



Bringing Advanced Characterisation to Industry

Simon Jacques

About us

- Finden is a UK Ltd company
- Operating for 1 year
- 4 unique clients
- Consists of two academics
 - Extensive synchrotron experience
 - X-ray & spectroscopic methods for materials characterisation
 - High throughput methods
 - Crystallography & Chemistry
- As academics we are based at RCaH Diamond. Company located in Oxfordshire, UK

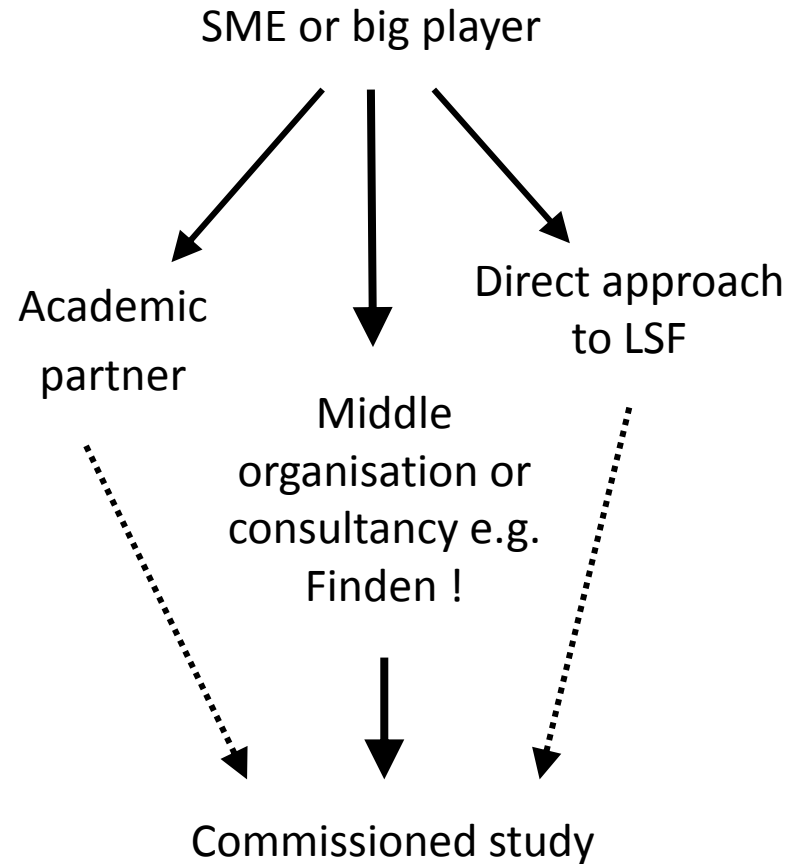
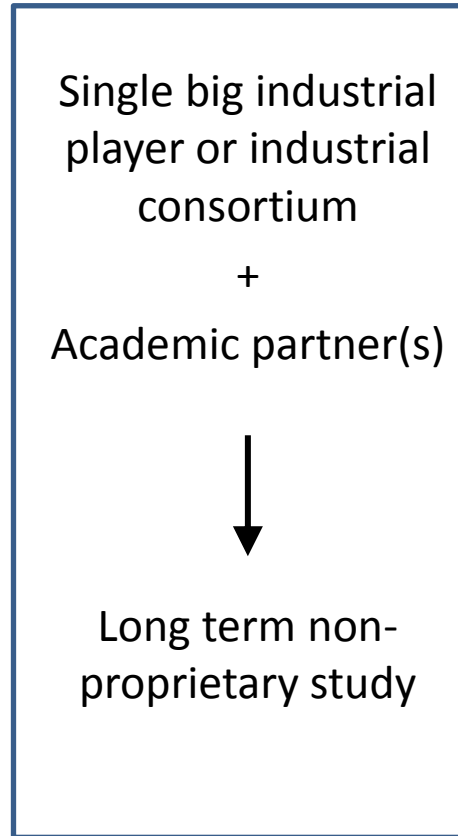
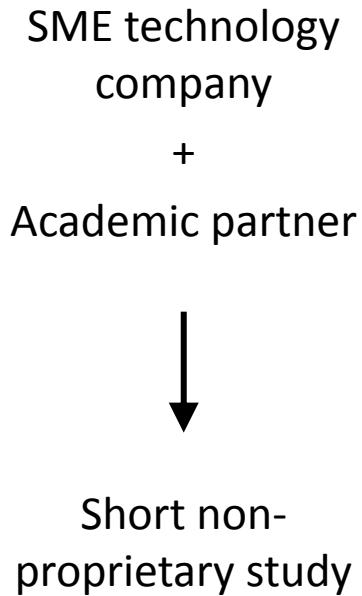


