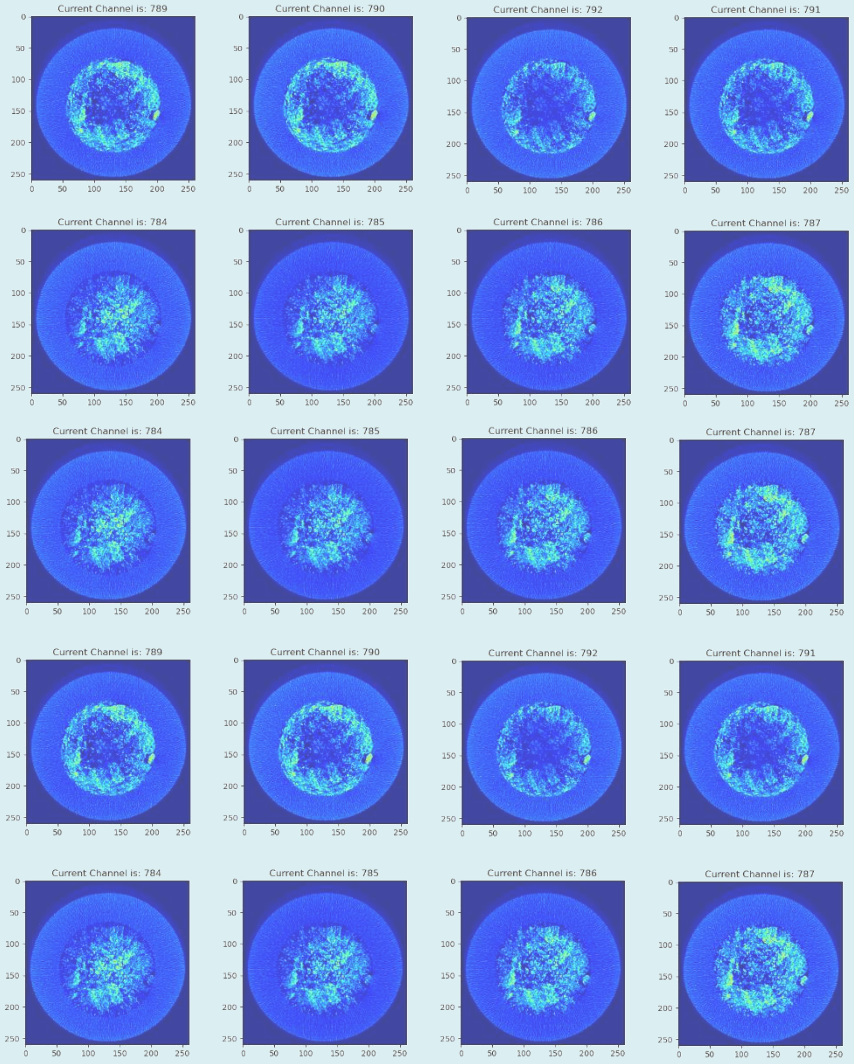

Quantifying thermal gradients across the bed of a magnetic induction reactor using *in situ* XRDCT

Lucy Costley-Wood, Asun Molina Esquinas, Andy Beale

UCL

Research Complex at Harwell

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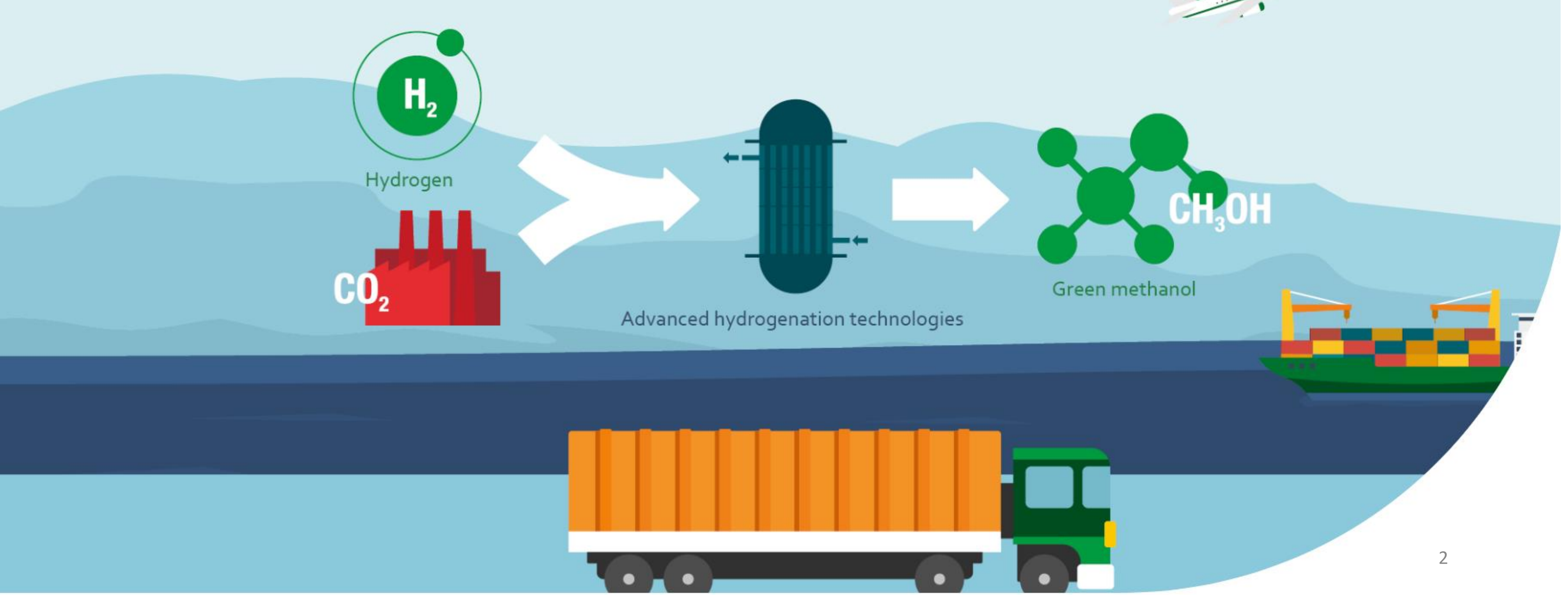
Reducing carbon emissions by optimising the CO_2 hydrogenation to produce green methanol



AIMPLAS
INSTITUTO TECNOLÓGICO DEL PLÁSTICO

ALIÉNOR
Tailor-made solutions

CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

Fraunhofer
ICT

PDC
Process Design Center

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東京大学
THE UNIVERSITY OF TOKYO

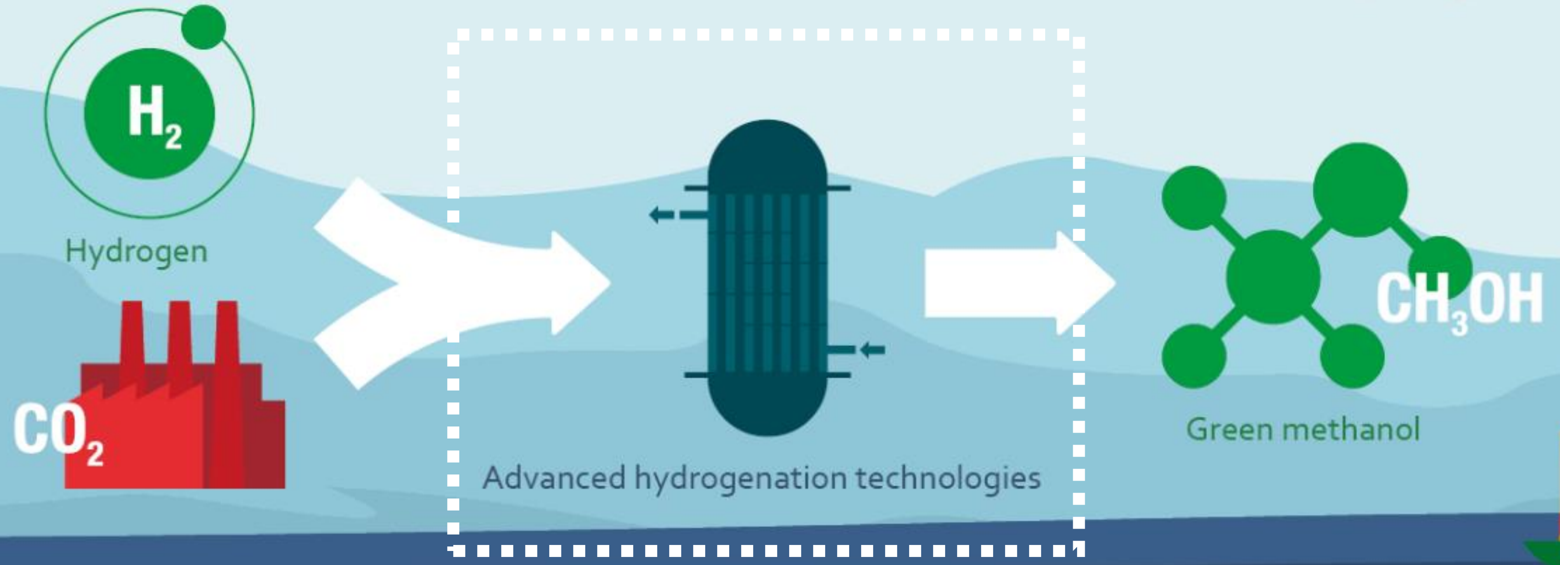
Reducing carbon emissions by optimising the CO_2 hydrogenation to produce green methanol

