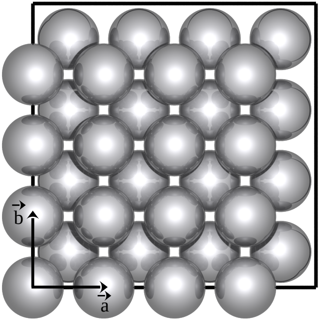
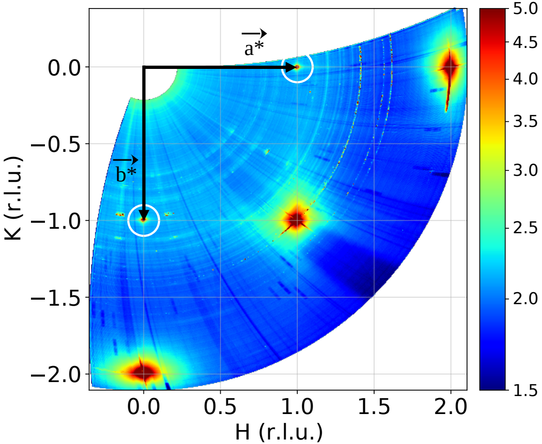
80	10	Removal of all signals
5	10	Decreased surface roughness
0	10	Weak strain changes
0	0	Return to clean surface but with lower roughness
5	0	Rotated lattices also visible. Surface oxide measured later.

Does the Pt(100) surface exhibit the same behaviour?

Pt(100)



Atoms on the Pt(100) surface follow a square arrangement.

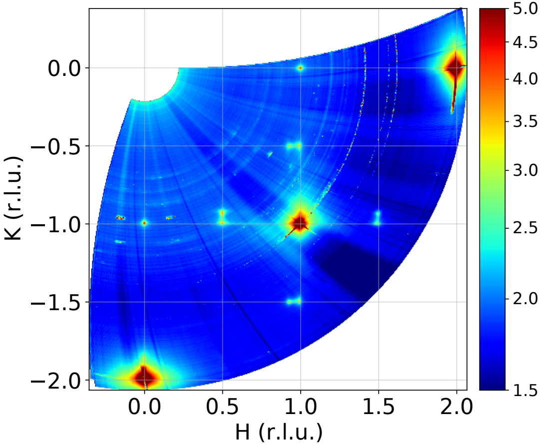


Pt(100) bulk-terminated structure reciprocal space in-plane map (Argon).

Pt(100): structures appear under 80 mbar of O_2

Argon (mbar)	NH_3 (mbar)	O_2 (mbar)
500	0	0
420	0	80
410	10	80
485	10	5
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.



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500	0	0
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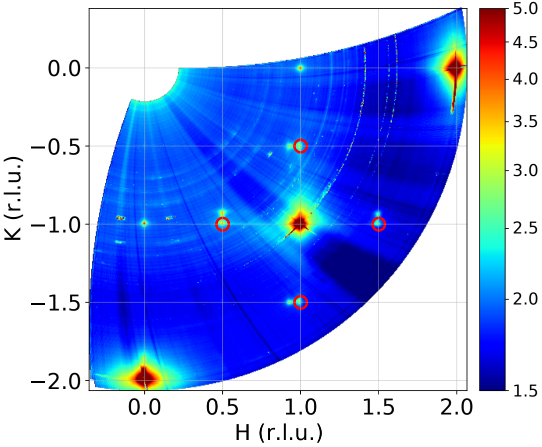
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.

Two family of peaks, one shifted from the other.



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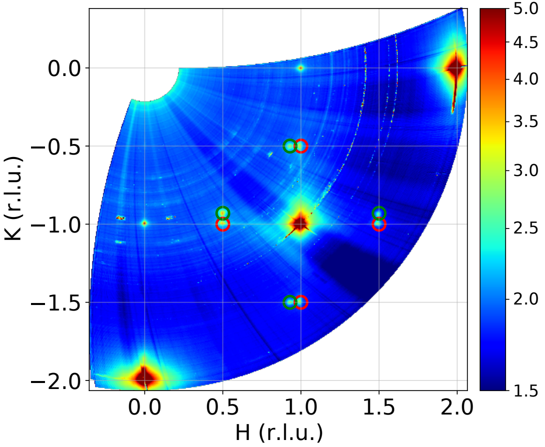

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485	10	5
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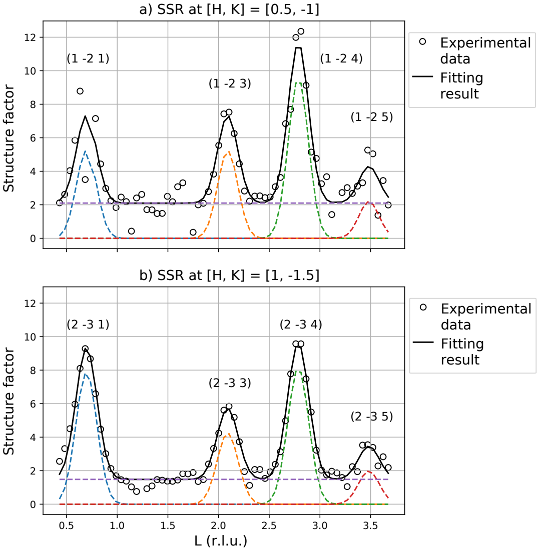
495	0	5

Partial pressures during reaction cycle.
In experimental order.

Two family of peaks, one shifted from the other.

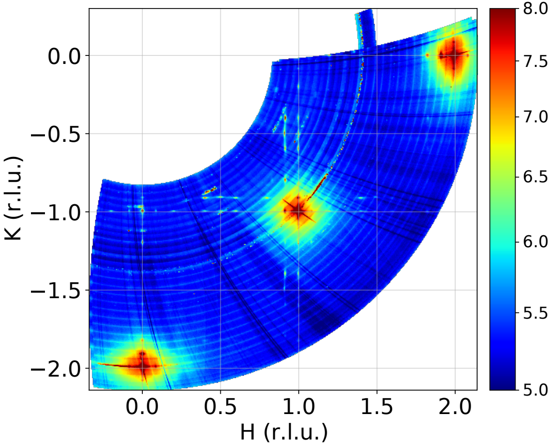
Pt(100)-(2 × 2) bulk Pt_3O_4 is formed!



Pt(100): reaction conditions, O_2 / NH_3 : 8

Argon (mbar)	NH_3 (mbar)	O_2 (mbar)
500	0	0
420	0	80
410	10	80
485	10	5
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.



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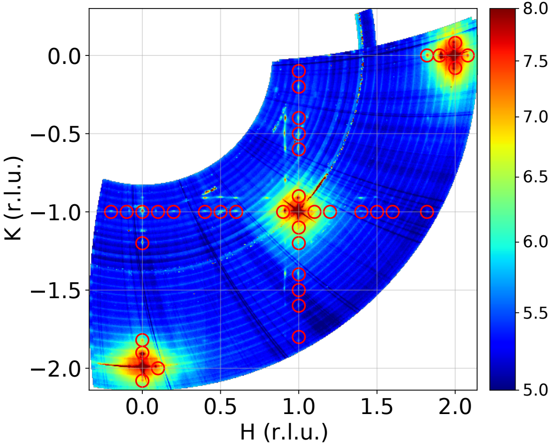
500	0	0
420	0	80
410	10	80
485	10	5
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.

Reaction conditions favour NO .



(10 × 10) reconstructions observed.

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Argon (mbar)	NH_3 (mbar)	O_2 (mbar)
500	0	0
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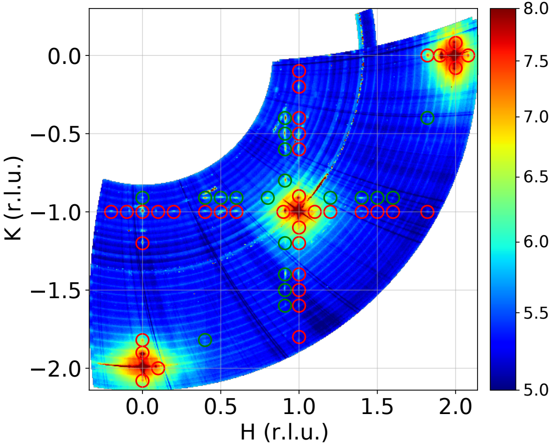
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.

Reaction conditions favour NO .

Two family of peaks, one shifted from the other.

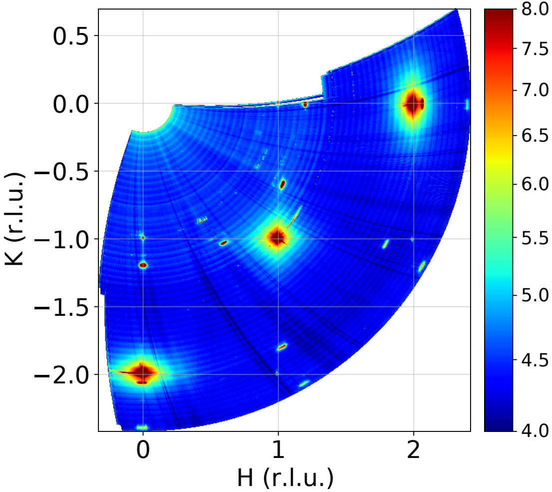


(10 × 10) reconstructions observed.

Pt(100): reaction conditions, O_2 / NH_3 : 0.5

Argon (mbar)	NH_3 (mbar)	O_2 (mbar)
500	0	0
420	0	80
410	10	80
485	10	5
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.



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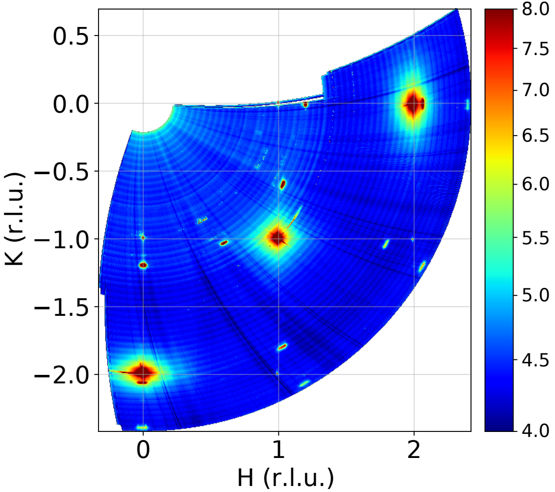
Argon (mbar)	NH_3 (mbar)	O_2 (mbar)
500	0	0
420	0	80
410	10	80
485	10	5
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.

Lowering O_2 pressure to conditions favoring N_2 .



Pt(100): reaction conditions, O_2 / NH_3 : 0.5

Argon (mbar)	NH_3 (mbar)	O_2 (mbar)
500	0	0
420	0	80
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490	10	0
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Partial pressures during reaction cycle.
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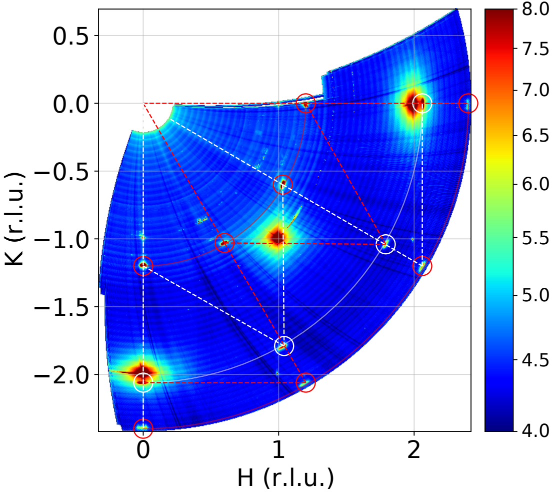
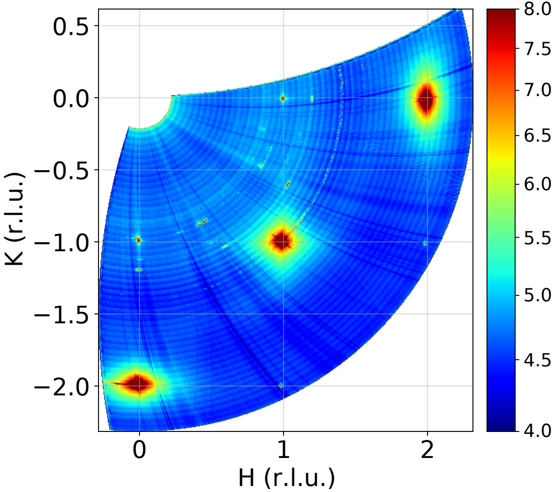


→ Pt(100)-Hex reconstruction.

Pt(100): only ammonia

Argon (mbar)	NH_3 (mbar)	O_2 (mbar)
500	0	0
420	0	80
410	10	80
485	10	5
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.



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500	0	0
420	0	80
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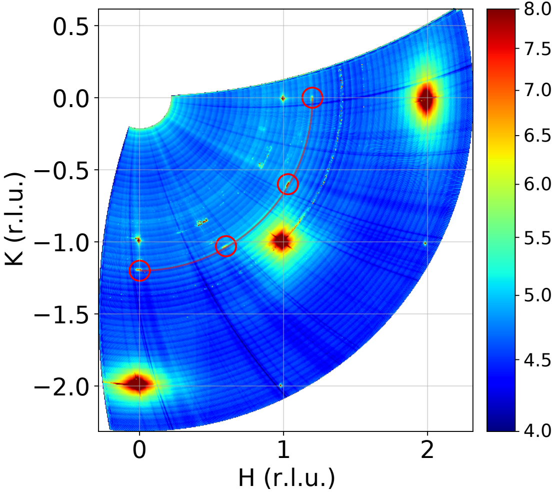
485	10	5
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.