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Access to LSF



Project Construct

2 year project – 1 Post Doc (\$200 k)

Proposed stationing partners (infrastructure)



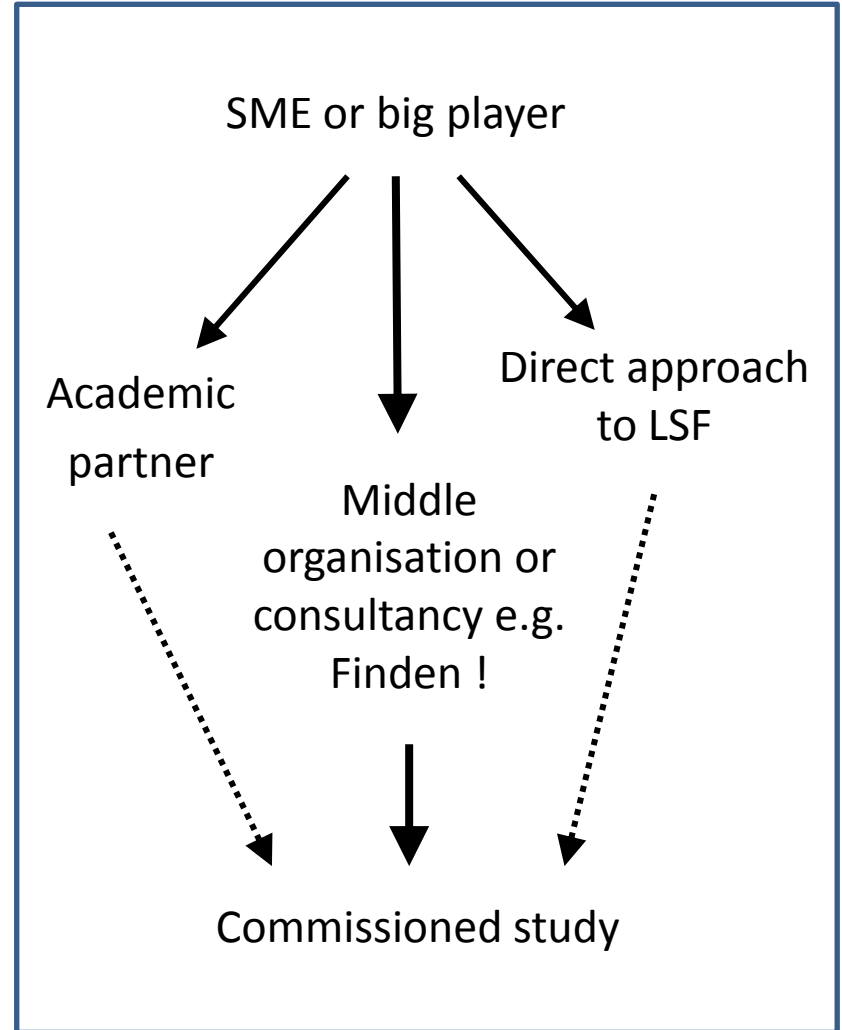
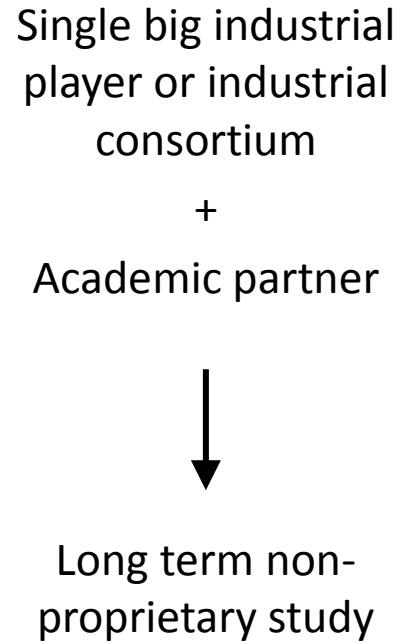
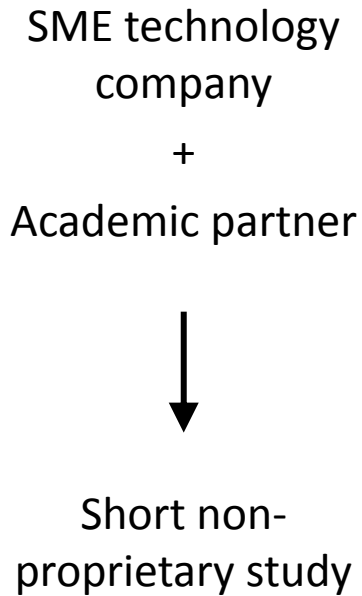
Non proprietary not without its issues or significant costs !