東京工業大学
Tokyo Institute of Technology

UNIVERSIDAD DE ALMERÍA

UCL

MANCHESTER 1824
The University of Manchester



New generation of catalyst systems

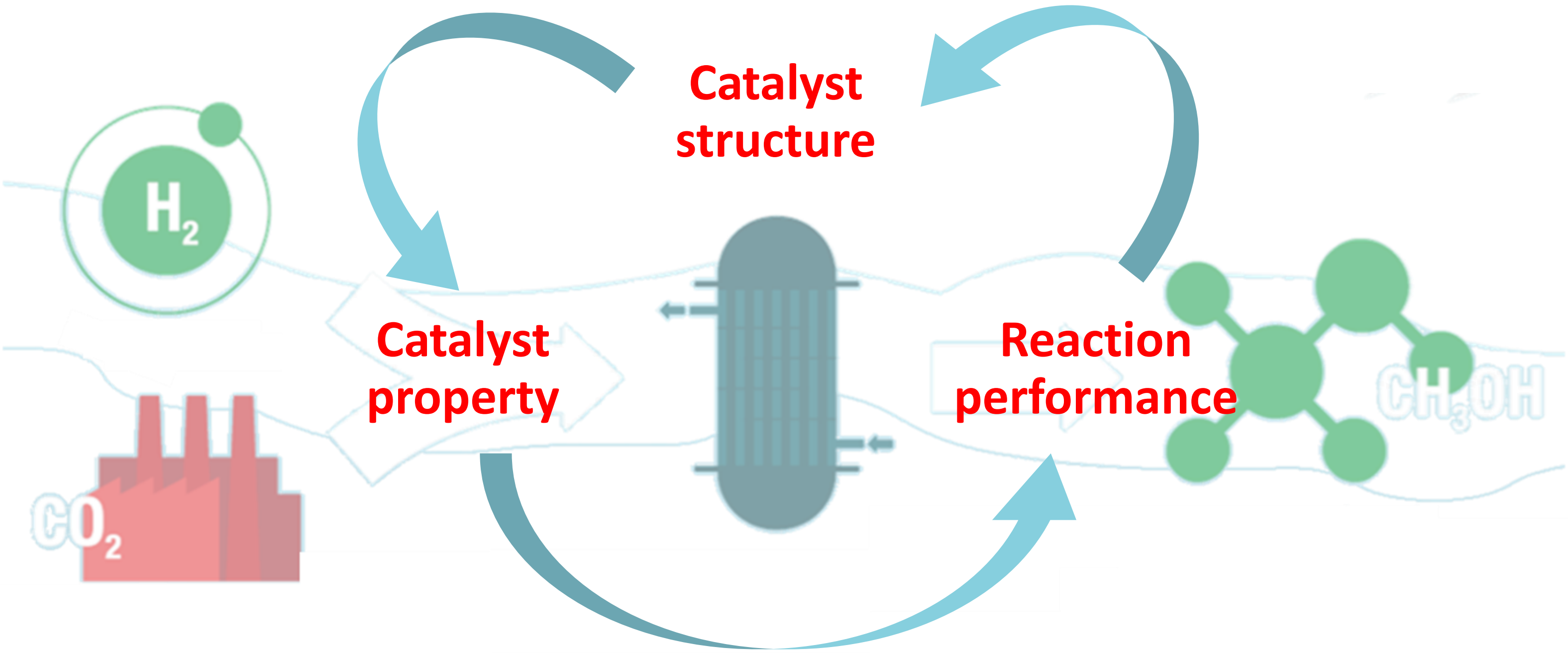
Advanced reactor systems

Microwave heating

Magnetic induction

Plasma induction

Our role in the Laurelin project

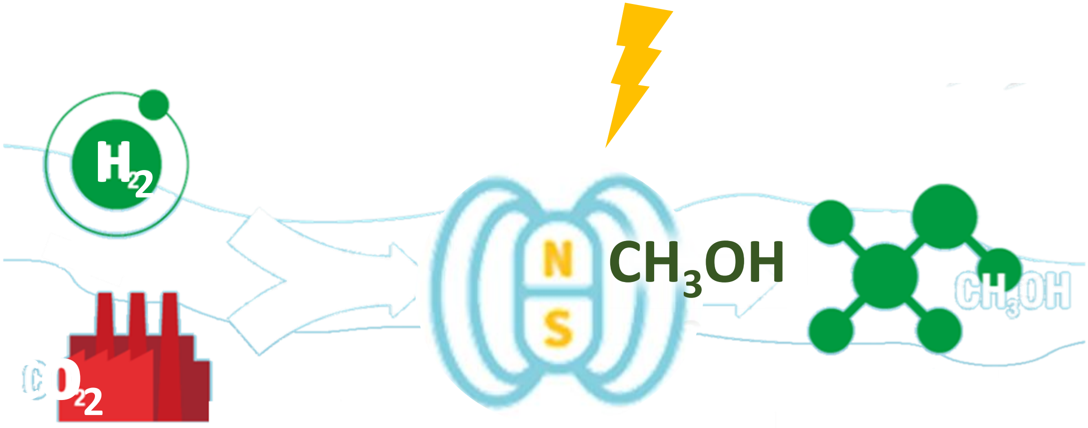


Novel reactors require new catalysts

Operando experiments more relevant to reactor design

Magnetic induction

CSIC



Catalysts

Magnetic properties

Indirect thermal heating

More energy efficient

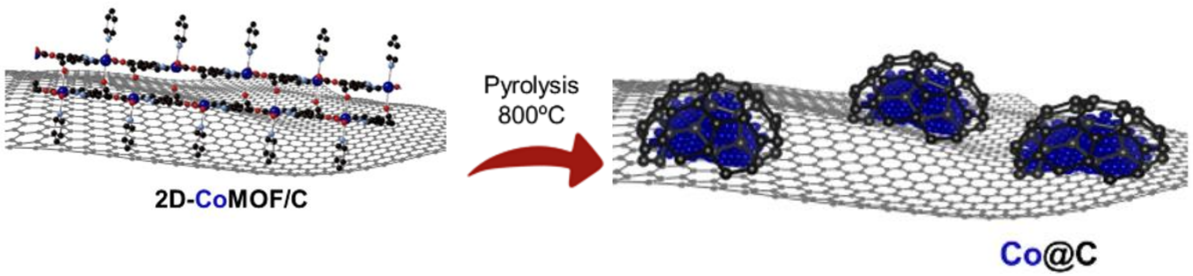
Difficult to determine:

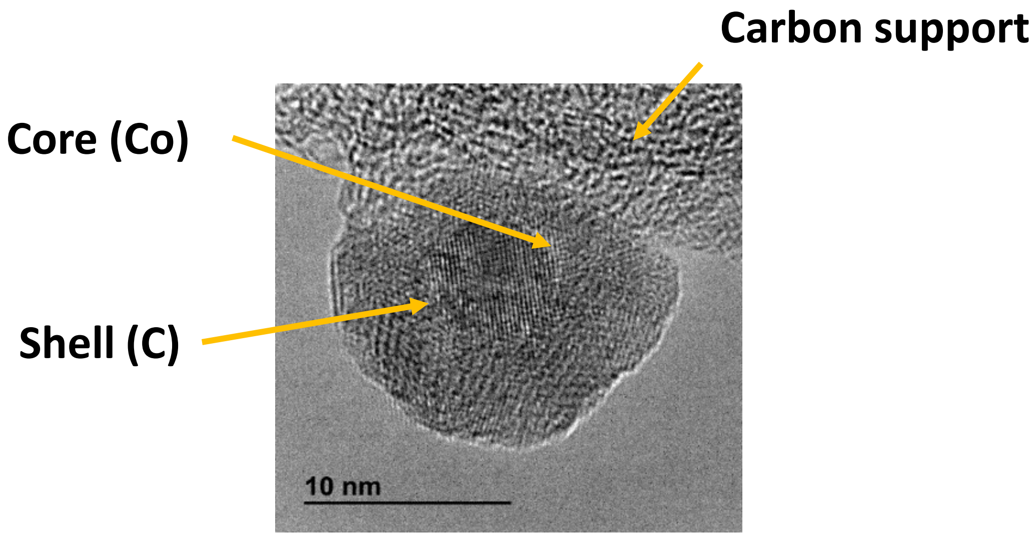
- Temperature of catalyst
- Any thermal gradients

X-ray Diffraction Computed Tomography (XRDCT)

Operando magnetic induction: Co/C XRDCT

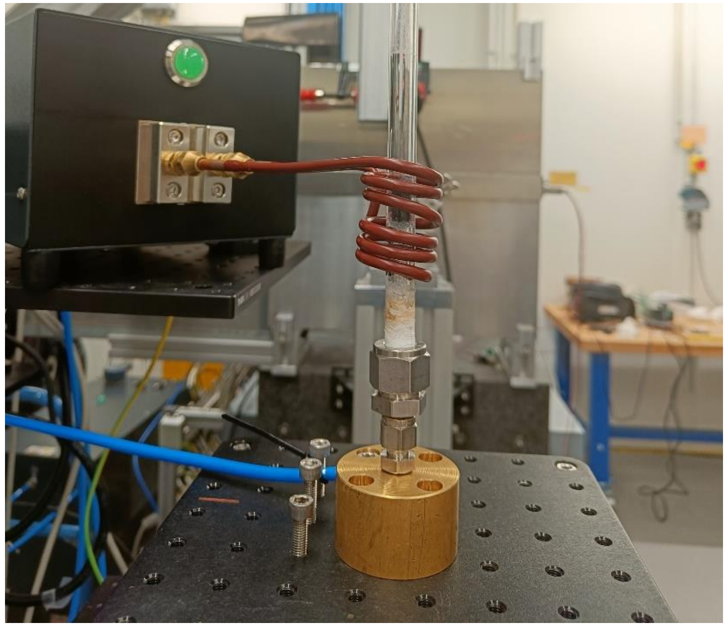
P21.2





Determination of the operating temperature of the catalyst during magnetic induction experiments using XRDCT