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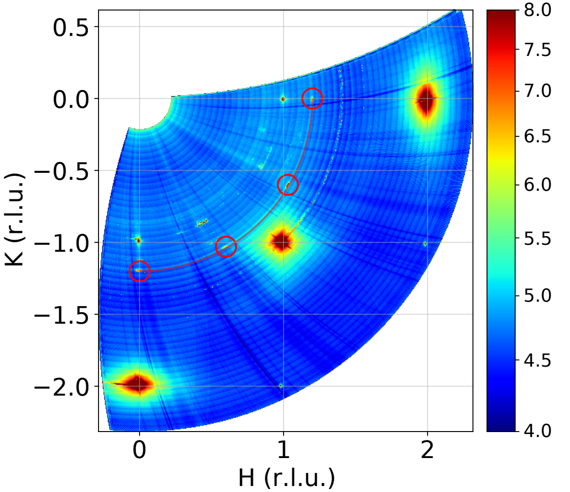
Argon (mbar)	NH_3 (mbar)	O_2 (mbar)
500	0	0
420	0	80
410	10	80
485	10	5
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.



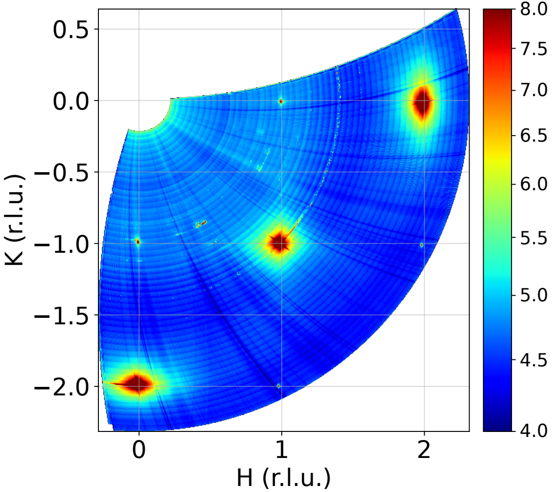
Pt(100)-Hex reconstruction linked to catalytic reaction?

Pt(100): back to inert atmosphere

Argon (mbar)	NH_3 (mbar)	O_2 (mbar)
500	0	0
420	0	80
410	10	80
485	10	5
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.

The initial surface is reproducible.

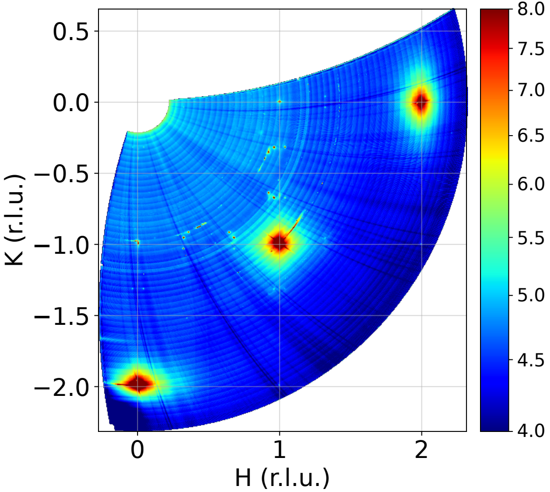


Removing the reagents brings back the Pt(100) bulk-terminated structure.

Pt(100): low oxygen pressure (5 mbar)

Argon (mbar)	NH_3 (mbar)	O_2 (mbar)
500	0	0
420	0	80
410	10	80
485	10	5
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.

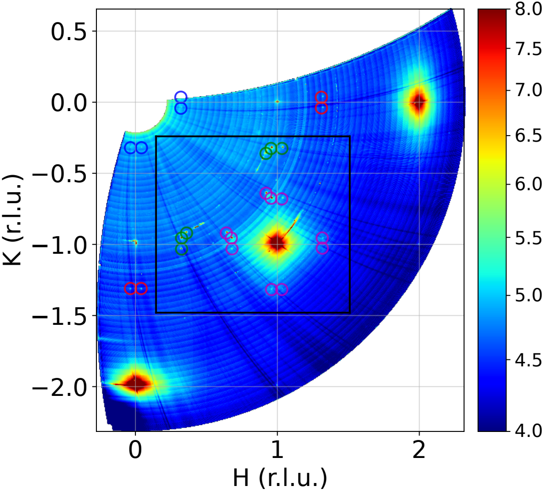


Pt(100): low oxygen pressure (5 mbar)

Argon (mbar)	NH_3 (mbar)	O_2 (mbar)
500	0	0
420	0	80
410	10	80
485	10	5
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.

Multiple new peaks appear!



Pt(100): low oxygen pressure (5 mbar)

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500	0	0
420	0	80
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485	10	5
490	10	0
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495	0	5

Partial pressures during reaction cycle.
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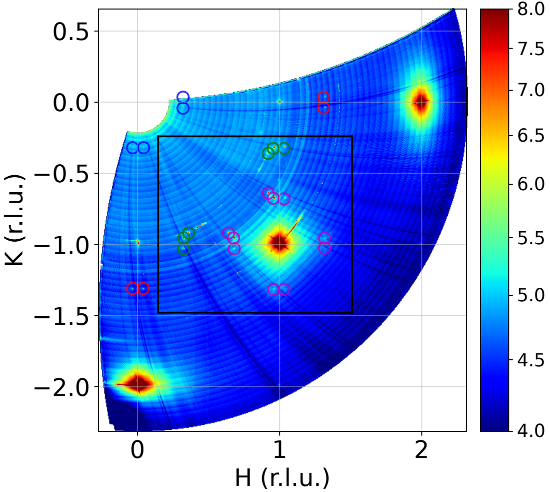

Pt(100)-Hex reconstruction linked to catalytic reaction!

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Partial pressures during reaction cycle.
In experimental order.

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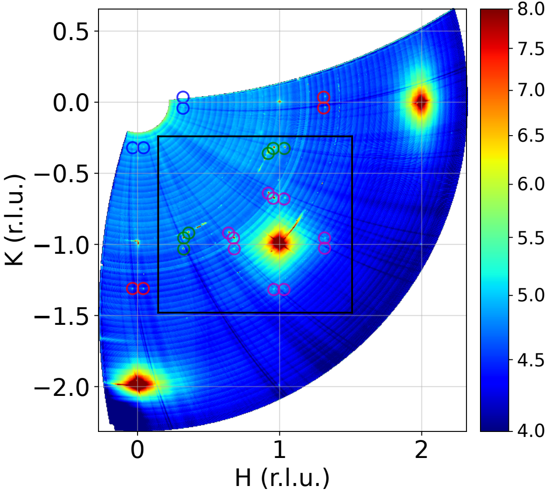


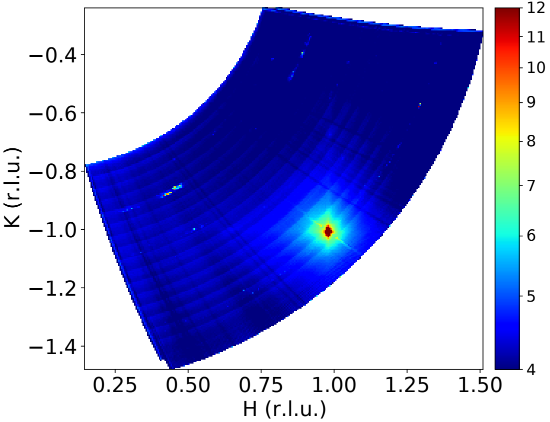
Pt(100)-Hex reconstruction linked to catalytic reaction!

Pt_3O_4 does not form at lower oxygen pressure!

Pt(100): Low oxygen pressure (5 mbar)

Argon (mbar)	NH_3 (mbar)	O_2 (mbar)
500	0	0
420	0	80
410	10	80
485	10	5
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.



Pt(100): Low oxygen pressure (5 mbar)

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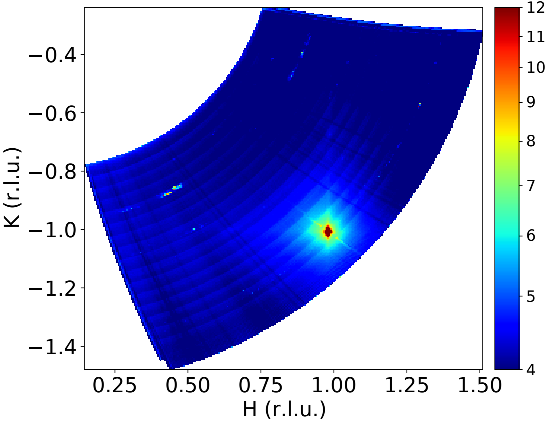
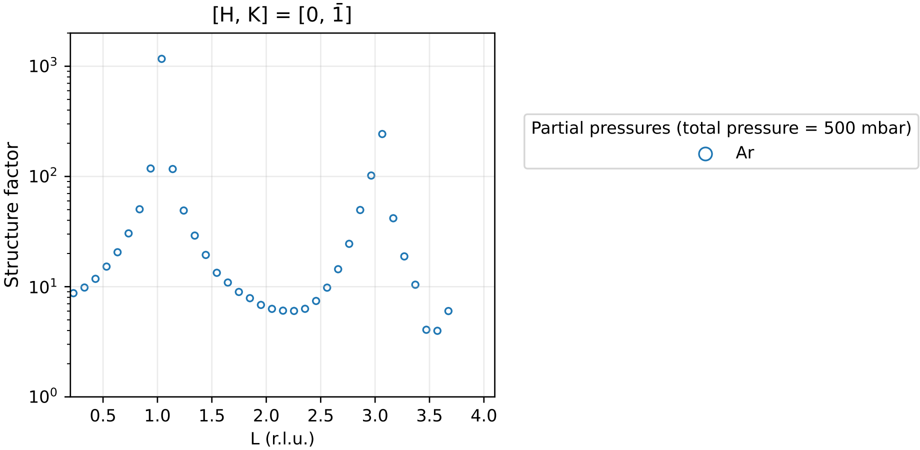
Partial pressures during reaction cycle.
In experimental order.

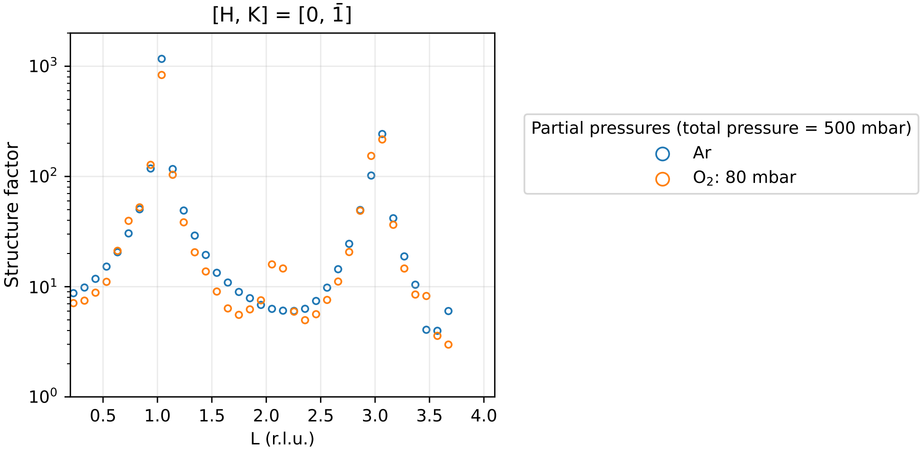


Transient structures!

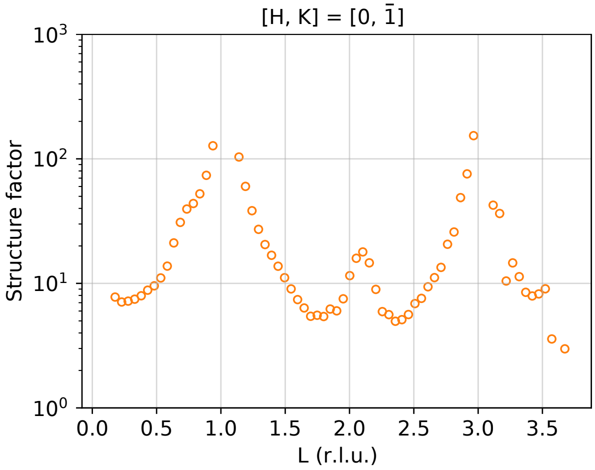
Pt(100): crystal truncation rods

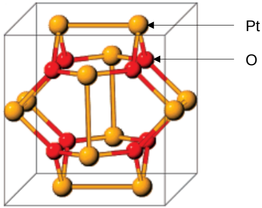


Pt(100): crystal truncation rods



Pt(100): Pt_3O_4 contribution to Pt(100) CTR



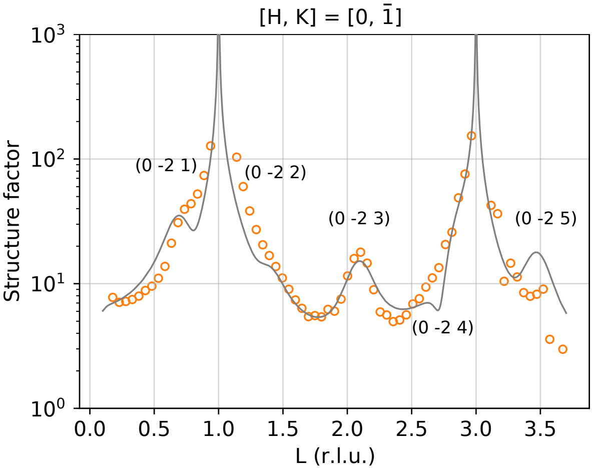


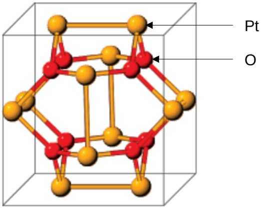
Pt_3O_4 unit cell[5].