HE institution – overheads (typically > 25 %) in northern Europe

IP – ownership/publication clearance times

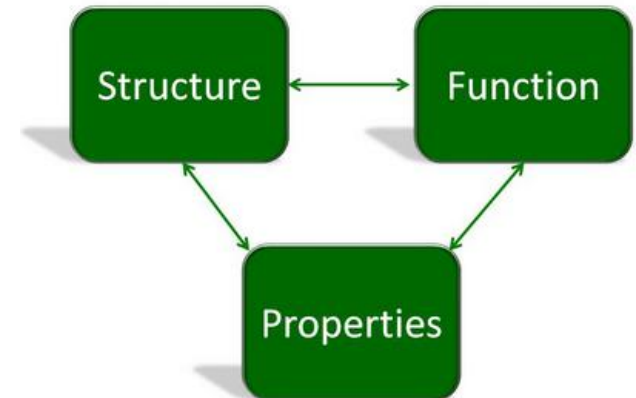
Recruitment – satisfying requirements of project partners

Access to LSF



About Finden

- As Finden Ltd, we aim to provide an efficient alternative
- Standard & advanced characterisation to further understanding of structure-function-property
- Chemical analysis under both static and in real time under operating conditions
- Services
 - X-ray absorption spectroscopy (XANES EXAFS)
 - X-ray diffraction and scattering
 - Infra Red Spectroscopy
 - Raman Spectroscopy
 - UV-Vis Spectroscopy
 - Tomography
 - Diffraction tomography & other advanced methods
- Consultancy on
 - data processing
 - process/materials development





What we do and who we serve ?

- Largely focus on industrial catalytic problems (associated with fine chemical synthesis)
- Nature of catalysts is that they are specialist materials – expensive raw ingredients, often expensive to manufacture
- Improve lifetime, but also inline re-activation (initial vs. permanent deactivation)
 - Ex-situ analysis often misleading (passivation issues – sintering etc.)
 - Classic in-situ is not always representative
- New technology companies (SME) / established big players
- Understand the requirements and the goals
- Help industry:
 - Pose questions
 - Choose characterisation methods
 - Design & perform experiments
 - Analyse and interpret data
 - Advise on how to improve products / processes

Our perception of industry barriers & motives

Barriers

- Industry traditionally hesitant to using large scale facilities (especially direct access)
- 'High' cost often quoted as an impediment to commitment
- Real cost is risk of not getting results and getting them in a reliable time frame
- Others !