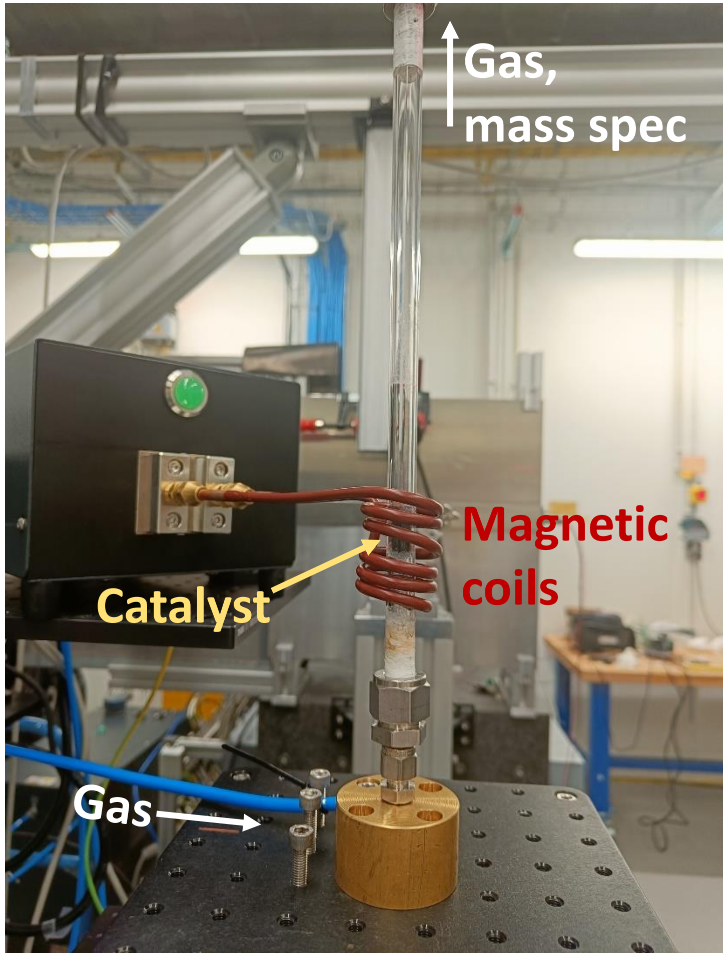
BL scientist: ***Zoltan*** *Hegedues*

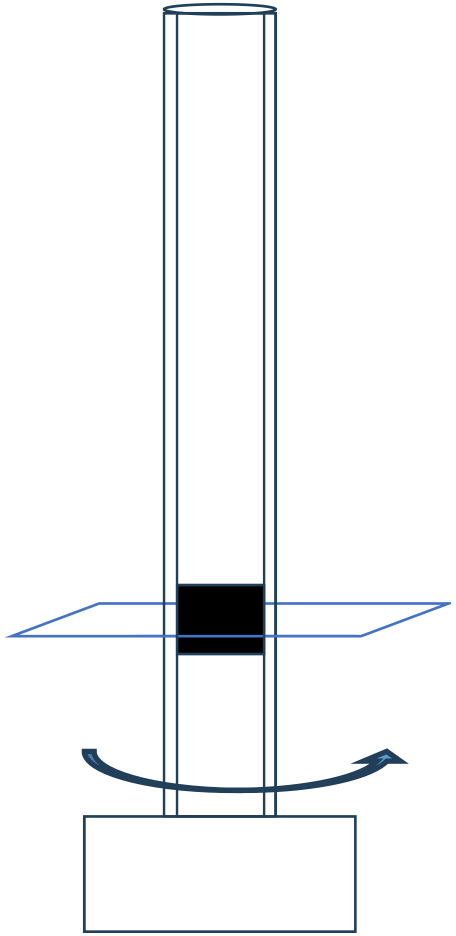


Operando magnetic induction: Co/C XRDCT

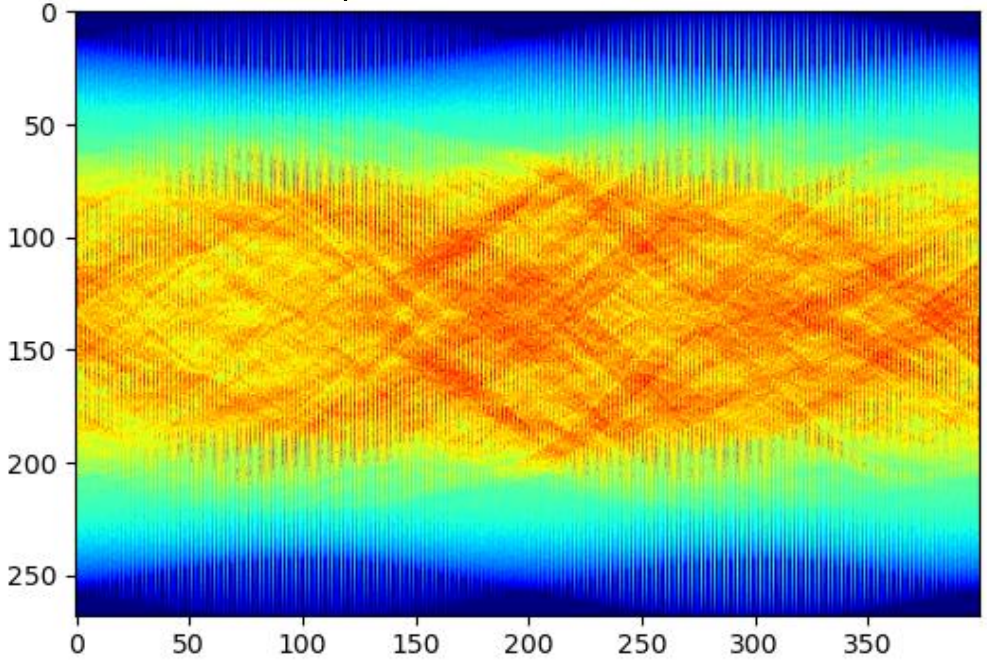
P21.2

XRDCT performed on **Co/C** at **0% and 100% magnetic power**. Get cross section of catalyst bed.





Scan across reactor, rotate 360/n, repeat.
Rotational step size 1.1°

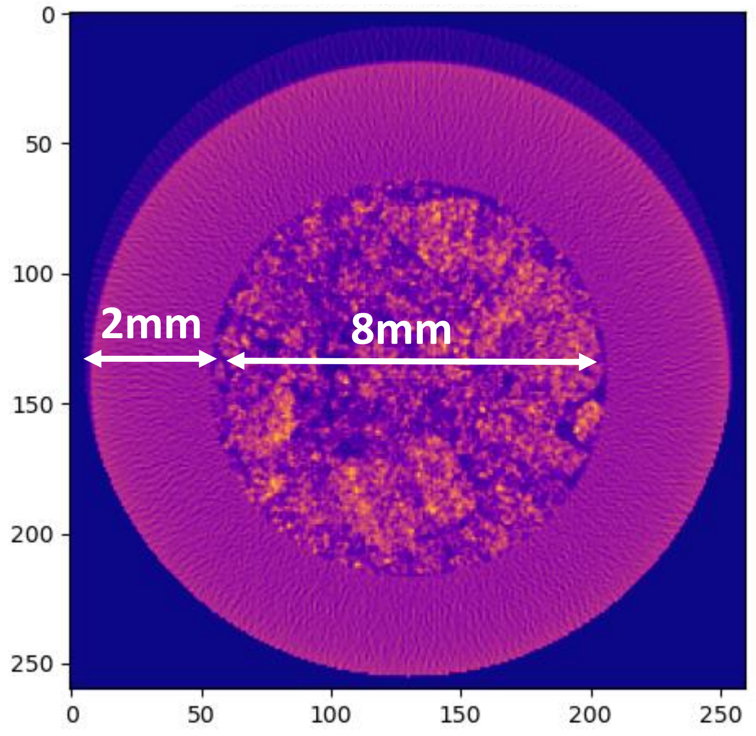


Creates sinogram, contains 85,000 XRD patterns!
Each vertical slices represents one horizontal line scan

Operando magnetic induction: Co/C XRDCT

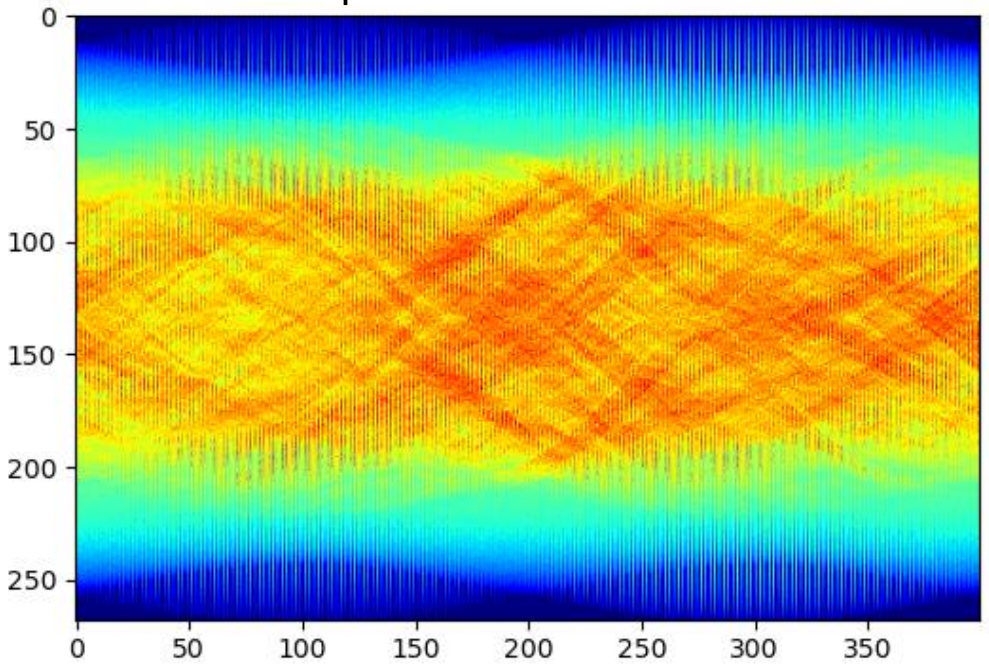
P21.2

XRDCT performed on **Co/C** at **0% and 100% magnetic power**. Get cross section of catalyst bed.