Pt_3O_4 is at the source of intensity on the Pt(100) CTR!

[5] Seriani *et al.* Catalytic Oxidation Activity of Pt_3O_4 Surfaces and Thin Films, Phys. Chem. B, 2006

Pt(100): Pt_3O_4 contribution to Pt(100) CTR





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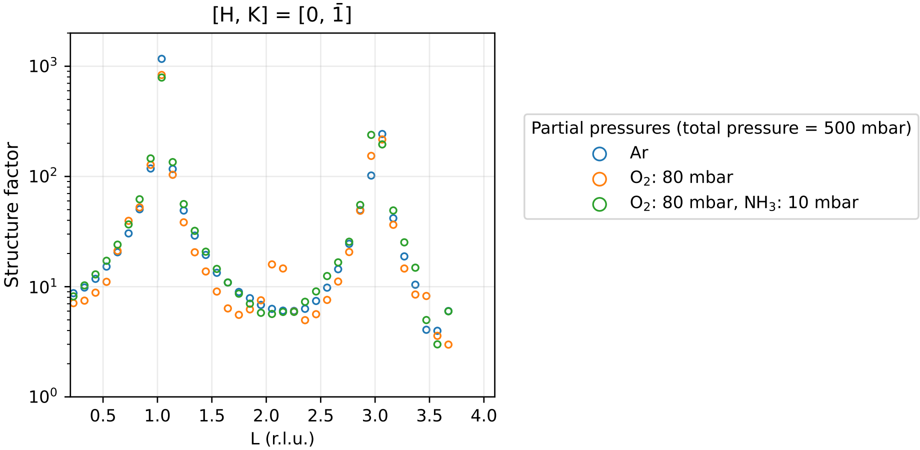
[5]Seriani *et al.* Catalytic Oxidation Activity of Pt_3O_4 Surfaces and Thin Films, Phys. Chem. B, 2006

Pt(100): crystal truncation rods



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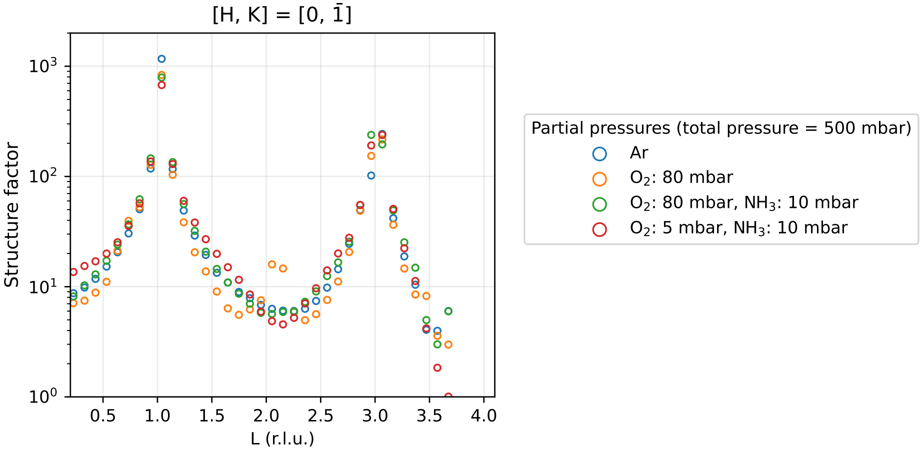

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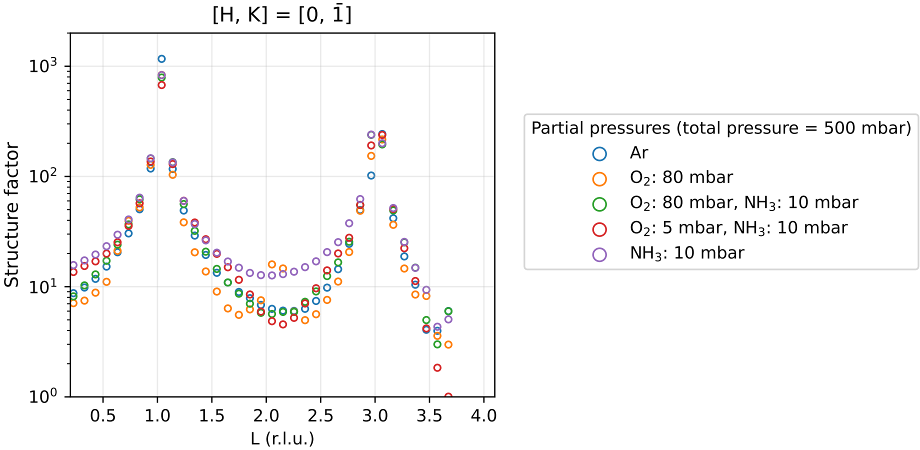

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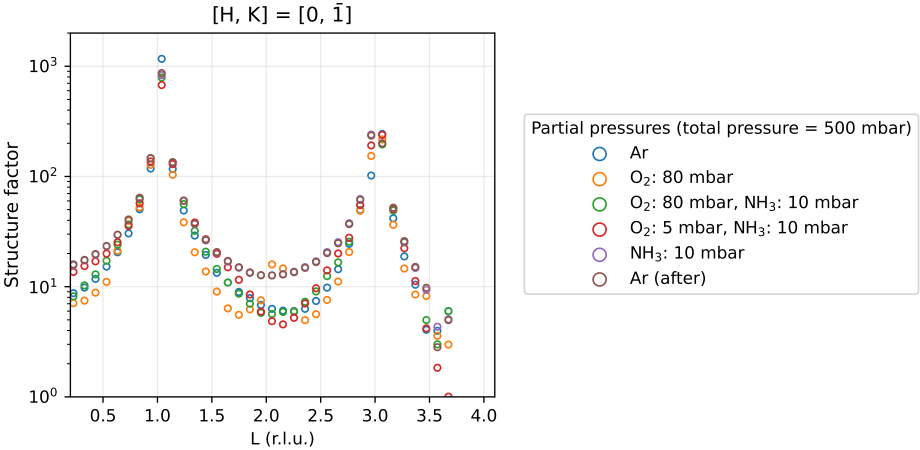

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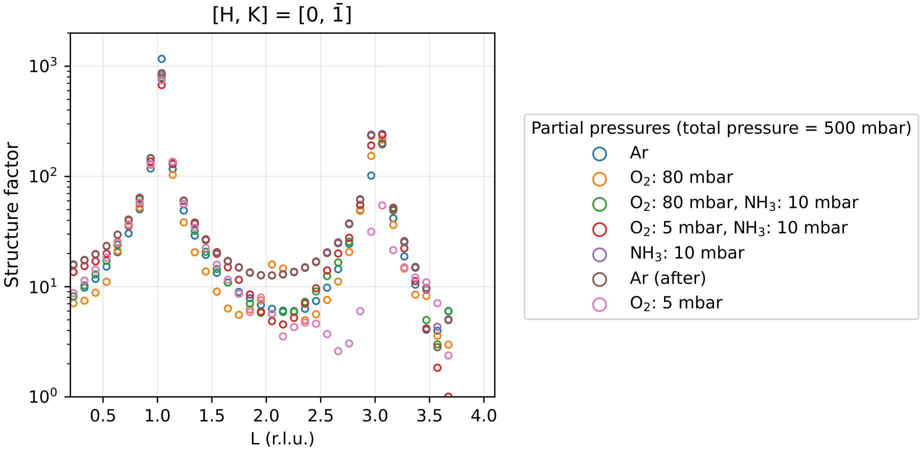

→ Important changes of roughness and surface strain are both visible.

Single crystals: summary

O_2 (mbar)	NH_3 (mbar)	Pt(111)	Pt(100)
80	0	Two rotated hexagonal lattices, Surface oxide after 9 h30 min. Increased surface roughness.	Pt(100)-(2 × 2) bulk Pt_3O_4, and signals shifted in H or K. Increased surface roughness.
80	10	Removal of all signals.	
5	10	Decreased surface roughness.	
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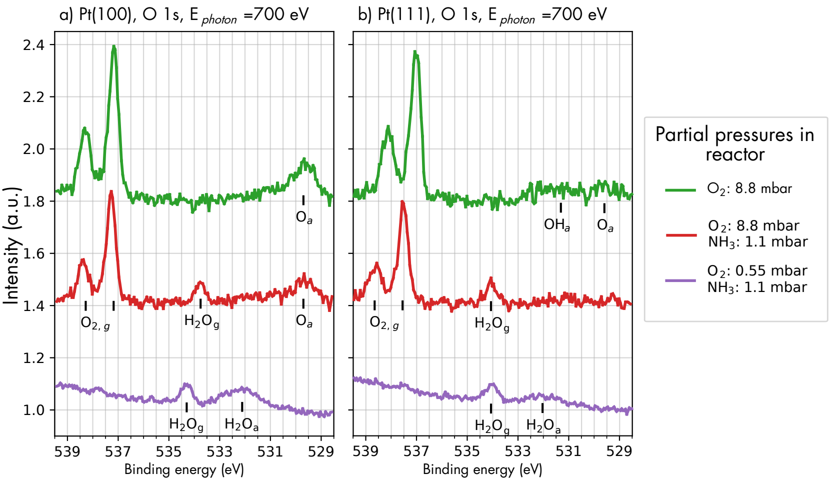
Can we identify the surface species responsible for the different behaviour?

X-ray photoelectron spectroscopy



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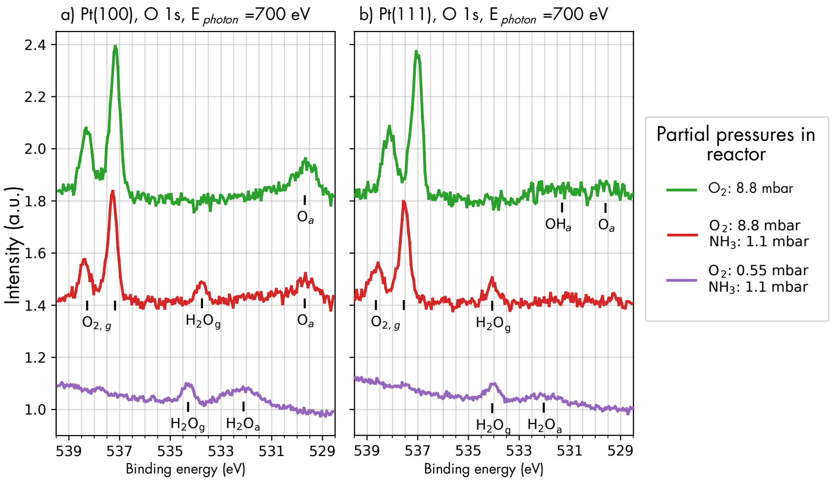

$P_{\mathrm{NO},(100)} > P_{\mathrm{NO},(111)}$, linked to oxygen adsorption?

Conclusion and perspectives

Conclusions

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- Study defect impact on strain and adsorption/catalytic properties.

I would like to thank the SOLEIL, CEA and ESRF staff for the support, and the ERC Carine as well as the GDR CohereX that supported the research.

Andrea Resta

Alessandro Coati

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Stéphane Labat

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Maxime Dupraz
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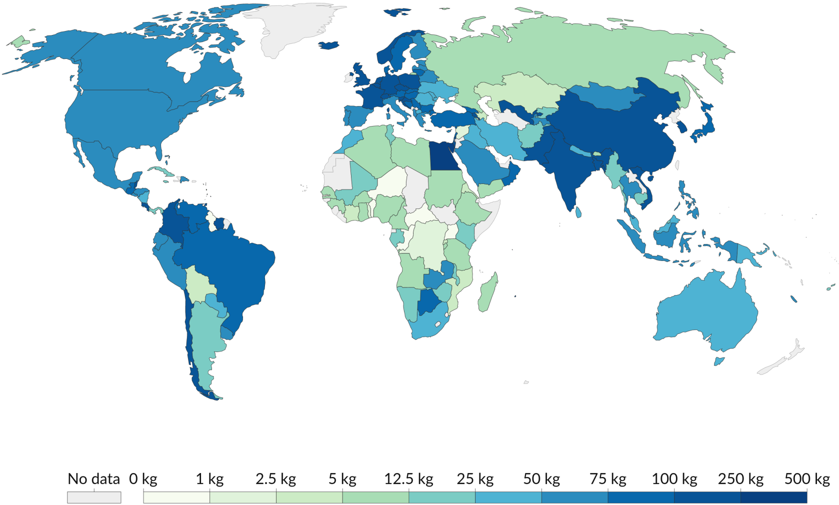
Clément Atlan
Steven Leake
Ewen Bellec
Edoardo Zatterin

Thanks to the members of the jury that have taken the time to follow this thesis!

Nitrogen fertilizer use per hectare of cropland, 2017

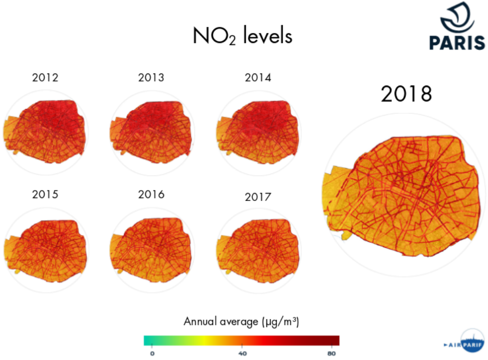
Application of nitrogen fertilizer, measured in kilograms of total nutrient per hectare of cropland.