Motivations

- General shift in focus – requirement to develop efficient processes (cost of raw materials; cost of preparing materials; environmental impact of preparation and process; recycling considerations); exploiting new opportunities
- Coupling of materials to make devices – understanding their function

Our perception of industry barriers & motives

Bias against using LSF largely a misnomer since:

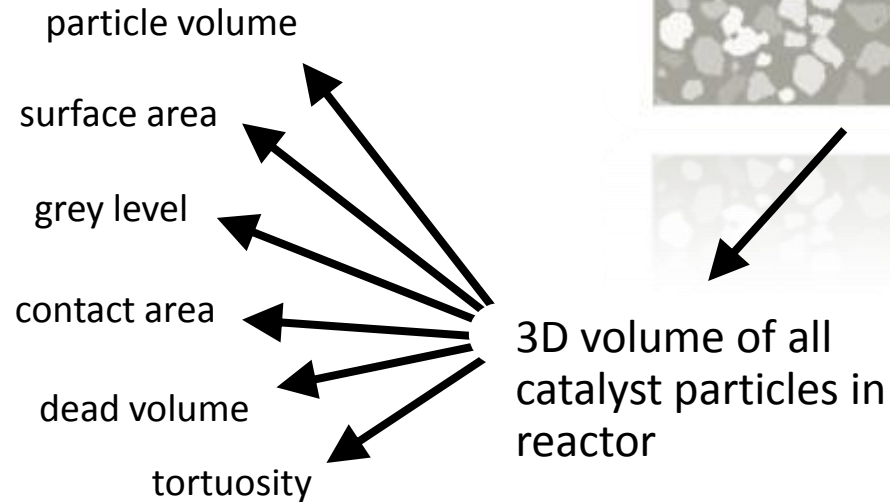
- Asking the right question ? (LSF black box)
- Do expts not achievable by conventional measurements
- In situ – becomes highly relevant
- Tried and tested methods argument – i.e. those benchmarked (not worse than lab !)
- High flux / recording allows large volume of work to be completed
- On-the-fly results processed data into recognisable format (what you get in the lab) allow adaption
- Ways to mitigate risk – free or low cost proof-of-concept studies
- Rapid access ?

Example of traditional characterisation

- Industrial partner wants to investigate the poor performance of a reactor (prescriptive)
- Whole field reactor (3 x 2.5 x 30 cm casing) studied using lab based CT (6 & 20 μ m resolution)
- First carry out small proof-of-concept study



**Improved
bed !**



SR better route

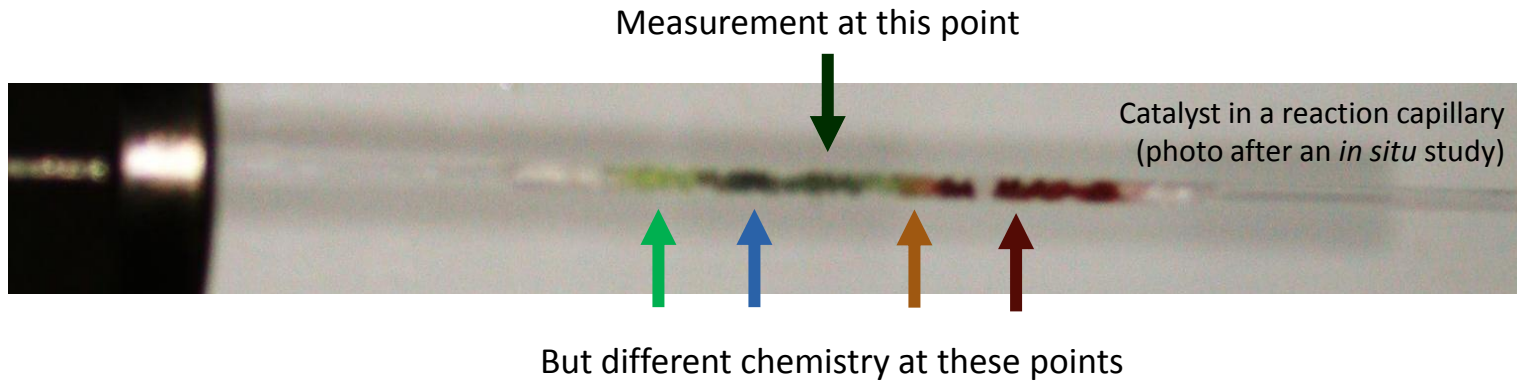
- Ca. €7000 study (Whole sample characterisation i.e. post proof-of-concept)
- Including 10 hours scan time @ ca. €2700
- 8 hour SR shift ca. €3300
- Easily 5 x samples
- SR → higher quality results (better contrast; higher resolution)
- Measurement of choice – combine with other measurements
- Raw data quicker (virtue of centralised computing cluster)