Reconstruction

Scan across reactor, rotate 360/n, repeat.
Rotational step size 1.1°



Extract 1D patterns for any and every pixel.

BEAMSTOP Finden commercial software

Operando magnetic induction: Co/C XRDCT

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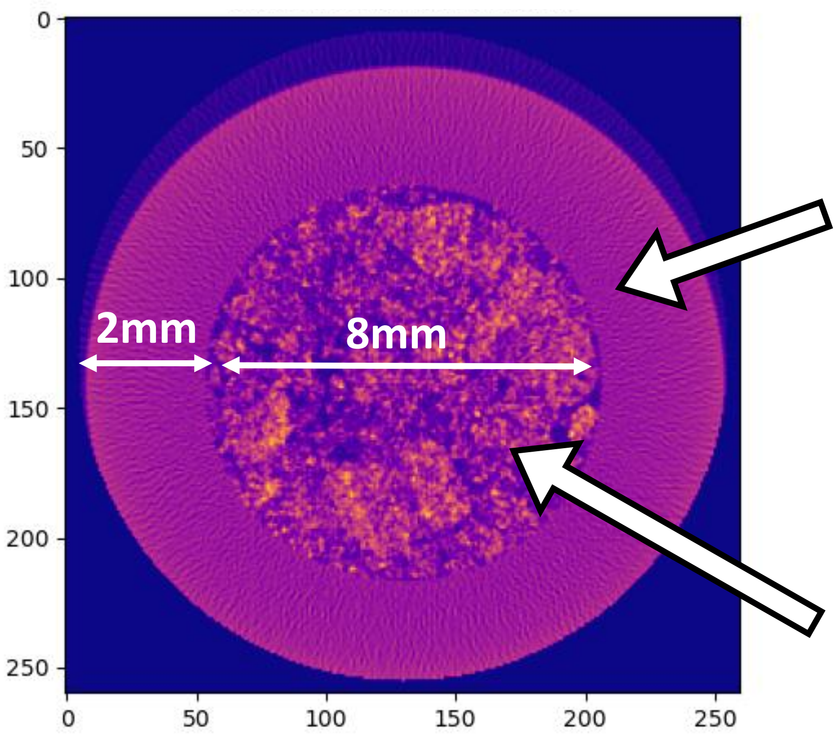
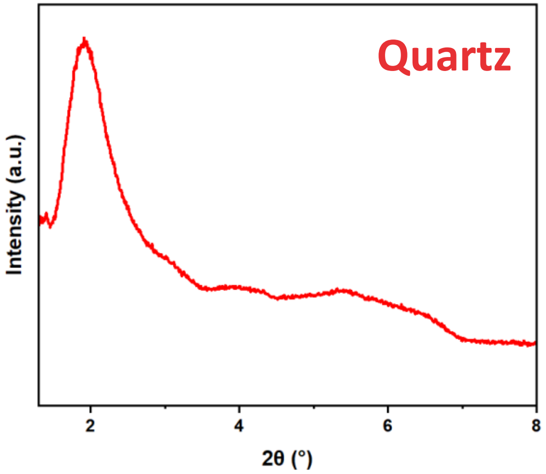
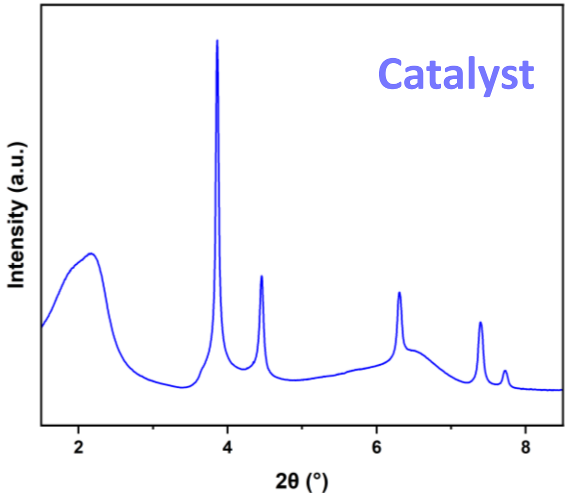
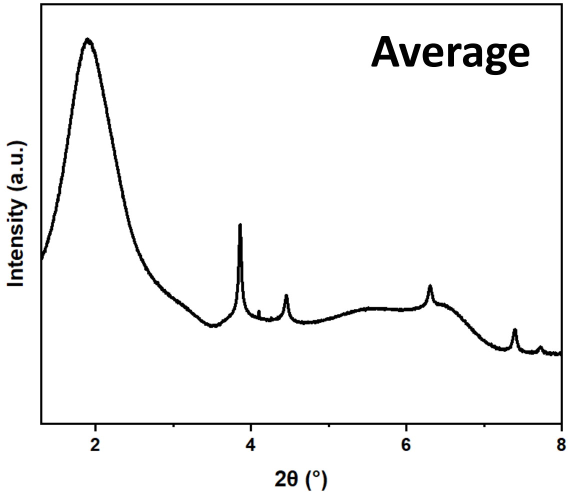
XRDCT performed on **Co/C** at **0% and 100% magnetic power**. Get cross section of catalyst bed.



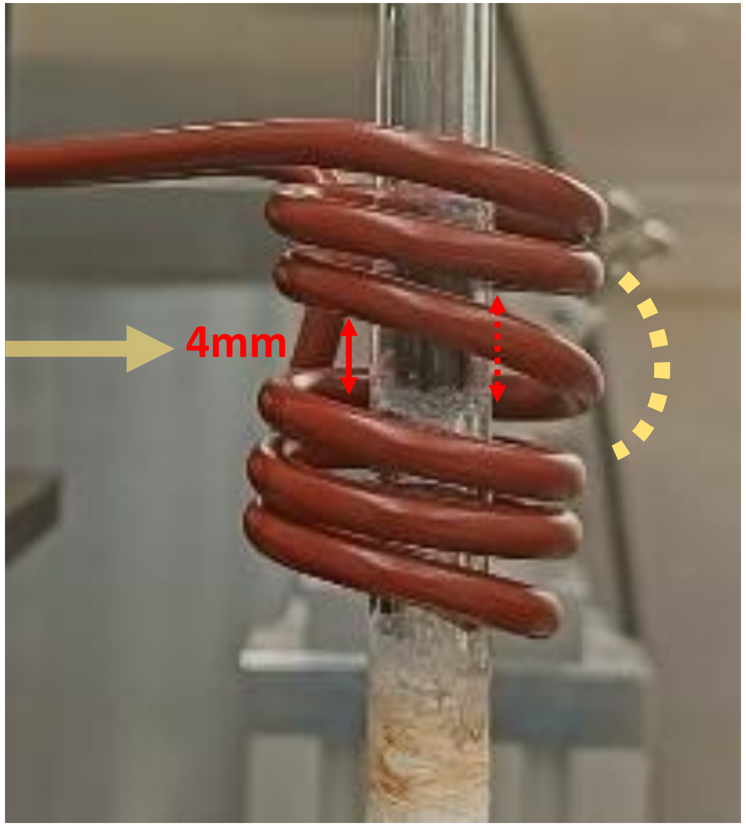






Problem solving

P21.2



Approximately 4 mm inlet, 8 mm outlet for beam

- Q_{max} 7.25Å^{-1}, required 90keV
- Small beam (27µm, slits)

4mm quartz total

- Again, high energy

Clipping Fe coils

- Over-saturate detector (not healthy)
- Use absorbers to work out limits

Long path length (parallax)

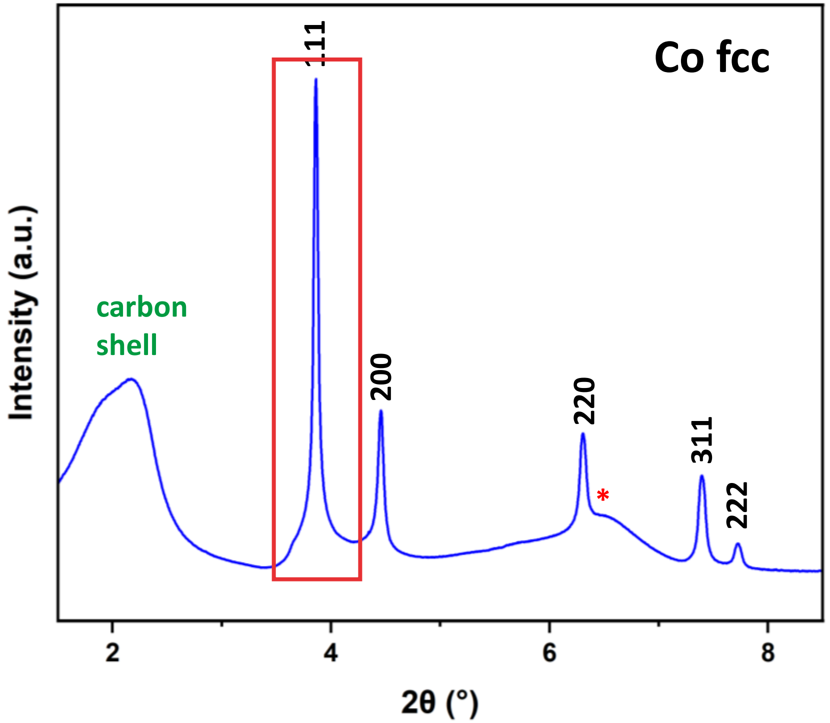
- Measure full 360°
- Compare peak widths across reconstructed scan