Source: UN Food and Agricultural Organization (FAO)

OurWorldInData.org/fertilizers •

Environmental impact: NO_x



Annual limit of 40 µg/m^3, adapted from[6].

[6] État de la qualité de l'air à Paris, 2023

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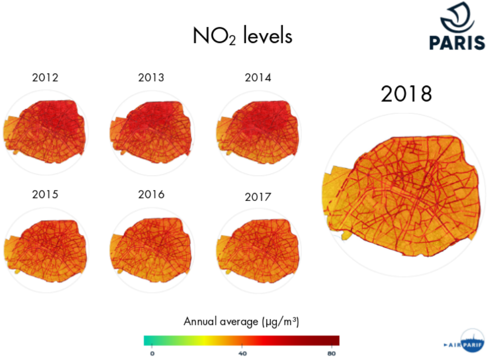

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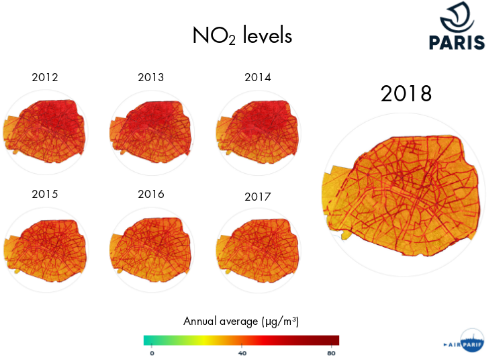

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- NO_x have a dramatic impact (toxic, corrosive, form smog and acid rain).
- Reducing NO_x possible with NH_3, but un-reacted NH_3 also toxic and corrosive.

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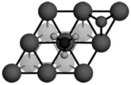
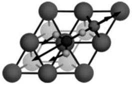
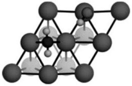
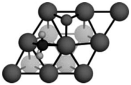
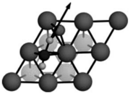
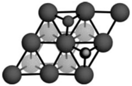
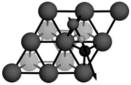
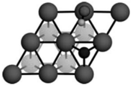
Reaction mechanism

Reaction	Reactant state	Transition state	Product state
$NH_3 + O$			
$NH_2 + O$			
$NH + O$			

[7] Imbihl *et al.* Catalytic ammonia oxidation on platinum: Mechanism and catalyst restructuring at high and low pressure, PCCP, 2007

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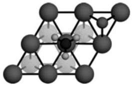
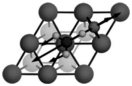
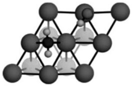
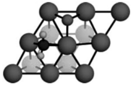
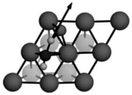
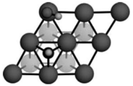
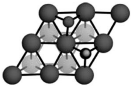
$NH_3 + O$			
$NH_2 + O$			
$NH + O$			

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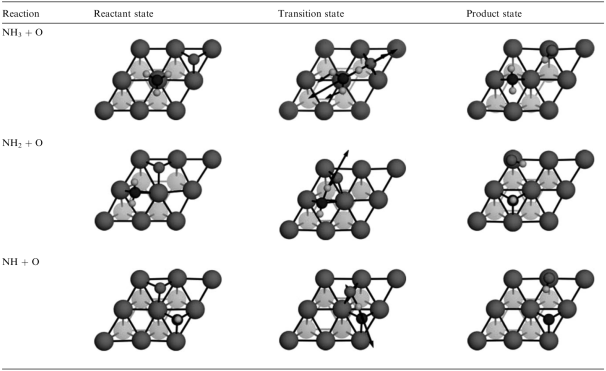

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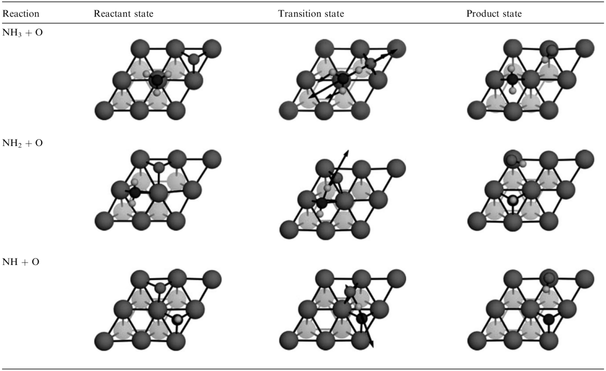

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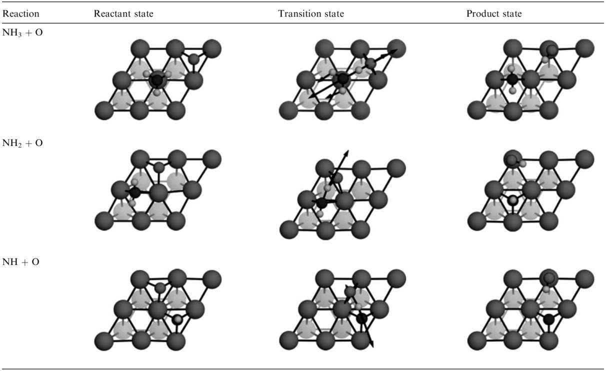

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- Low oxygen coverage $\rightarrow N_2$, high oxygen coverage $\rightarrow$NO.

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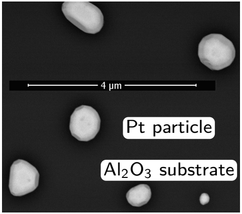

SEM image of epitaxied Pt particles (collaboration with Pr. Rabkin - TECHNION).

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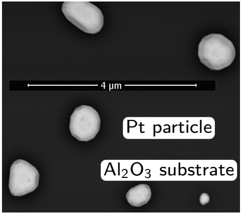

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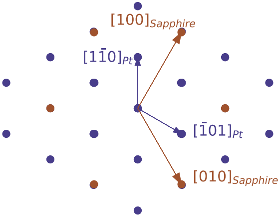

Real space epitaxy relationship.

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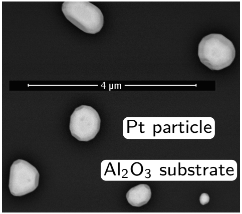

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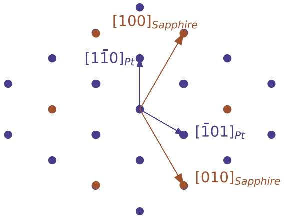

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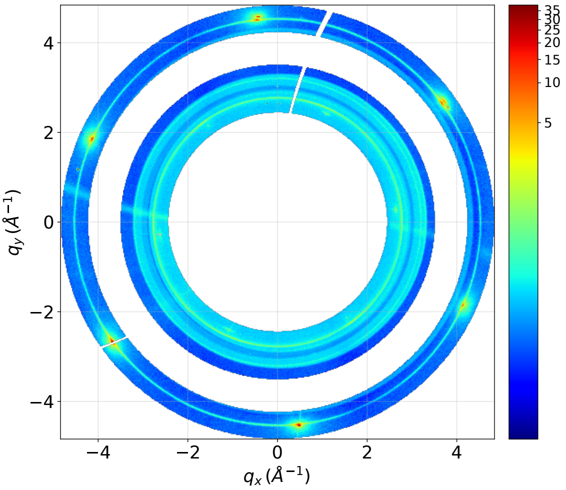

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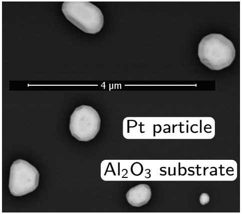

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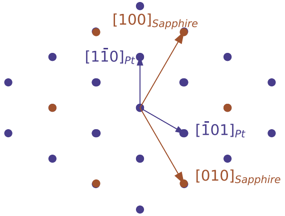

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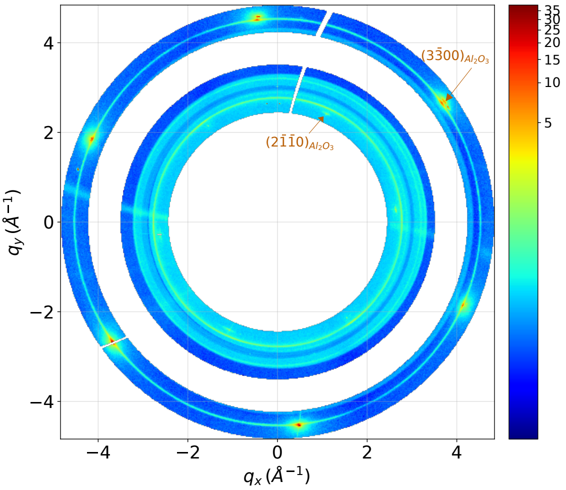

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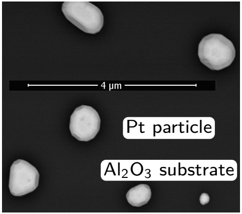

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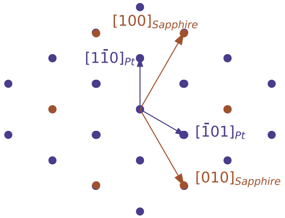

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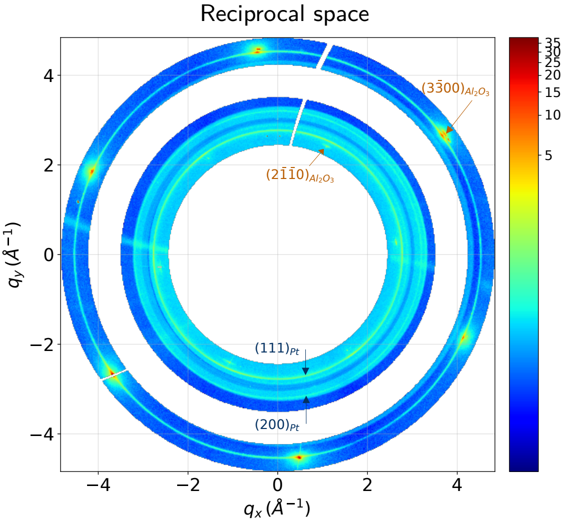

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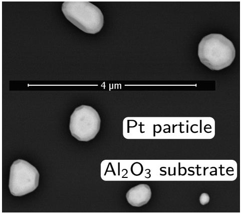

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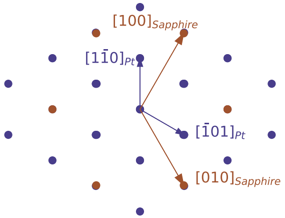

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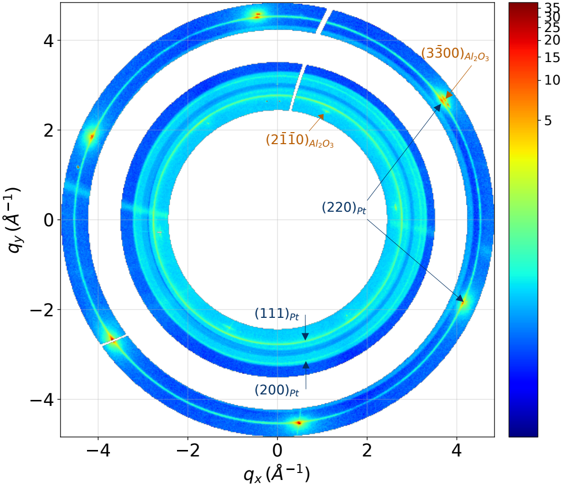
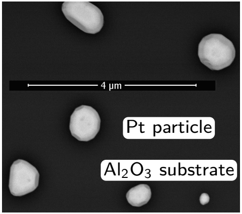
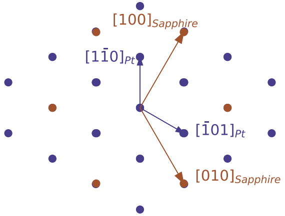


Pt(111)||α-Al_2O_3(0001) epitaxy

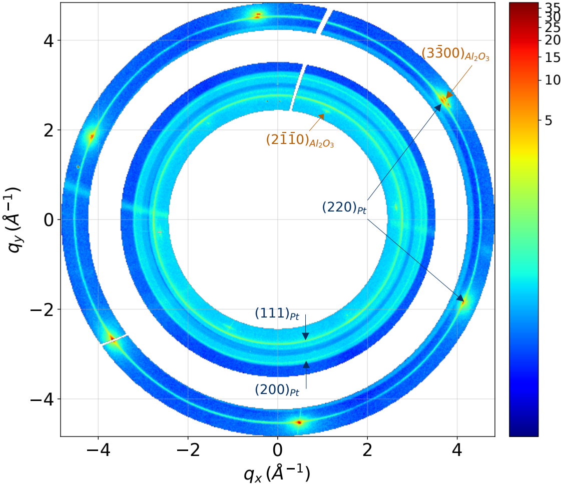


SEM image of epitaxied Pt particles (collaboration with Pr. Rabkin - TECHNION).