***Advanced characterisation:
Moving from packed bed models to real systems***

- Shifting to real samples
- Accepting samples are heterogeneous by accident or design
- Recognising limits of techniques

The packed bed model



- Miniature of industrial process
- Use gas delivery / heating apparatus to model process conditions
- Convenient for characterisation by methods sensitive to chemistry (e.g. *in situ* XRD)
- Real catalysts are rarely crushed and sieved powder fractions !
- Single point studies do not tell us the whole story
 - true on small and large scale ($\mu\text{m} \rightarrow \text{m}$)
 - true in both the bed and indeed catalyst bodies

reactant(s)

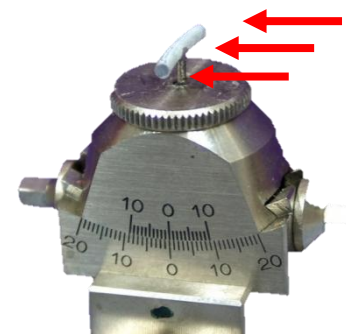
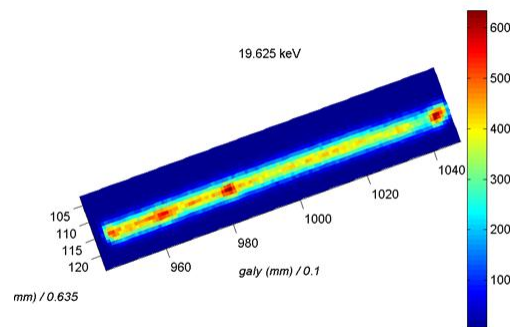


Using real samples

- Supported catalysts – preferred industrial method is to use packed bed structures of catalytic bodies
- mm or μm sized objects
- High energy X-rays can penetrate thick objects
- Efficiency of entire industrial process dependent on the performance *per se*



product(s)

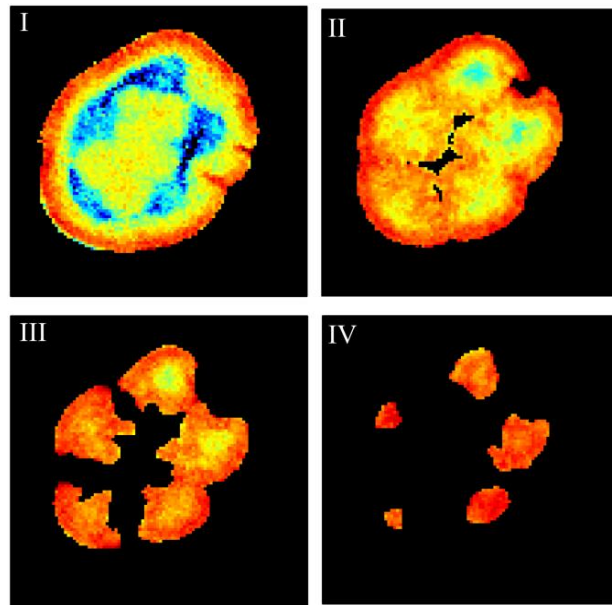


Tomography shows us that there are variations inside the catalytic body; Co/Mo on alumina