0% magnetic power

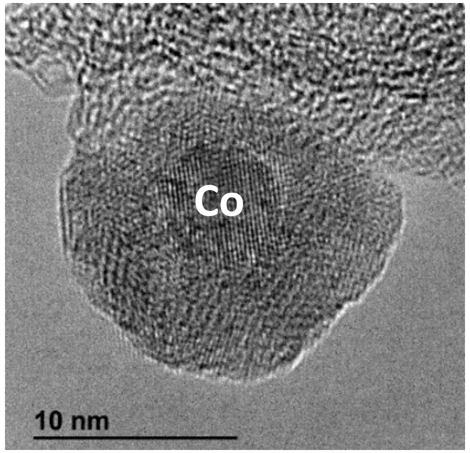
P21.2

PXRD of catalyst shows Co fcc reflections, intensity ratios indicate stacking faults.

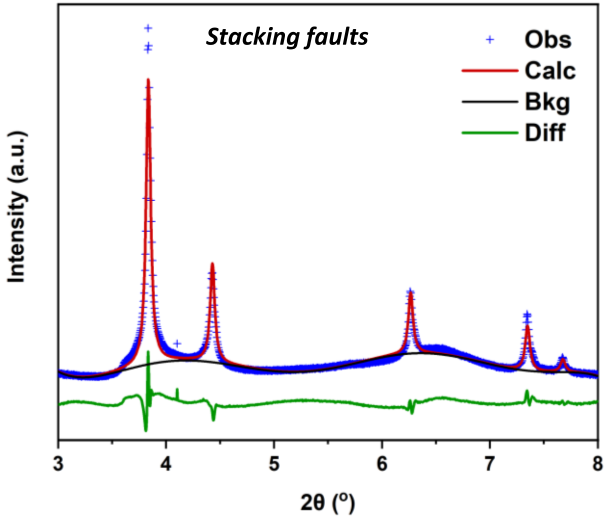
Large broad reflections from partially crystalline carbon shell.



PXRD of Co@C at room temperature, 90 keV, average integration from XRDCT



Representative image of one Co@C NP

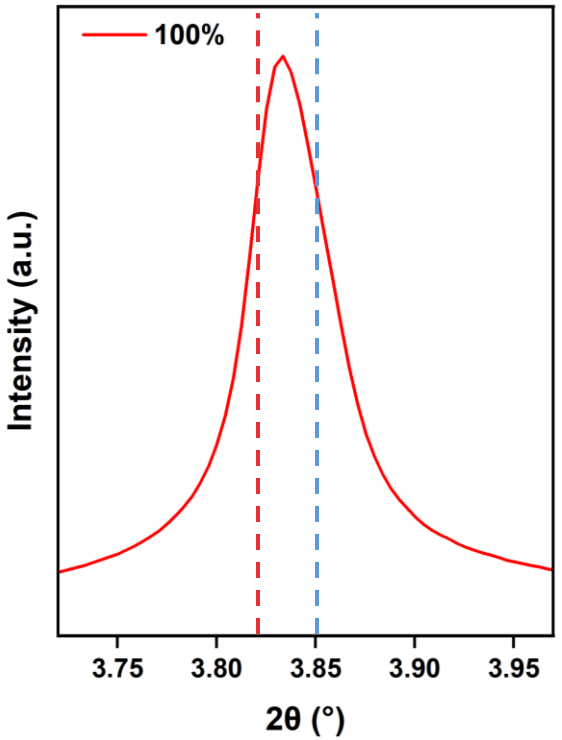


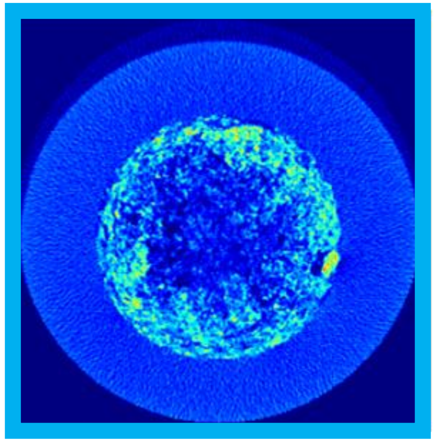
Refined pattern using GSAS II.

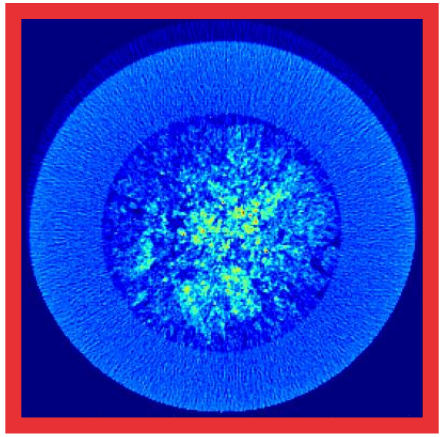
Lattice param.	3.542 Å
Size	16 nm
M/D ratio	1.49
wR	10 %

100% magnetic power

Reconstruct using intensity from specific 2θ positions





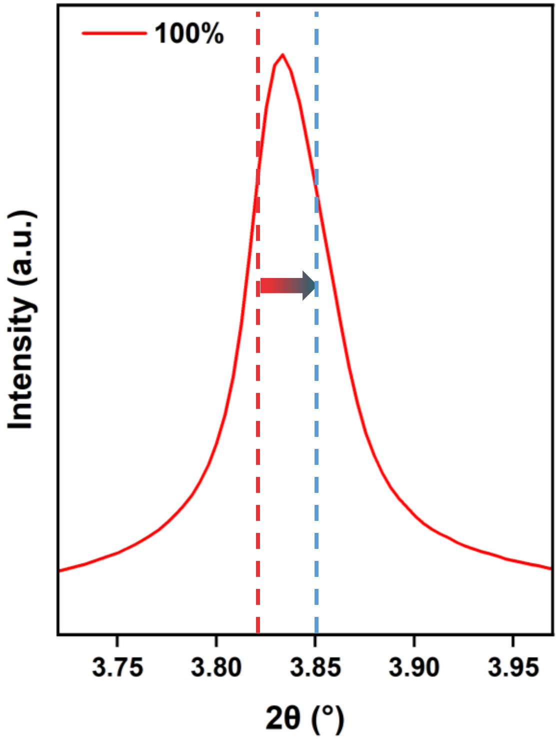


Peak asymmetry due to overlapping Co phases

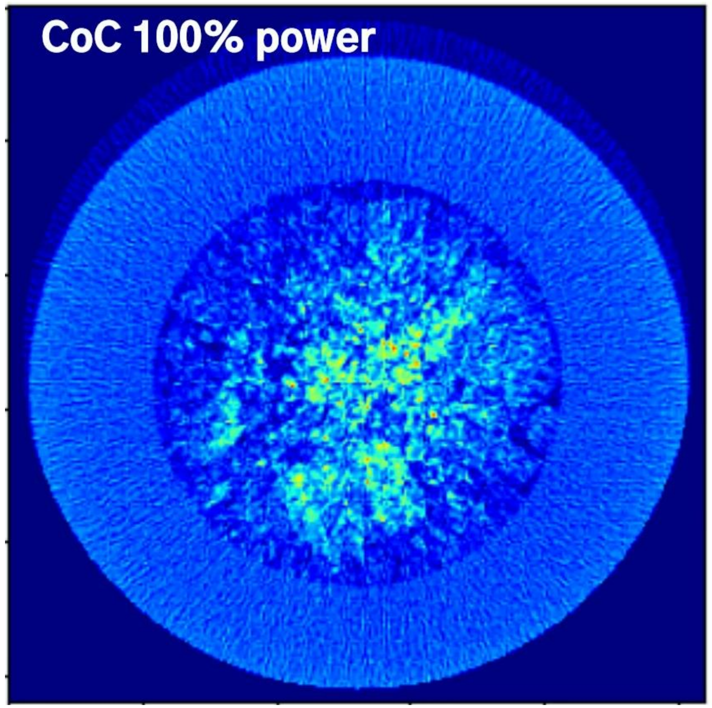
Strong thermal gradients within the reactor.

Most thermally expanded Co in centre.