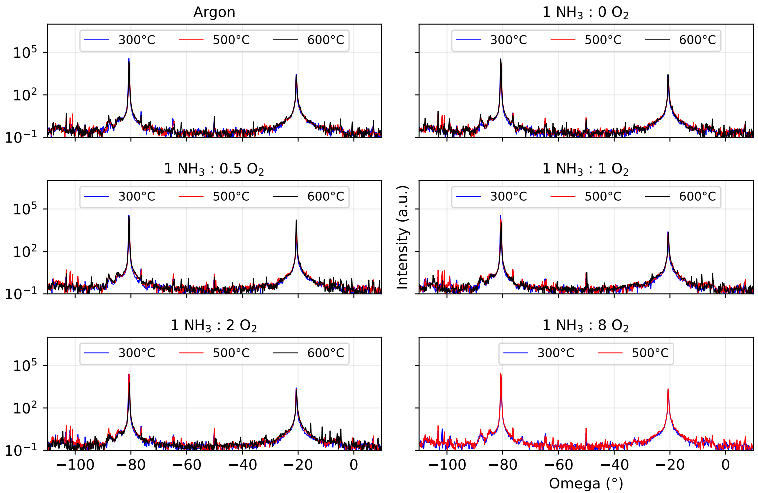
Real space epitaxy relationship.

Reciprocal space

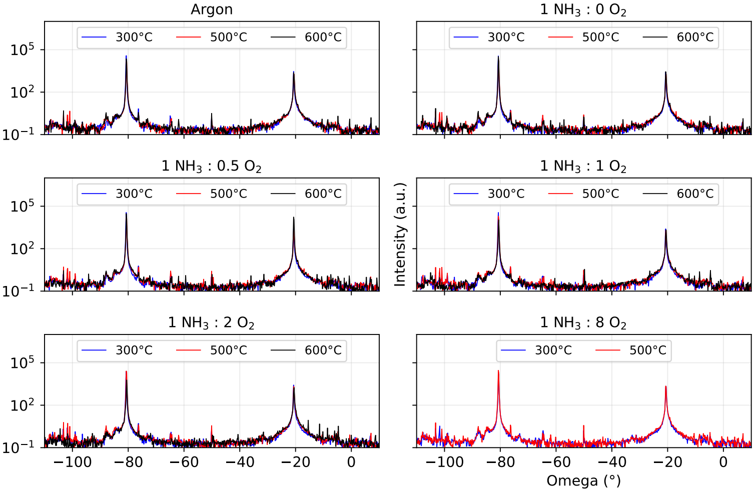


$\rightarrow$ (111)-orientated Pt particles on substrate.

Pt(111)||α-Al_2O_3(0001) epitaxy

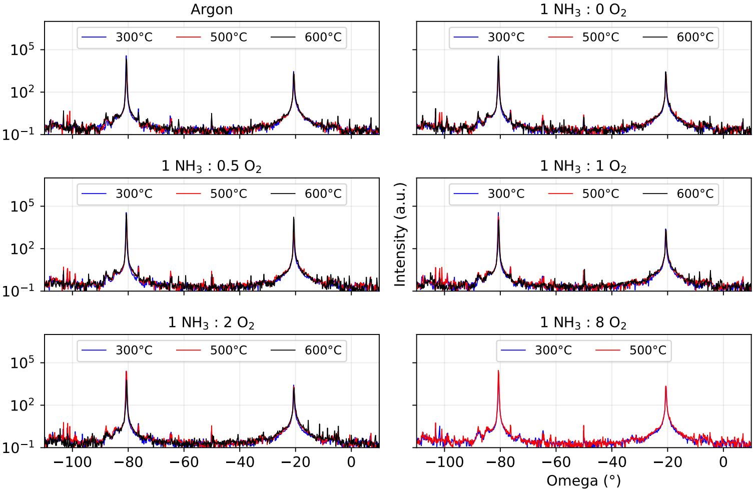


Pt(111)||α-Al_2O_3(0001) epitaxy



No change of intensity for the Pt Bragg peaks during the reaction.

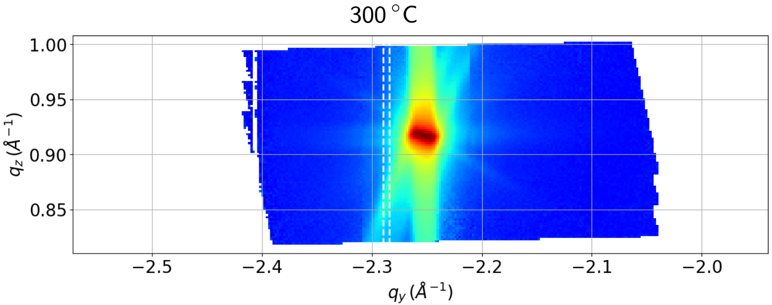
Pt(111)||α-Al_2O_3(0001) epitaxy

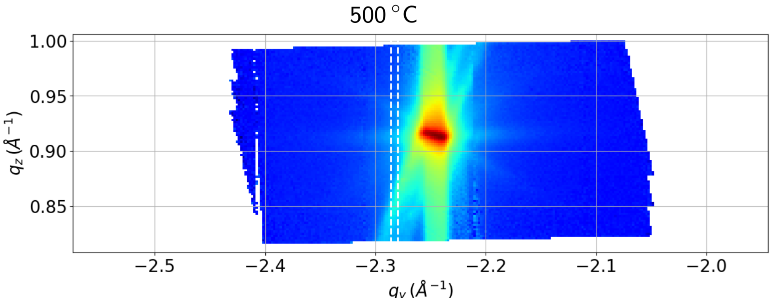


No change of intensity for the Pt Bragg peaks during the reaction.

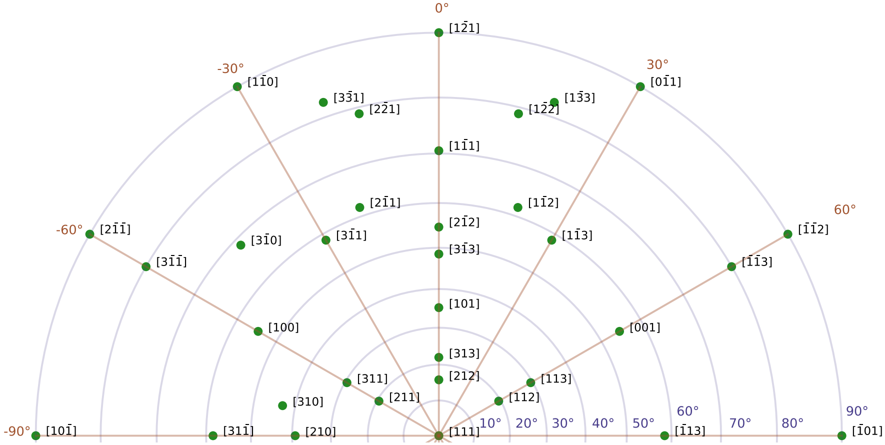
$\rightarrow$ Stable epitaxy up to 600 °C, 80 mbar of O_2 and 10 mbar of NH_3.

{110} facet signal during SXRD



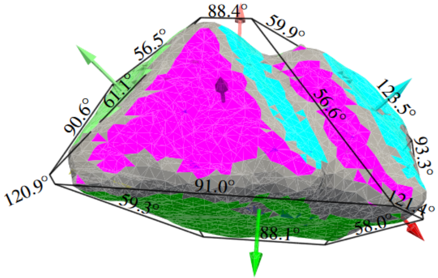


Collective behaviour of Pt particles



[111] stereographic projection (for a face-centred cubic lattice).

Facets retrieval



A mesh is constructed from the particle voxels.

A mesh of the surface is created by the marching-cubes algorithm, resulting in a surface made out of triangles, that in 3D can take up to 26 different orientations.

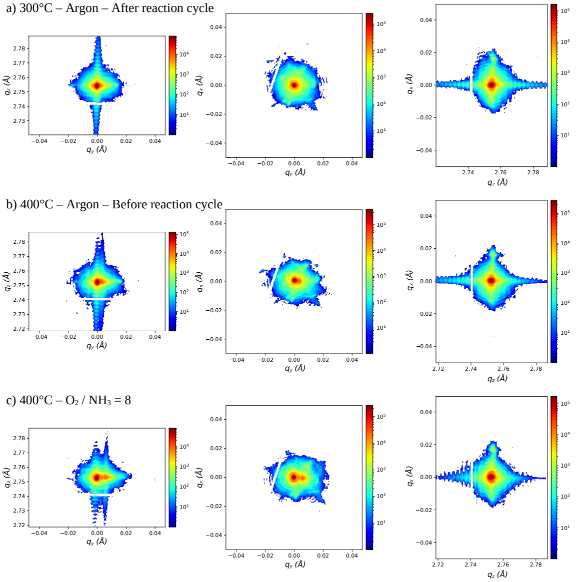
The surface is then smoothed to remove the steps created by the voxel size.

The main parameters to retrieve the facets are[1]:

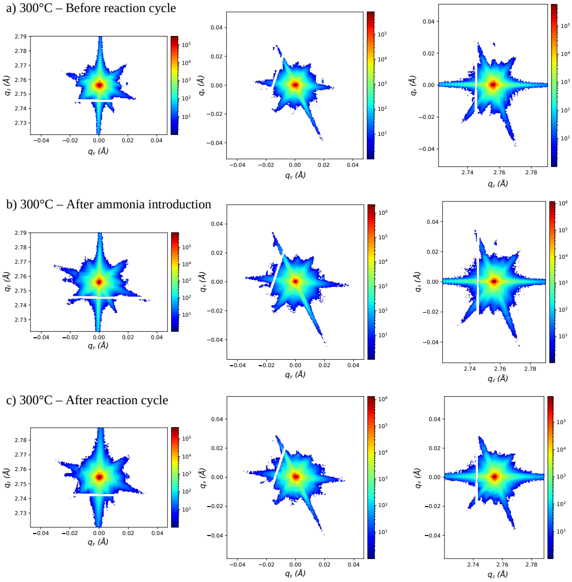
- facet normal direction.
- facet size.
- roughness tolerance.

[1]Facet Analyser: ParaView plugin for automated facet detection and measurement of interplanar angles of tomographic objects. Grothausmann, R., Beare, R. (2015) The MIDAS Journal

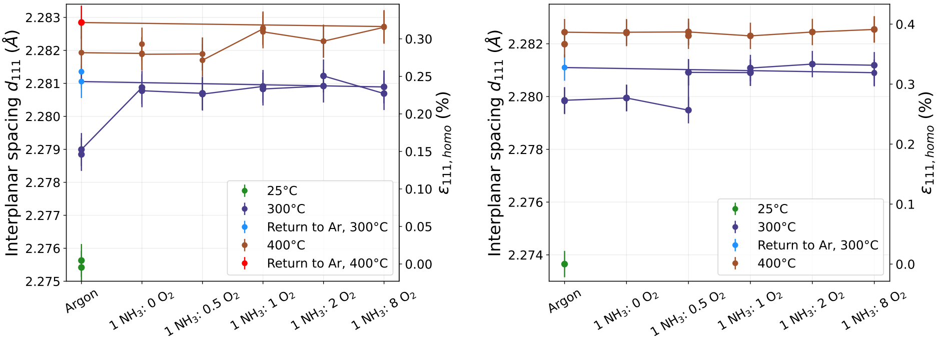
Diffraction patterns - small particle $\varnothing \approx 350\,\mathrm{nm}$



Diffraction patterns - large particle $\varnothing \approx 800\,\mathrm{nm}$



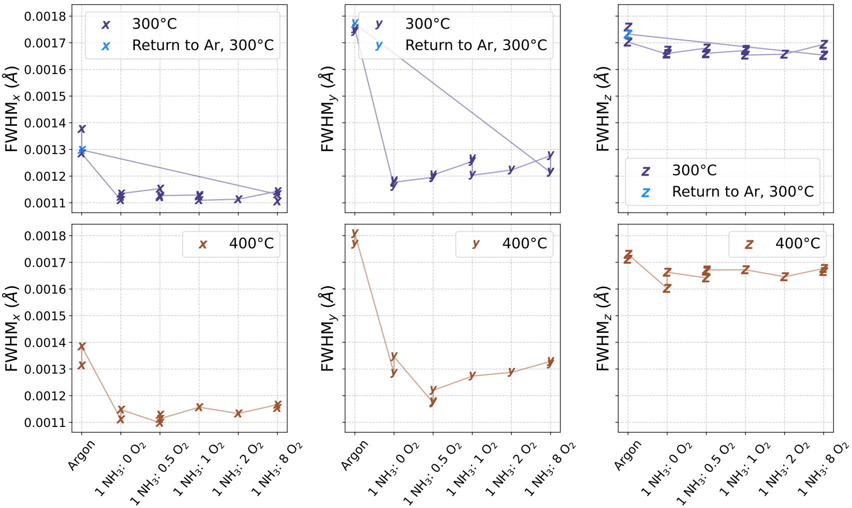
Homogeneous strain



Average interplanar spacing d_{111} evolution for small (left, $\varnothing \approx 350\,\text{nm}$) and large particle (right, $\varnothing \approx 800\,\text{nm}$) as a function of the ammonia to oxygen ratio.

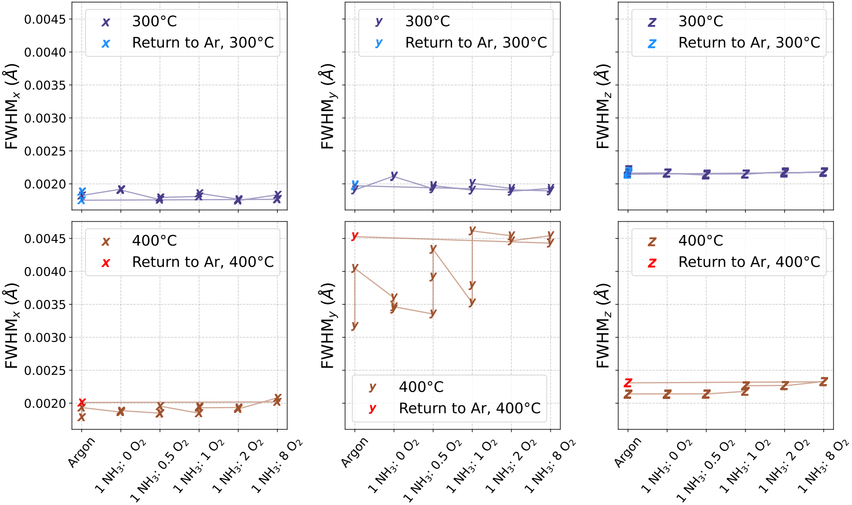
$\rightarrow$ Different behaviours are observed!