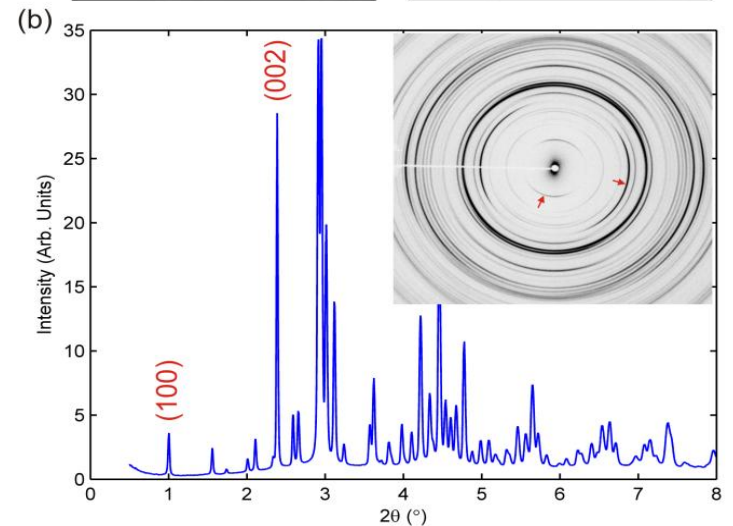
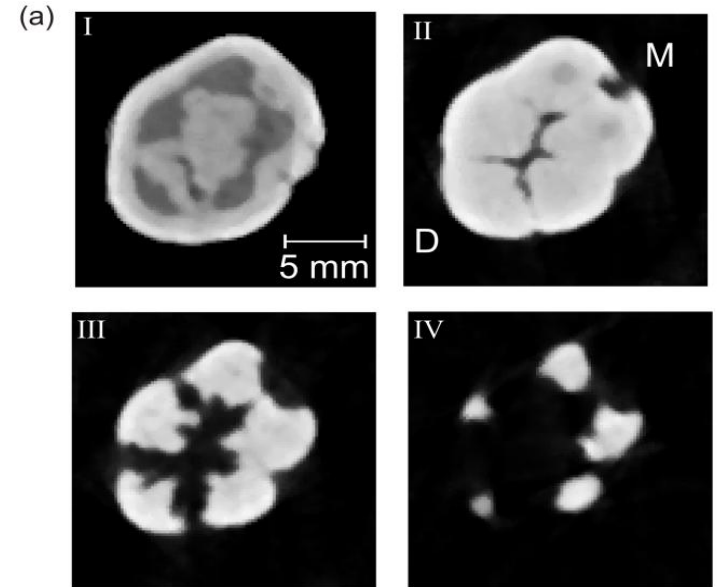
Support materials provide gas permeable environments with high SA