100% magnetic power



From most shifted to least shifted Co

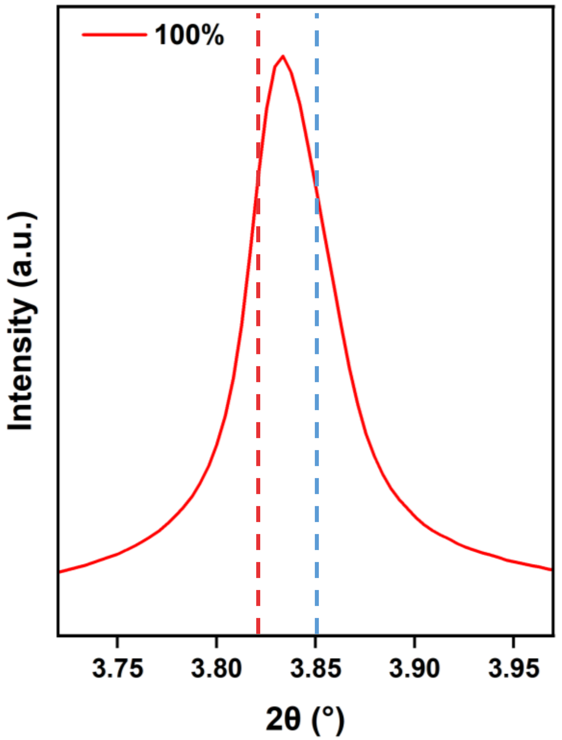


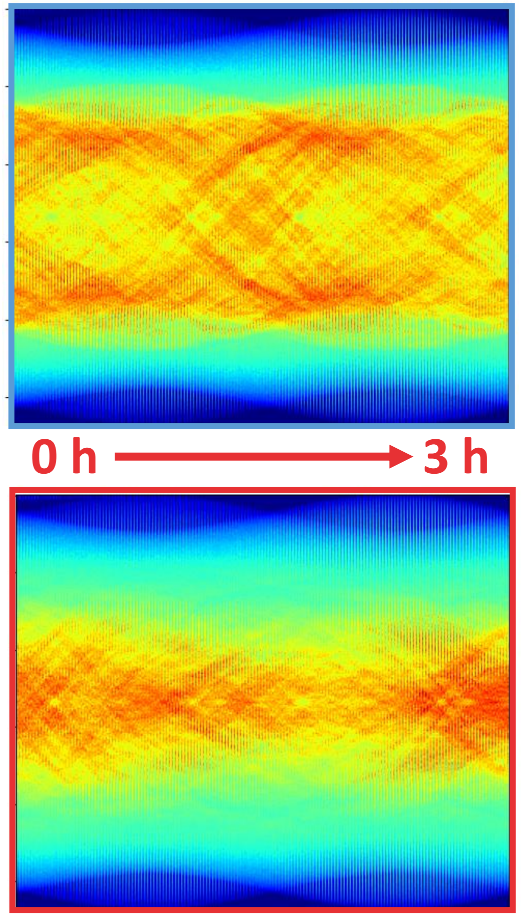
Repeated for room temperature sample to ensure not artifact of reconstruction

100% magnetic power

P21.2

Temporary/mild gradients common in conventional reactors
Use sinograms to see if temperature equilibrates





Intensity from more expanded Co in centre of reactor.

Temperature gradient persists over 3 hours, doesn't become homogeneous. Rapid and constant source of heat loss.

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Why gradients?

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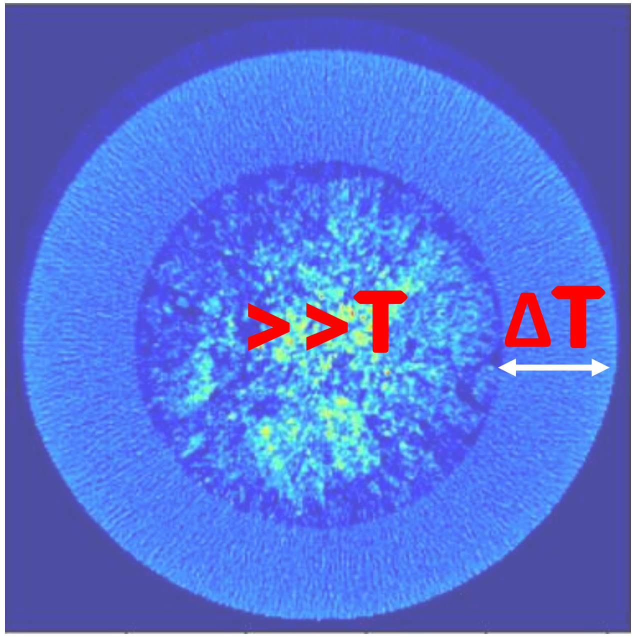
P21.2

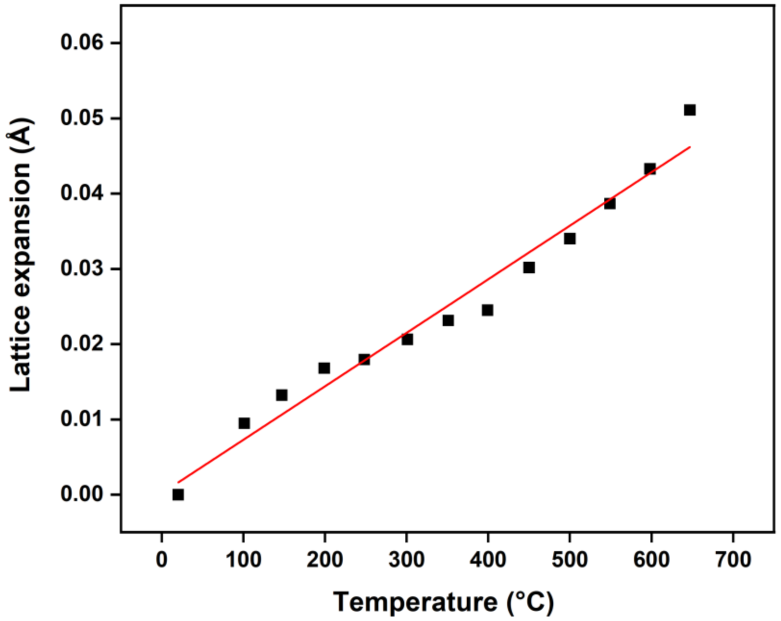
- No external heating as for furnace type reactors
- Quartz walls acting as heat sink



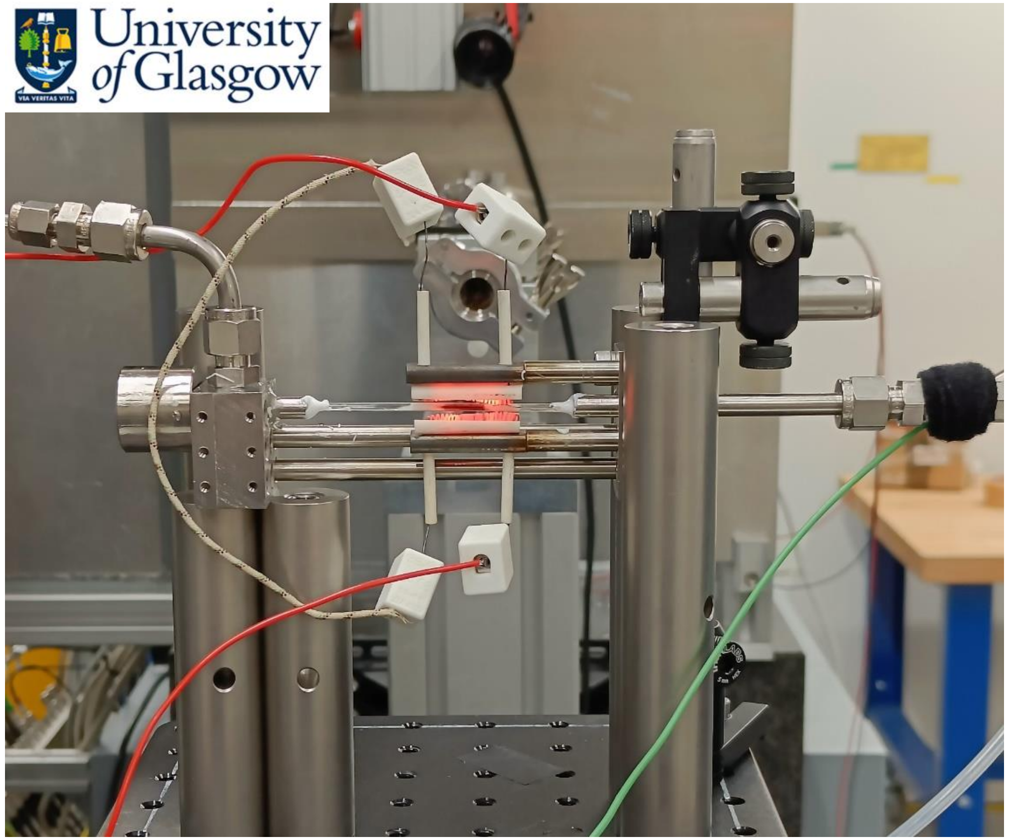
- *So what is the actual temperature?*

Thermal calibrations

Thermal calibrations using same sample, high temperature cell belonging to Emma Gibson

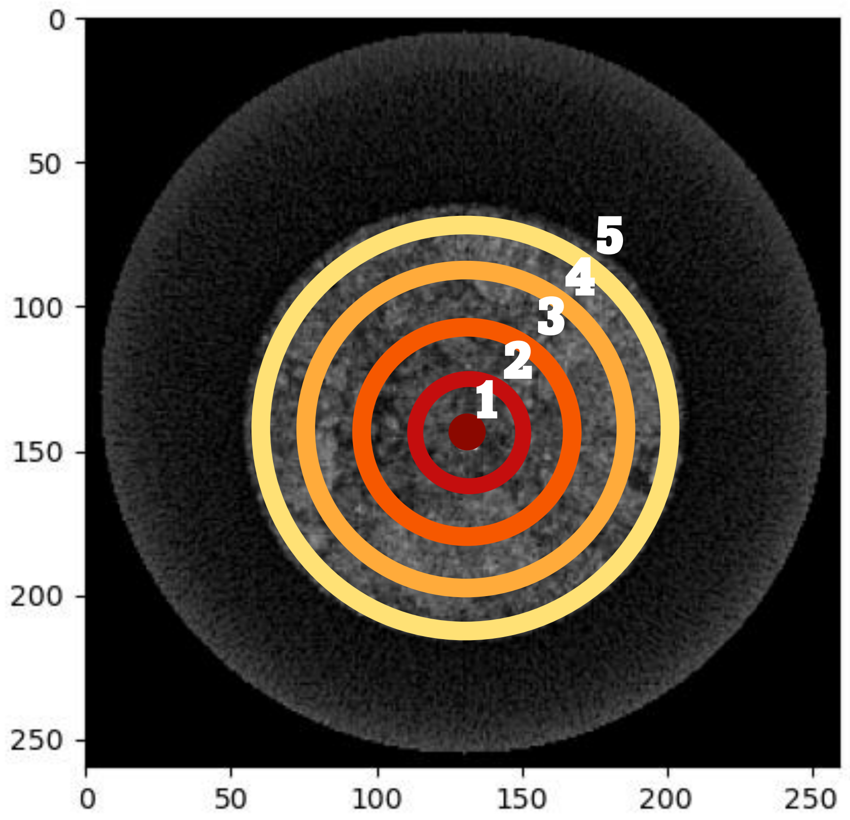


Observed some non-linearity, likely due to small NPs and thick carbon shell.