Strain evolutions - large particle $\varnothing \approx 800\,\mathrm{nm}$



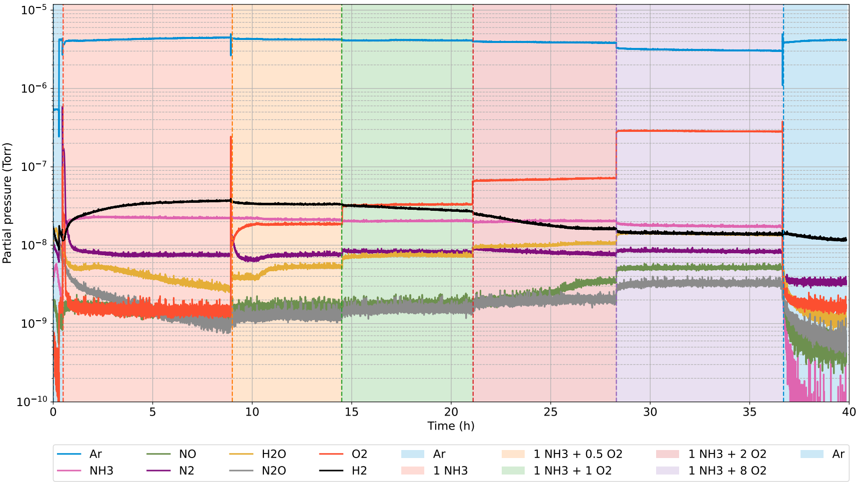
Large variation of the FWHM at 300 °C and 400 °C during ammonia introduction / removal.

Strain evolutions - small particle $\varnothing \approx 350\,\mathrm{nm}$

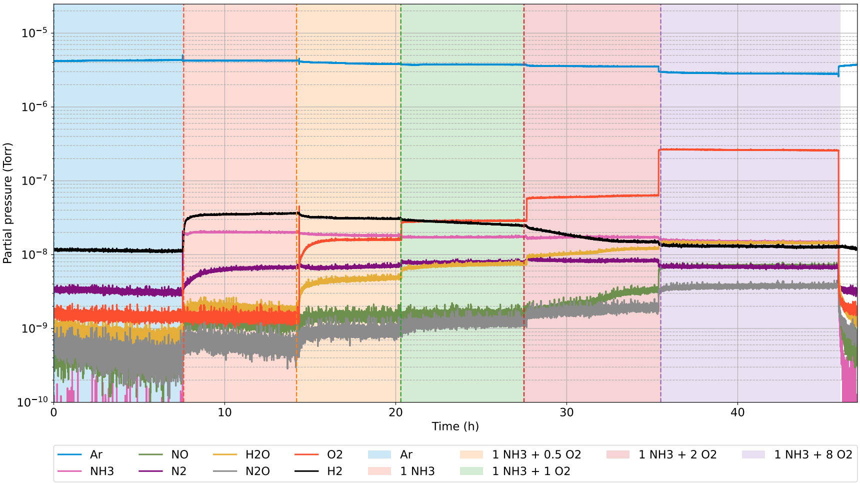


Large variation of the FWHM at 400 °C during reaction.

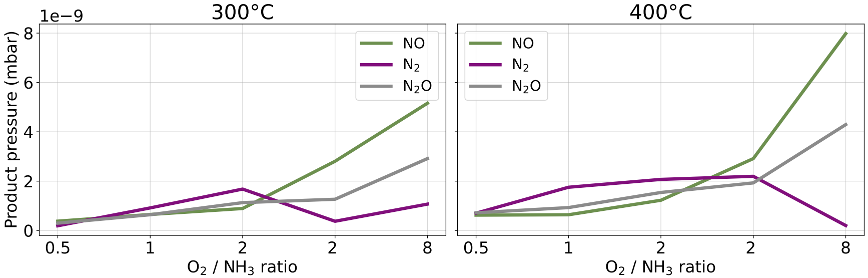
Pt particles: RGA signals during BCDI (300°C)



Pt particles: RGA signals during BCDI (400°C)



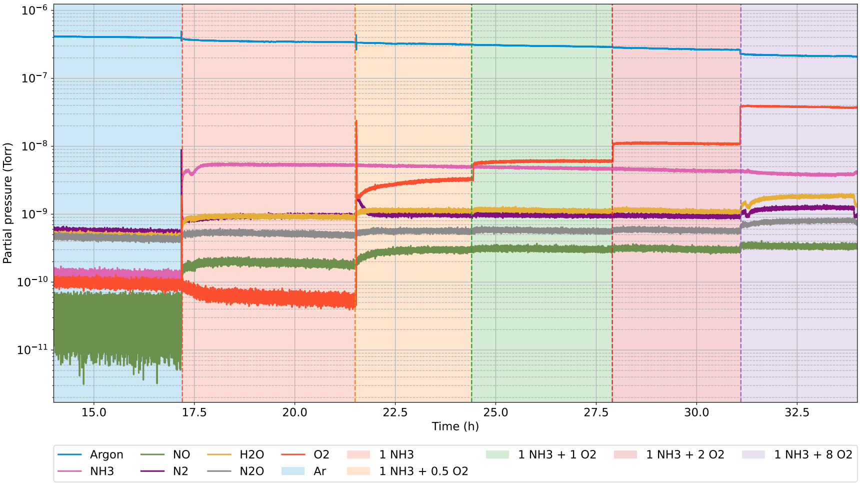
Pt particles: RGA signals during BCDI



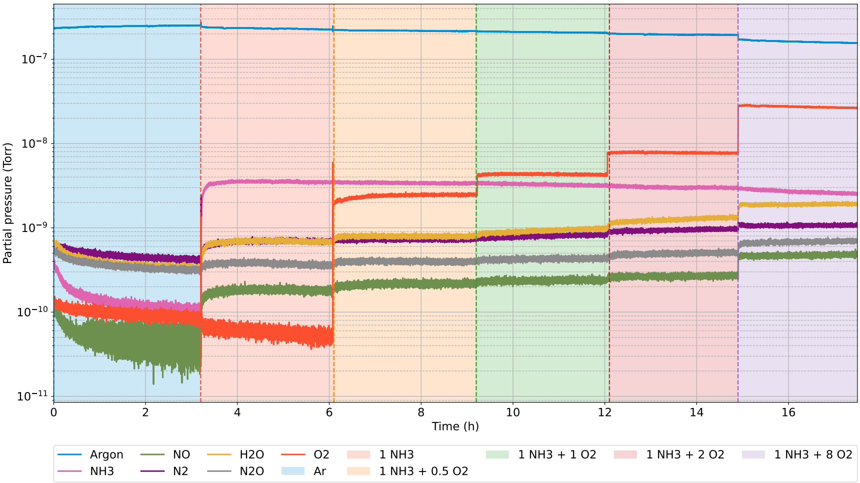
Similar behaviour as reported in literature.

Transition observed when O_2 / NH_3 : 2 $\rightarrow$ increased selectivity towards NO.

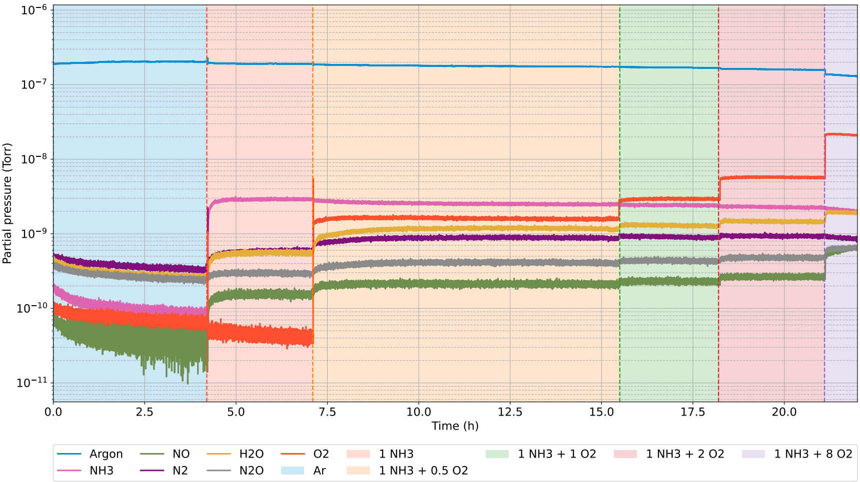
Pt particles: RGA signals during SXRD (300°C)



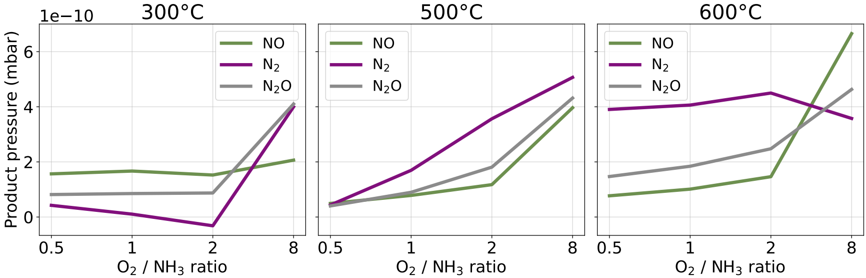
Pt particles: RGA signals during SXRD (500°C)



Pt particles: RGA signals during SXRD (600°C)

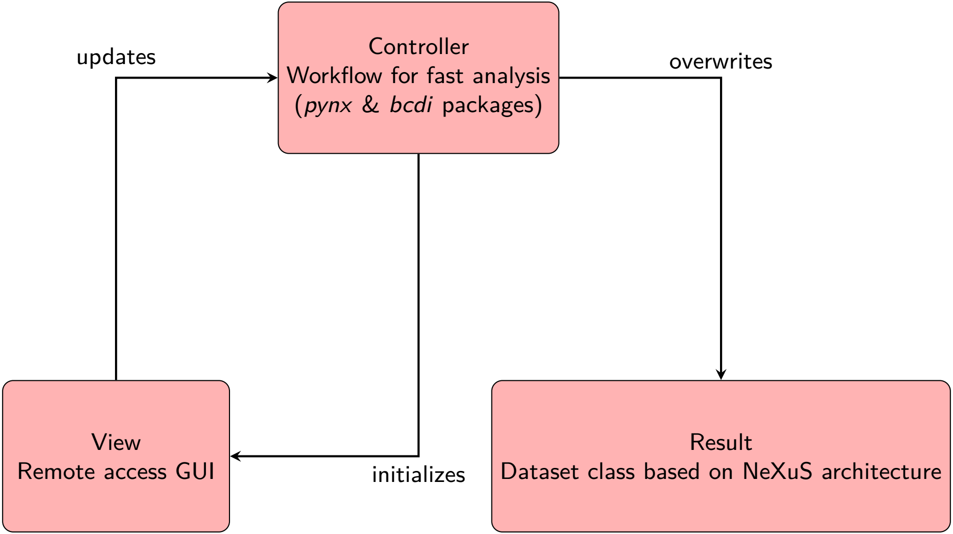


Pt particles: RGA signals during SXRD



Similar behaviour as reported in literature.

Software architecture



Software architecture

Controller
Workflow for fast analysis (pynx, bcdi, ...)

overwrites

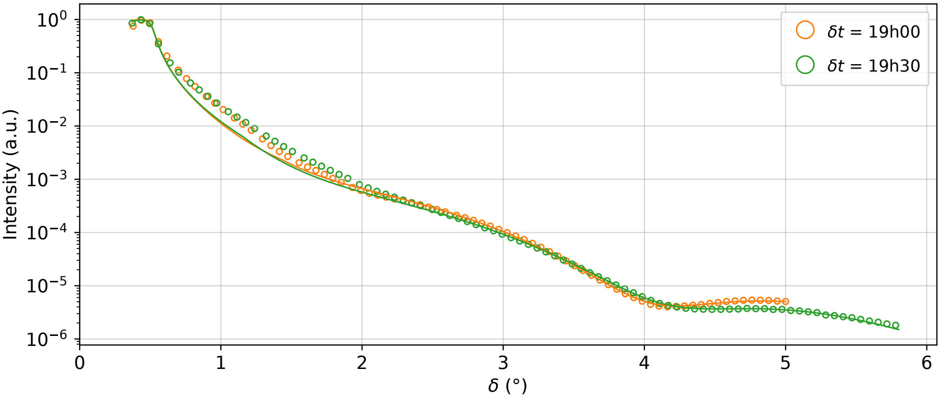
Result
Dataset class based on
NeXuS architecture

Advanced users can use terminal scripts for quick analysis.