Advanced characterisation

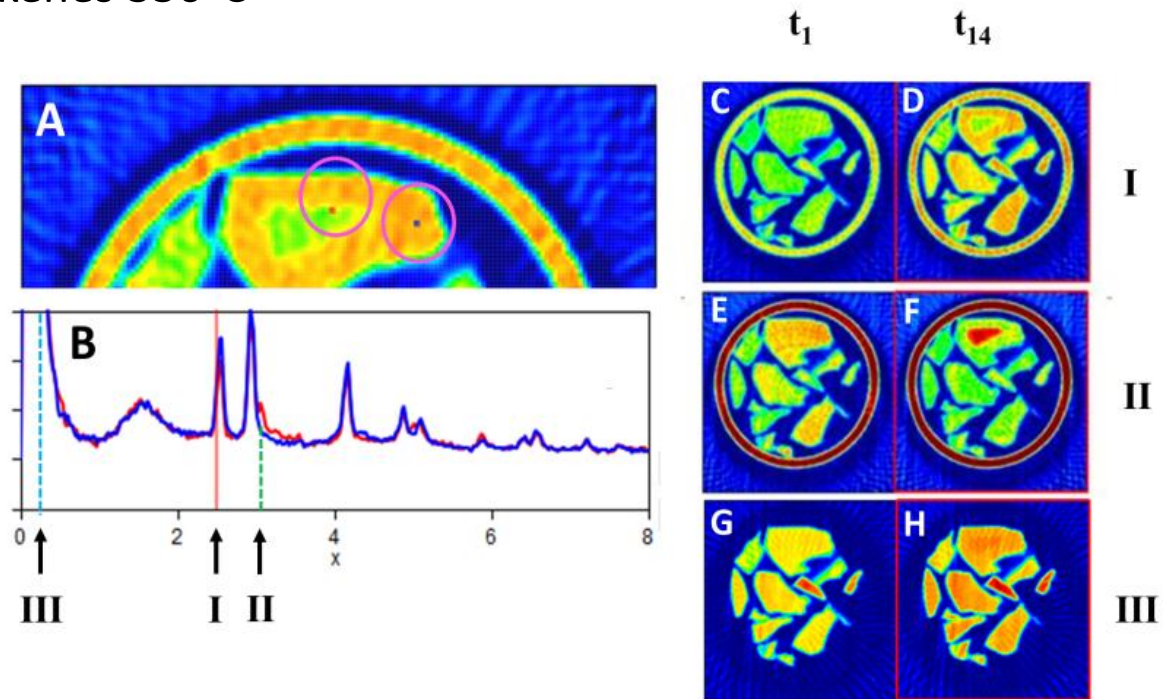
- In situ XRD-CT using high flux high energy X-rays (synchrotron technique)
- Combination of X-ray tomography and XRD
- Powerful non-destructive technique gives XRD signal at each point in **bulk samples**
- Any extractable feature in XRD can be mapped
- Open to conventional analysis



Crystallite size



- **Map evolving chemistry**
- Can discriminate sample from in-situ rig or container
- Industrial catalyst
- Calcination → activation → FT at atmospheric pressure
- Short chain alkanes/alkenes 350°C
- 5 μm resolution



In operando study of industrial FT catalyst using PDF-CT.

A raw intensity components of the reconstructed diffraction for this slice. B shows two reconstructed patterns blue and red spectra from the pixel positions circled in A. The maps C-H are maps of raw diffraction intensity at positions I, II and III in the diffraction pattern; where I and II correspond to positions associated with Bragg peaks for CoO and fcc Co respectively. Position III corresponds to a SAX signal which perhaps can be rationalised with PDF later. C,E & G and D,F & H show these components at times t_1 and t_{14} respectively. These images illustrate that spatial changes in time can readily be observed. .

Our experience

- *Advanced* characterisation is logical progression
- Fairly similar to standard methods
- Easy to convince Industrial partners / clients of the value of such characterisation methods once engaged
- Proof-co-concept is convincing step
- They are not demanding accreditation or benchmarking
- They look to us pre and post-study as to the value of data
- Timely that such characterisations are readily available

Our bottlenecks / issues

- Lag. From initial contact to commissioned study
- Lag. From 1st work to next commission
- Rapid requirements. Results next week !
- Heightened awareness of obtaining the data
- Technical challenges dealing with large data sets

Papers

Pair Distribution Function Computed Tomography

Simon. D. M. Jacques et al.

Nature Communications 4 (2013)

Dynamic X-Ray Diffraction Computed Tomography Reveals Real-Time Insight into Catalyst Active Phase Evolution

Simon. D. M. Jacques et al.

Angewandte Chemie International Edition 50 (43) p10148 (2011)

Probing ZnAPO-34 Self-Assembly Using Simultaneous Multiple in Situ Techniques

Andrew M. Beale et al.

The Journal of Physical Chemistry C 115(14) p6331 (2011)

Active phase evolution in single Ni/Al₂O₃ methanation catalyst bodies studied in real time using combined μ -XRD-CT and μ -absorption-CT

Matthew. G. O'Brien et al.

Chemical Science 3(2) p509 (2012)

Noninvasive Spatiotemporal Profiling of the Processes of Impregnation and Drying within Mo/Al₂O₃ Catalyst Bodies by a Combination of X-ray Absorption Tomography and Diagonal Offset Raman Spectroscopy

Emma K. Gibson et al.

ACS Catalysis 3 (3) p339 (2013)