Thermal calibrations

P21.2

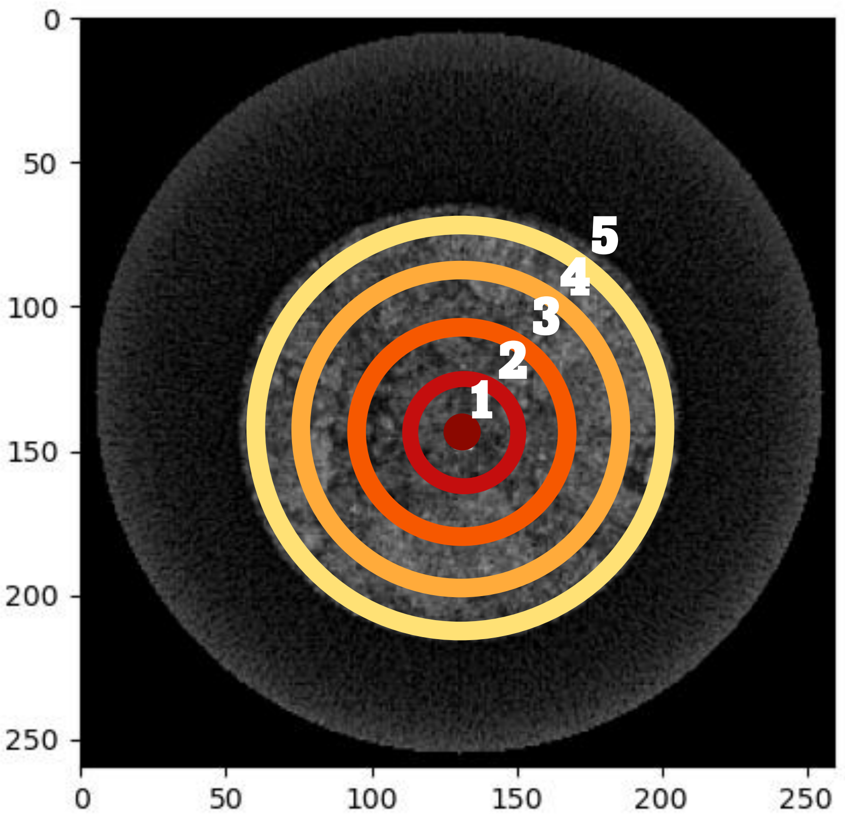


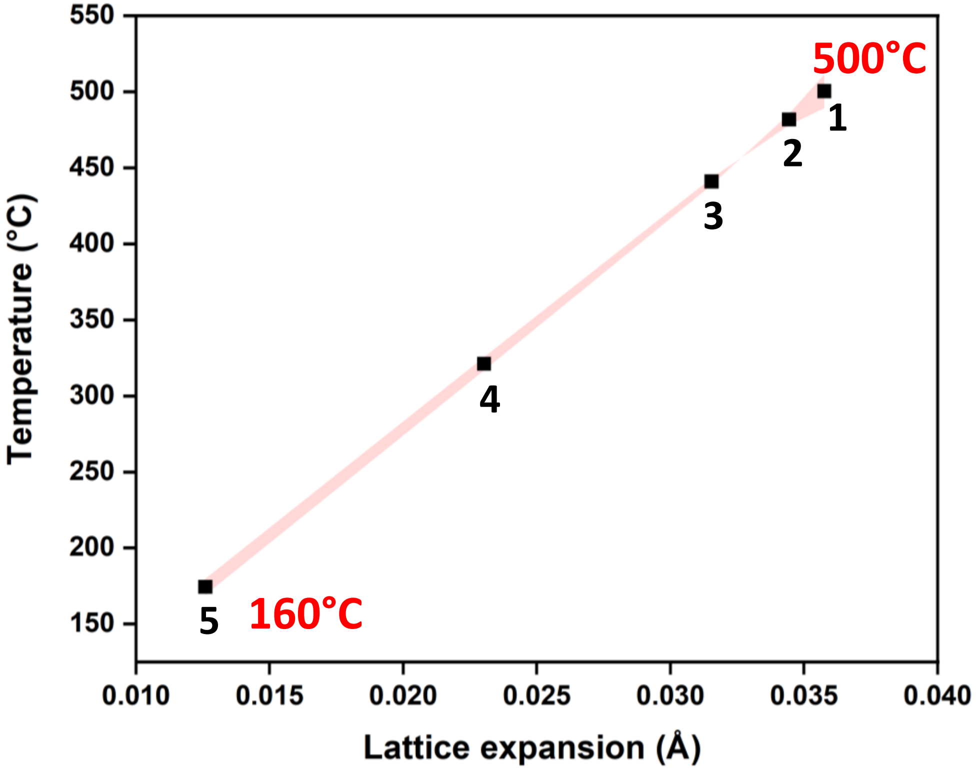
Split the bed into 5 zones, integrate patterns only within these masks.

Create 5 mean patterns at 5 different distances from centre of the bed

	Lattice parameter (Å)
0% power	3.542
100% power	
Zone 1	3.578
Zone 2	3.576
Zone 3	3.573
Zone 4	3.565
Zone 5	3.555

Thermal calibrations



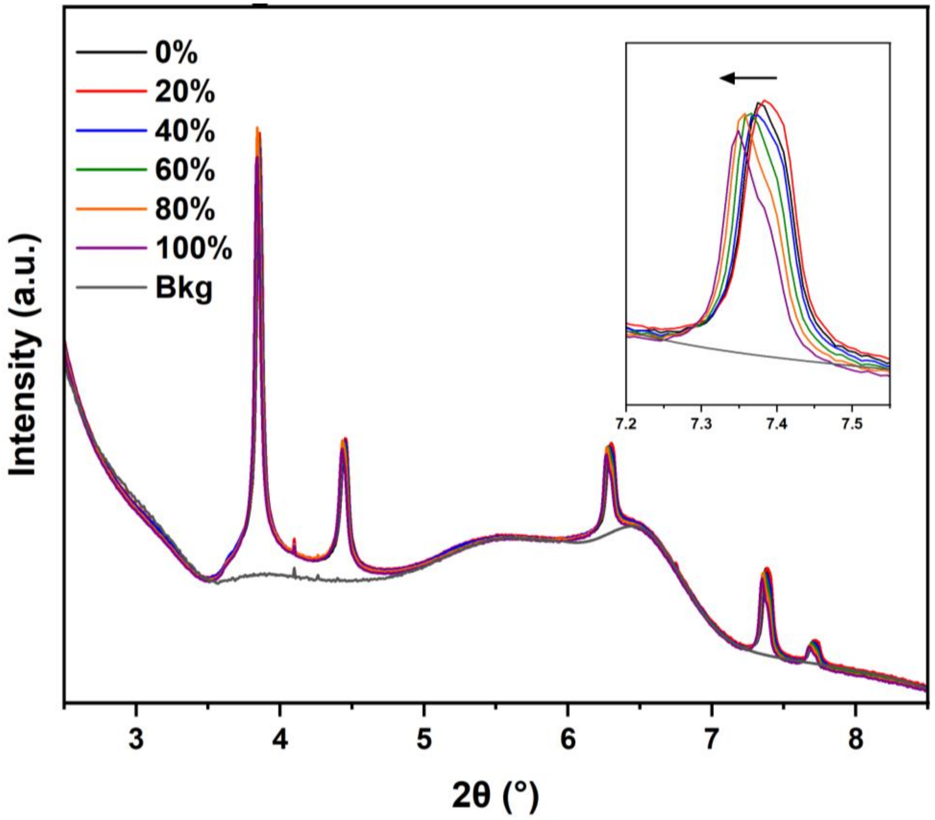


Temperature variation of up to 340 °C across bed!

Why we need XRDCT

P21.2

Operando point XRD, same catalyst, same set-up.