Gwaihir video example

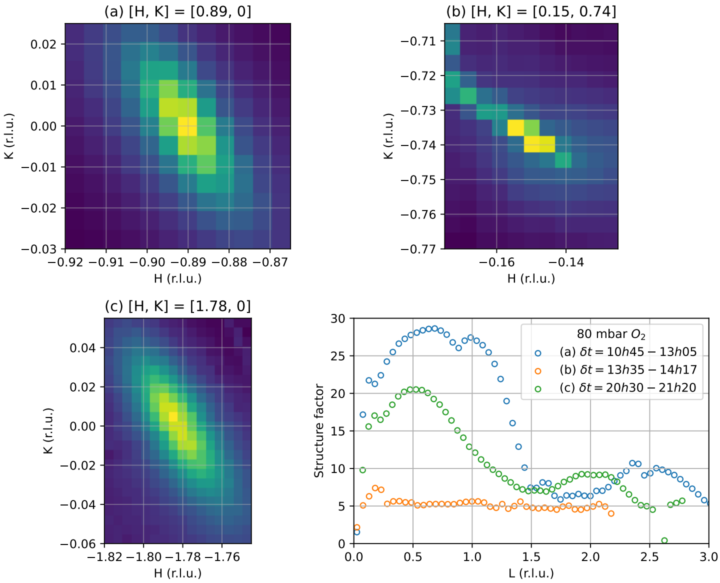
External users first approach to BCDI.

Pt(111): structures appear under 80 mbar of O_2

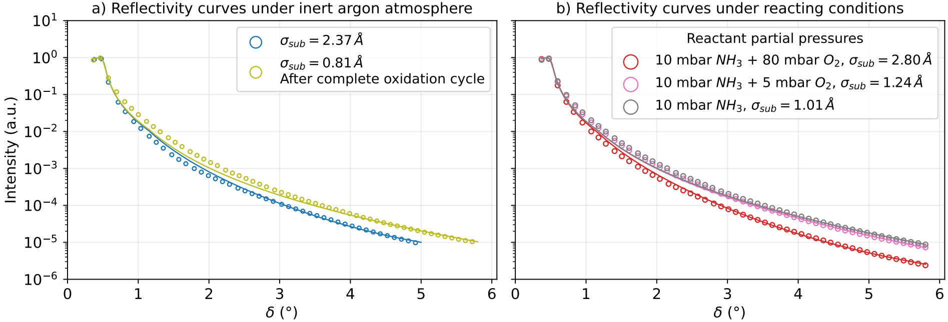


Reflectivity measurements indicate the presence of a 14 Å thick layer.

Pt(111): structures appear under 80 mbar of O_2

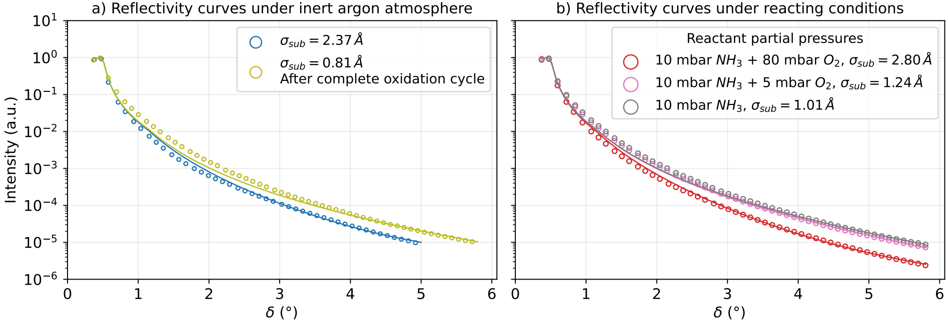


Pt(111): reflectivity during ammonia oxidation



High roughness under oxygen, and important O_2 / NH_3 ratios.

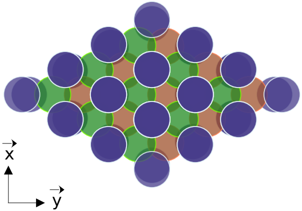
Pt(111): reflectivity during ammonia oxidation

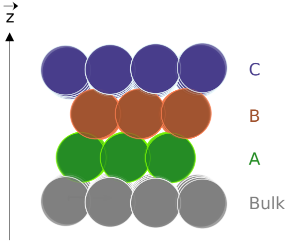


High roughness under oxygen, and important O_2 / NH_3 ratios.

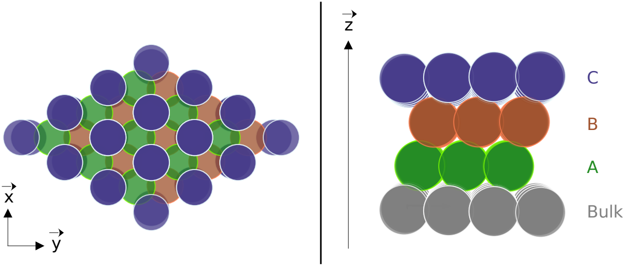
Low roughness under low O_2 / NH_3 ratios, and ammonia.

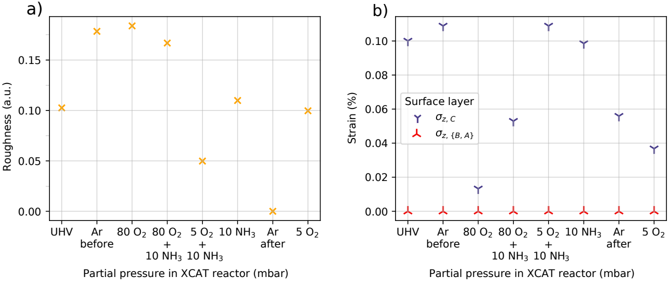
Pt(111): crystal truncation rods



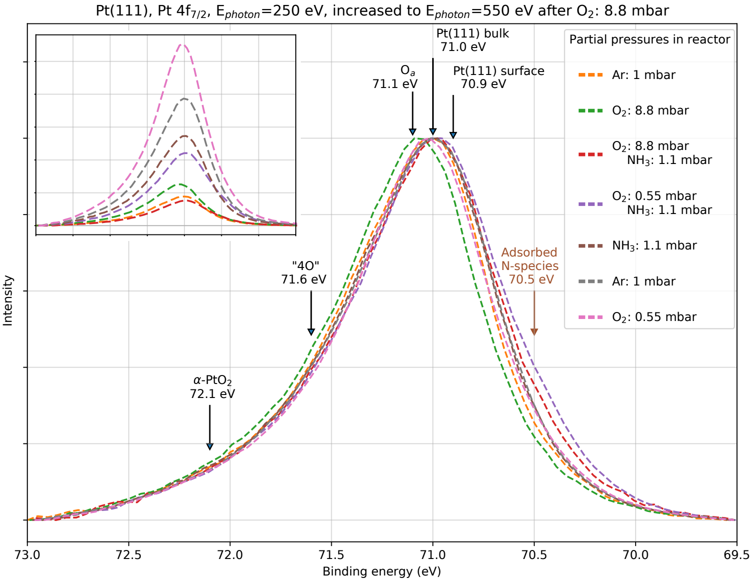


Pt(111): crystal truncation rods

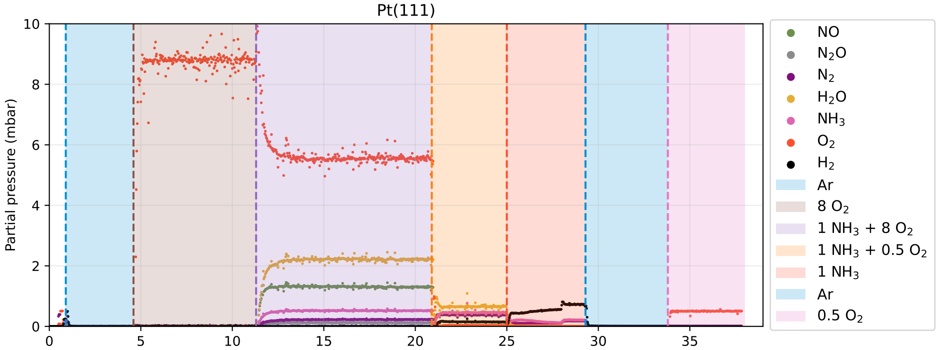




Pt(111): x-ray photoelectron spectroscopy



Pt(111): x-ray photoelectron spectroscopy

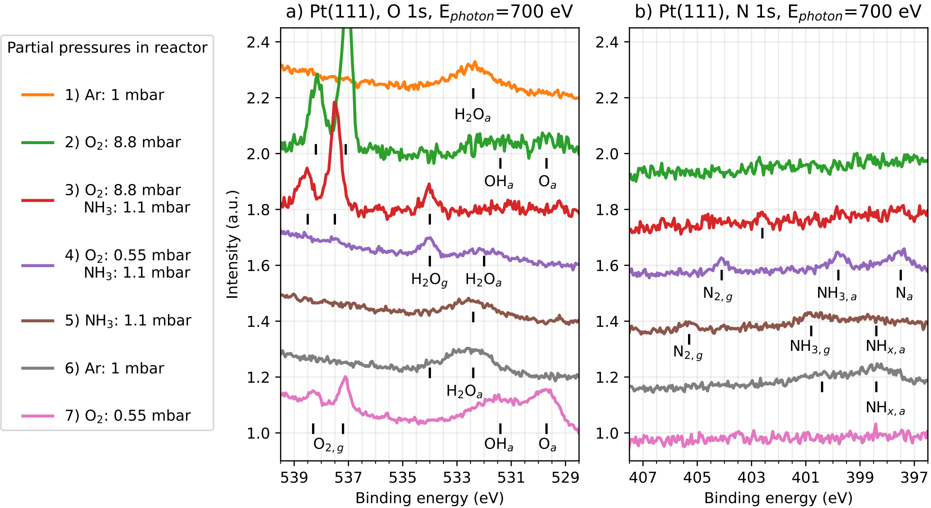


Pt(111): x-ray photoelectron spectroscopy

Partial pressures (mbar)	Ar	1	0	0	0	0	1	0
	NH_3	0	0	1.1	1.1	1.1	0	0
	O_2	0	8.8	8.8	0.55	0	0	0.55
Gas signals (decreasing pressure order)		Ar	O_2	O_2, H_2O, NO NH_3, N_2, N_2O	H_2O, NH_3 N_2, H_2	H_2, NH_3 N_2	Ar	O_2
N 1s: peak positions		No data	No peak	402.6 eV	404.1 eV 399.8 eV 397.5 eV	405.3 eV 400.8 eV 398.4 eV	400.4 eV 398.4 eV	No peak
Attributed surface species				Not indexed	$N_{2,g}$ $NH_{3,a}$ N_a	$N_{2,g}$ $NH_{3,g}$ $NH_{x,a}$	$NH_{3,a}$ $NH_{x,a}$	
O 1s: peak positions		532.4 eV	538.2 eV 537.1 eV 531.4 eV 529.7 eV	538.5 eV 537.5 eV 534.0 eV	534.0 eV 532.0 eV	532.4 eV	534.0 eV 532.4 eV	538.3 eV 537.2 eV 531.4 eV 529.7 eV
Attributed surface species		H_2O_a	$O_{2,g}$ $O_{2,g}$ OH_a O_a	$O_{2,g}$ $O_{2,g}$ H_2O_g	H_2O_g H_2O_a	H_2O_a	H_2O_g H_2O_a	$O_{2,g}$ $O_{2,g}$ OH_a O_a

Indexing of peaks measured during ammonia oxidation of the Pt(111) surface.

Pt(111): x-ray photoelectron spectroscopy

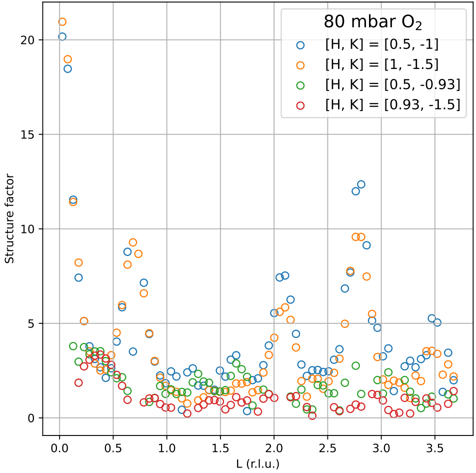


Pt(100): structures appear under 80 mbar of O_2

Argon (mbar)	NH_3 (mbar)	O_2 (mbar)
500	0	0
420	0	80
410	10	80
485	10	5
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.

Bulk Pt_3O_4 is formed epitaxied on the Pt(100) surface.

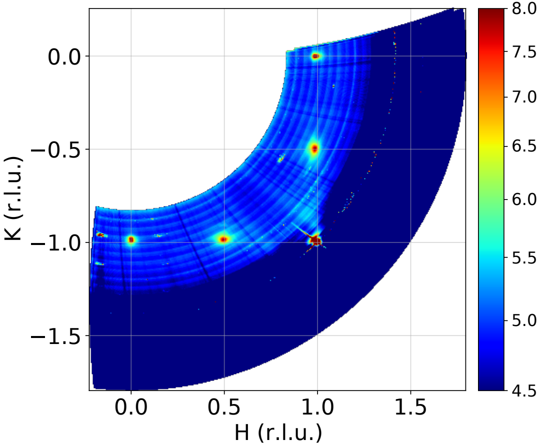


Pt(100): reaction conditions, O_2 / NH_3 : 8

Argon (mbar)	NH_3 (mbar)	O_2 (mbar)
500	0	0
420	0	80
410	10	80
485	10	5
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.

The addition of NH_3 removes the shifted peaks.

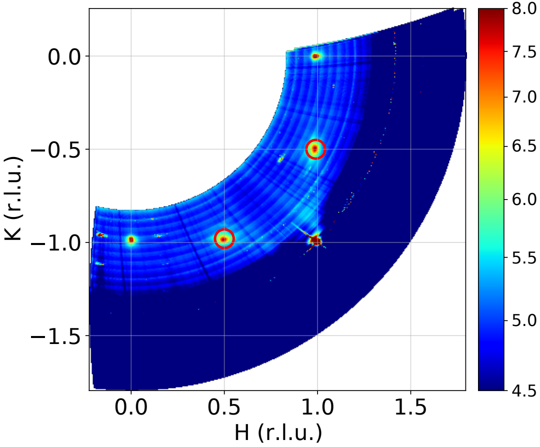


Pt(100): reaction conditions, O_2 / NH_3 : 8

Argon (mbar)	NH_3 (mbar)	O_2 (mbar)
500	0	0
420	0	80
410	10	80
485	10	5
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.