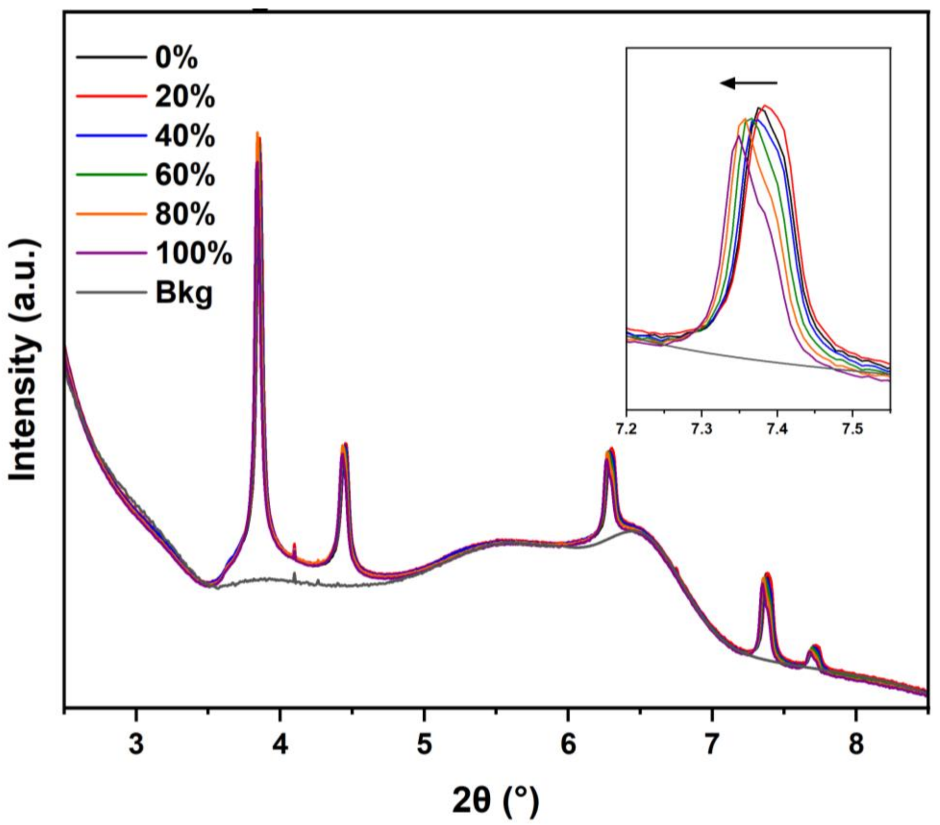


Increasing magnetic field strength during CO_2 conversion.

Why we need XRDCT

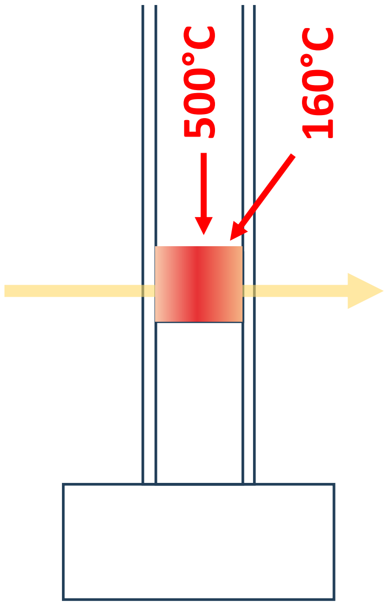
P21.2

Operando point XRD, same catalyst, same set-up.



Increasing magnetic field strength during CO_2 conversion.

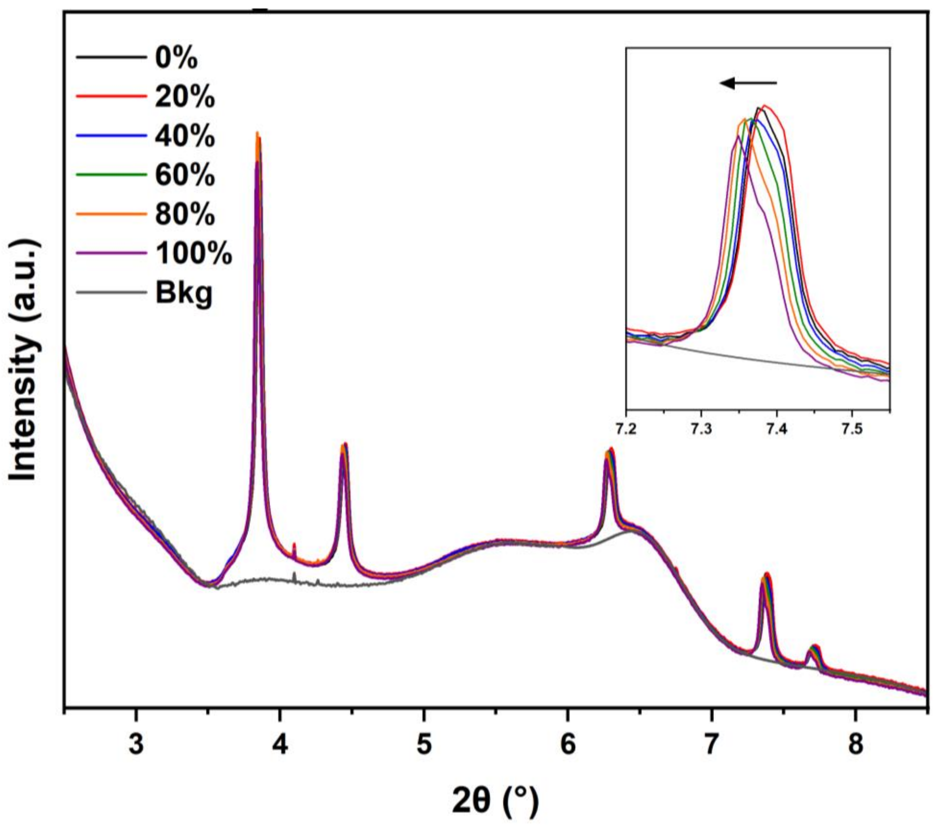
- *As catalyst temperature increases, peak shape becomes asymmetric*
- *Overlap of differently expanded Co due to thermal gradients*



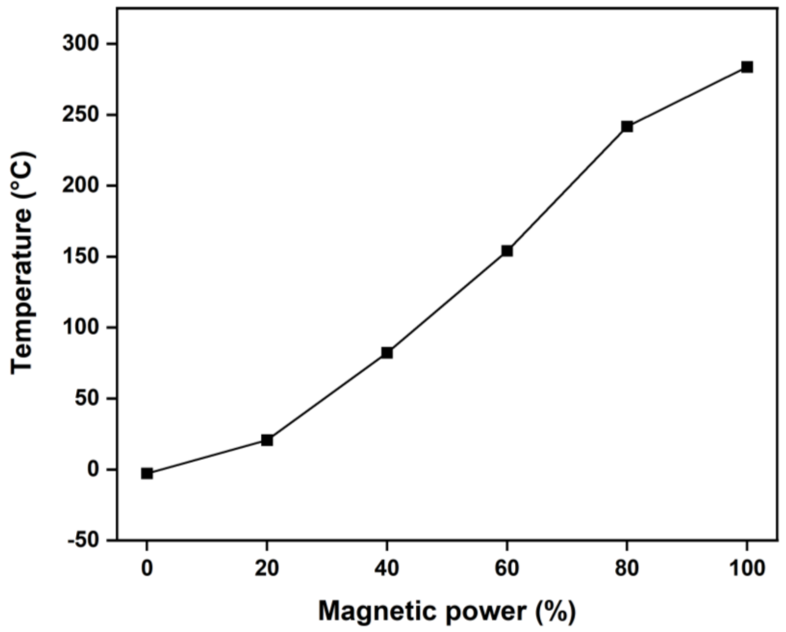
Why we need XRDCT

P21.2

Operando point XRD, same catalyst, same set-up.

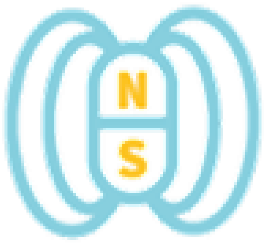


Increasing magnetic field strength during CO_2 conversion.



- *Fit multiple Co phases*
- *Majority of catalyst volume in cooler part of reactor*
- *Temperature is underestimated.*

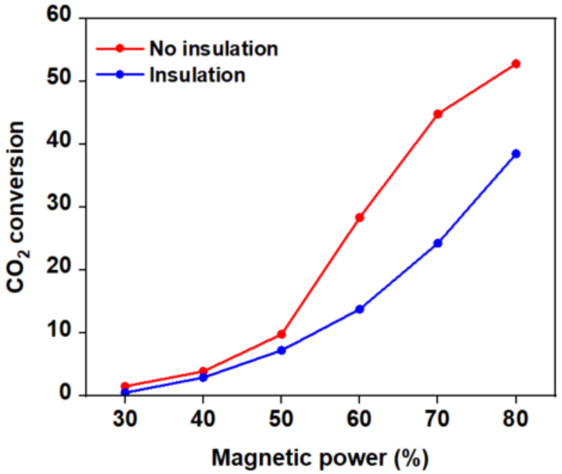
Conclusions & next steps



Operando measurements allow understanding and improvement of **catalysts** *and* **reactors**

Especially necessary as catalysis aims to move away from conventional heating.

→ **Heat mapping** by **XRDCT** resulted in **improved reactor design**



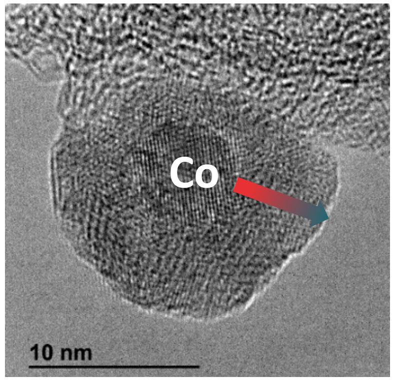
Addition of simple heating jacket improves conversion by up to 14%

Next steps…

We now know the temperature of the **Co** core

But how efficient is the ***heat transfer*** *to the reacting species?*

→ Compare temperatures of **SiC** and **catalyst** in a mixed bed



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Acknowledgements

UCL

Andy Beale
Matt Potter
Asun Molina Esquinas

CSIC

Pascual Oña Burgos
Luis Miguel Martinez Prieto
Christian Cerezo Navarette
Silvia Gutiérrez Tarriño
JoseLuis del Río Rodríguez
Adrian Garcia Zaragoza

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DESY.

Zoltan Hegedues

Thanks for listening!

The LAURELIN project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 101022507