The addition of NH_3 removes the shifted peaks.



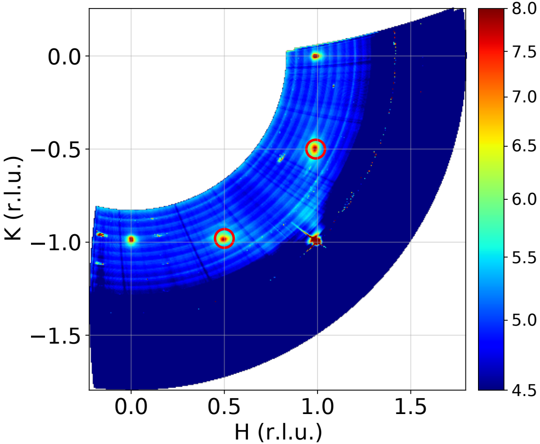
Peaks linked to Pt_3O_4 are still visible.

Pt(100): reaction conditions, O_2 / NH_3 : 8

Argon (mbar)	NH_3 (mbar)	O_2 (mbar)
500	0	0
420	0	80
410	10	80
485	10	5
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.

The addition of NH_3 removes the shifted peaks.



Peaks linked to Pt_3O_4 are still visible.

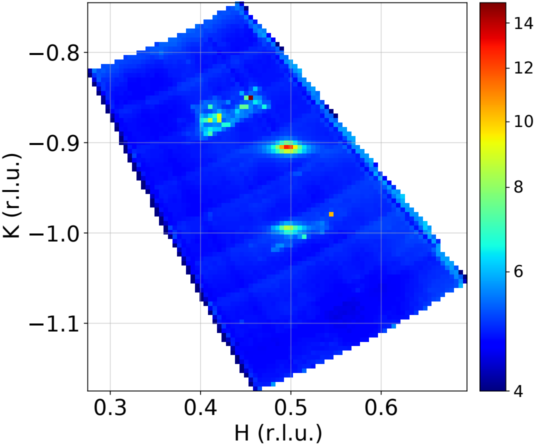
The heater has failed during the reacting conditions.

Pt(100): structures appear under 80 mbar of O_2

Argon (mbar)	NH_3 (mbar)	O_2 (mbar)
500	0	0
420	0	80
410	10	80
485	10	5
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.

The sample was cleaned and put again under oxygen atmosphere.

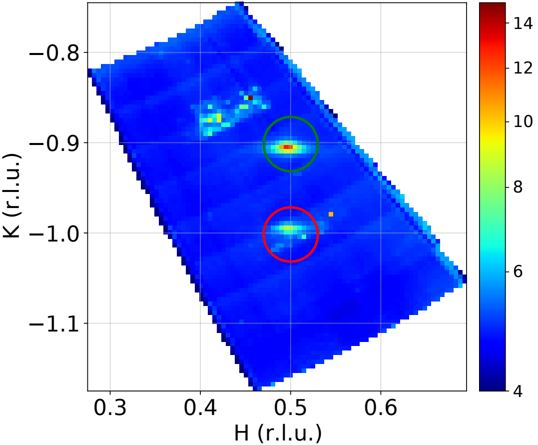


Pt(100): structures appear under 80 mbar of O_2

Argon (mbar)	NH_3 (mbar)	O_2 (mbar)
500	0	0
420	0	80
410	10	80
485	10	5
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.

The sample was cleaned and put again under oxygen atmosphere.



Similar in-plane signals are observed!

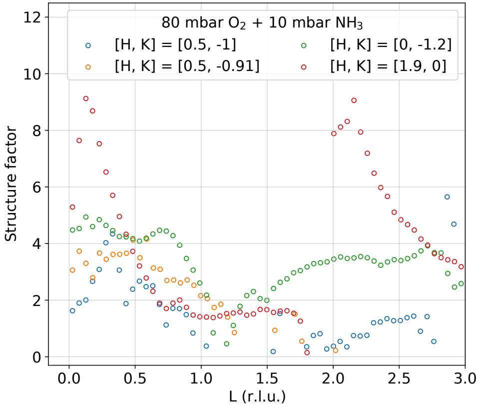
Pt(100): reaction conditions, O_2 / NH_3 : 8

Argon (mbar)	NH_3 (mbar)	O_2 (mbar)
500	0	0
420	0	80
410	10	80
485	10	5
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.

(10 × 10) reconstructions observed.

Reaction conditions favour NO .

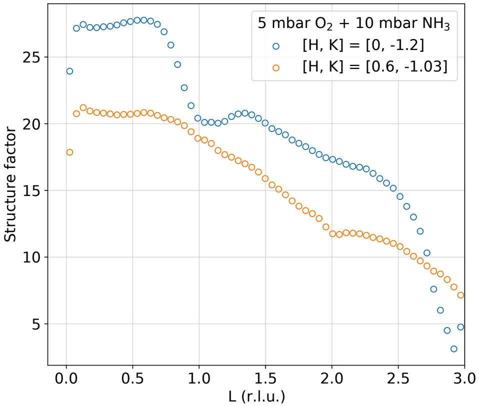


Pt(100): reaction conditions, O_2 / NH_3 : 0.5

Argon (mbar)	NH_3 (mbar)	O_2 (mbar)
500	0	0
420	0	80
410	10	80
485	10	5
490	10	0
500	0	0
495	0	5

Partial pressures during reaction cycle.
In experimental order.

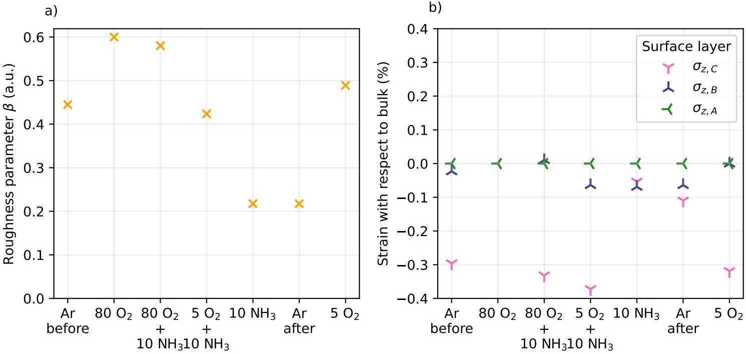
Lowering O_2 pressure to conditions favoring N_2 .



→ Pt(100)-Hex reconstruction.

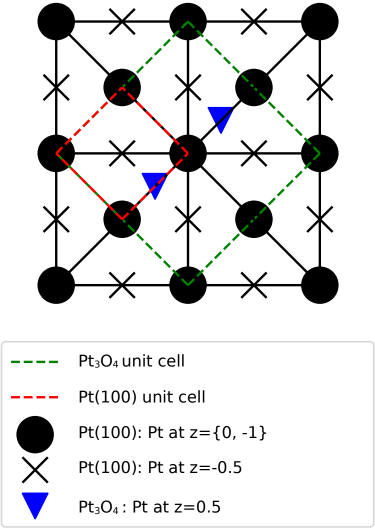
Pt(100)-Hex is a monolayer, responsible for N_2 selectivity?

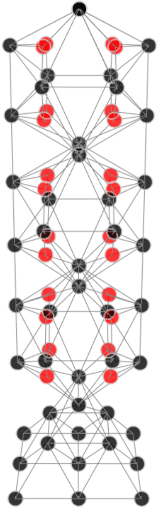
Pt(100): crystal truncation rods



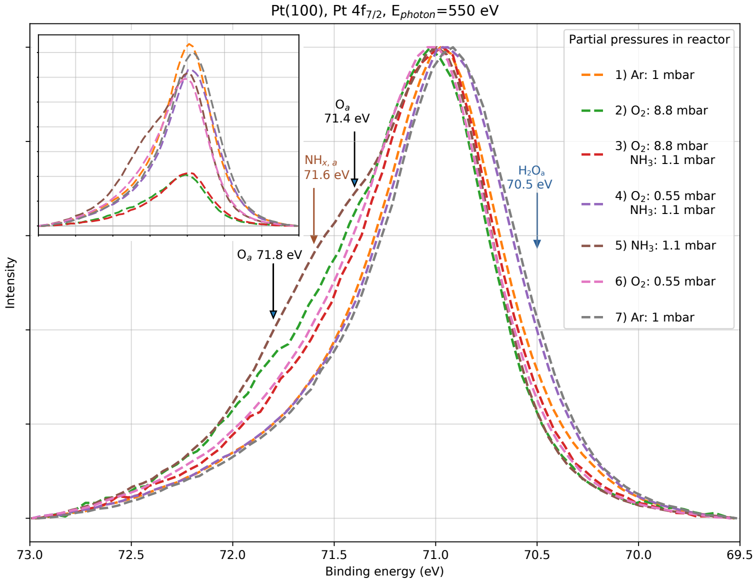
Important roughness and strain evolutions are measured!

Pt(100): Pt(100)-(2 × 2) bulk Pt_3O_4

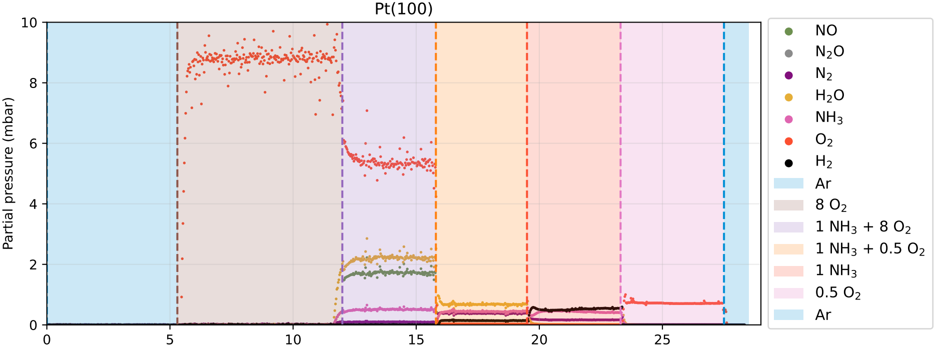




Pt(100): x-ray photoelectron spectroscopy



Pt(100): x-ray photoelectron spectroscopy

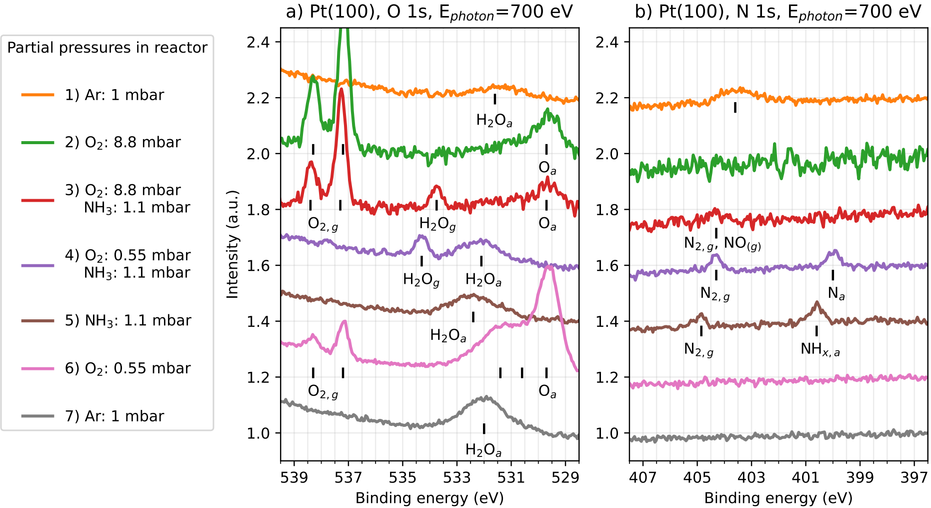


Pt(100): x-ray photoelectron spectroscopy

Partial pressures (mbar)	Ar	1	0	0	0	0	0	1
	NH_3	0	0	1.1	1.1	1.1	0	0
	O_2	0	8.8	8.8	0.55	0	0.55	0
Gas presence (decreasing pressure order)		Ar	O_2	O_2, H_2O, NO NH_3, N_2, N_2O	H_2O, NH_3 N_2, H_2	H_2, NH_3 N_2	O_2	Ar
N 1s: peak positions		403.6 eV	No peak	404.3 eV	404.3 eV 400.0 eV	404.9 eV 400.6 eV	No peak	No peak
Attributed surface species		Not assigned		$N_{2,g}$ & NO_g	$N_{2,g}$ N_a	$N_{2,g}$ $NH_{x,a}$		
O 1s: peak positions		531.6 eV	538.3 eV 537.2 eV 529.7 eV	538.4 eV 537.3 eV 533.7 eV 529.7 eV	534.3 eV 532.1 eV	532.4 eV	538.3 eV 537.2 eV 531.4 eV 530.6 eV 529.7 eV	532 eV
Attributed surface species		H_2O_a	$O_{2,g}$ $O_{2,g}$ O_a	$O_{2,g}$ $O_{2,g}$ H_2O_g O_a	H_2O_g H_2O_a	H_2O_a	$O_{2,g}$ $O_{2,g}$ O_a O_a O_a	H_2O_a

Indexing of peaks measured during ammonia oxidation of the Pt(100) surface.

Pt(100): x-ray photoelectron spectroscopy



Pt(111) & Pt(100): RGA signals during SXRD & XPS