sasol
reaching new frontiers

Photon and neutron sources: any good for industrial R&D?

E du Plessis

Sasol energy company - our global presence

sasol
reaching new frontiers

North America and Canada

North America and Canada

1 Lake Charles (Louisiana, USA)
2 Oil City (Pennsylvania, USA)
3 Richmond (California, USA)
4 San Francisco (California, USA)
5 Tucson (Arizona, USA)
6 Houston (Texas, USA)
7 Montney Basin, (Canada)
8 Calgary, (Canada)

South America

1 São Paulo (Brazil)

South America

Southern Africa

Southern Africa

1 Cape Town (SA)
2 Durban (SA)
3 Johannesburg (SA)
4 Sasolburg (SA)
5 Secunda (SA)
6 Harare (Zimbabwe)
7 Lusaka (Zambia)
8 Gaborone (Botswana)
9 Maputo (Mozambique)
10 Temane (Mozambique)
11 Mozambique (offshore)
12 Windhoek (Namibia)

Rest of Africa and Middle East

Rest of Africa and Middle East

1 Alexandria (Egypt)
2 Bandar Assaluyeh (Iran)
3 Doha (Qatar)
4 Ras Laffan (Qatar)
5 Dubai (UAE)
6 Tehran (Iran)
7 Escravos (Nigeria)
8 Nigeria (offshore)
9 Gabon (offshore)

Australasia

Australasia

1 Sydney (Australia)
2 Port Moresby (Papua New Guinea)
3 NW Shelf offshore (Australia)

Manufacturing/production Office Exploration Project New projects Research

our global presence

Western Europe

Eastern Europe

Europe

1 Birkenhead (UK)
2 Birmingham (UK)
3 Castletown (Isle of Man)
4 Farnham (UK)
5 London (UK)
6 St Andrews (UK)
7 Antwerp (Belgium)
8 Barcelona (Spain)
9 De Meern (The Netherlands)
10 Enschede (The Netherlands)
11 Paris (France)
12 Vordingborg (Denmark)
13 Brunsbüttel (Germany)
14 Hamburg (Germany)
15 Herne (Germany)
16 Marl (Germany)
17 Moers (Germany)
18 Witten (Germany)
19 Sarroch (Italy)
20 Milan (Italy)
21 Terranova dei Passerini (Italy)
22 Linz (Austria)
23 Augusta (Italy)
24 Bratislava (Slovak Republic)
25 Nováky (Slovak Republic)
26 Warsaw (Poland)
27 Moscow (Russia)

Central Asia, India and South East Asia

1 Shurtan (Republic of Uzbekistan)
2 Tashkent (Republic of Uzbekistan)
3 Mumbai (India)
4 State of Orissa (India)
5 Kertih (Malaysia)
6 Kuala Lumpur (Malaysia)
7 Singapore

Central Asia, India and South East Asia

Far East

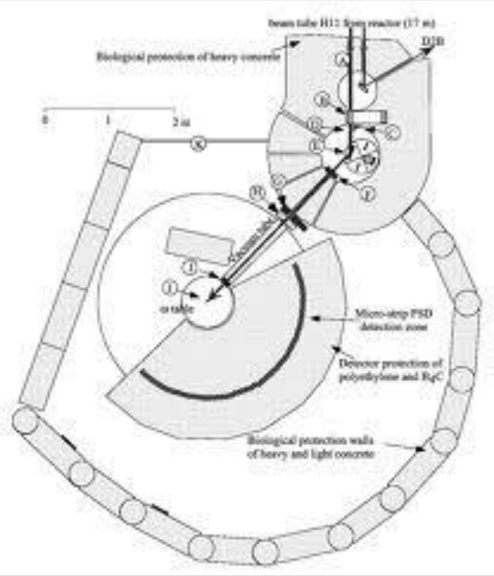
Far East

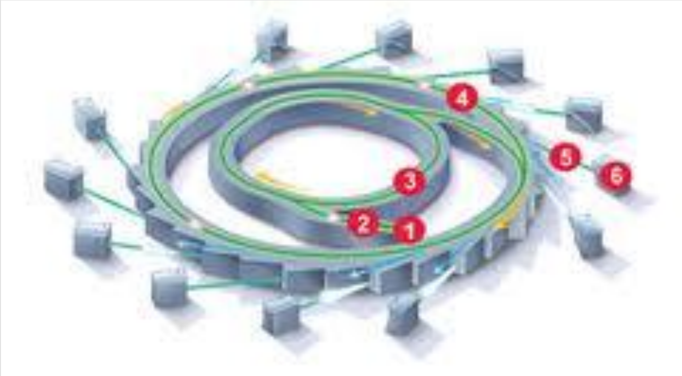
1 Beijing (China)
2 Dongguan (China)
3 Guangzhou (China)
4 Hangzhou (China)
5 Hong Kong (China)
6 Lianyungang (China)
7 Nanjing (China)
8 Ningxia Hui Autonomous Region (China)
9 Shanghai (China)
10 Oita (Japan)
11 Tokyo (Japan)
12 Yinchuan (China)

Manufacturing/production · Office · Exploration · Project · New projects · Research

Layout

- How we built contact
- How did we get started using neutrons and X-rays
- Synchrotron XRD/EXAFS – cost vs. benefit
- Academic/commercial beam time
- Team
- Lessons learnt
- How to improve value obtained from industrial access to light & neutron sources





How we built contact – conference/s

Science at Synchrotrons in SA

2007

Feb 2009: iThemba labs, SA: 65 researchers & policy makers, 58 postgrad students

Proposal writing workshop organized by prof Danie Hattingh (NMMU)

Proposal writing workshop

Synchrotron.org.za

ICTP/Hercules/schools

How we built contact - Students

XANES study of the susceptibility of nano-sized cobalt crystallites to oxidation during realistic Fischer-Tropsch synthesis

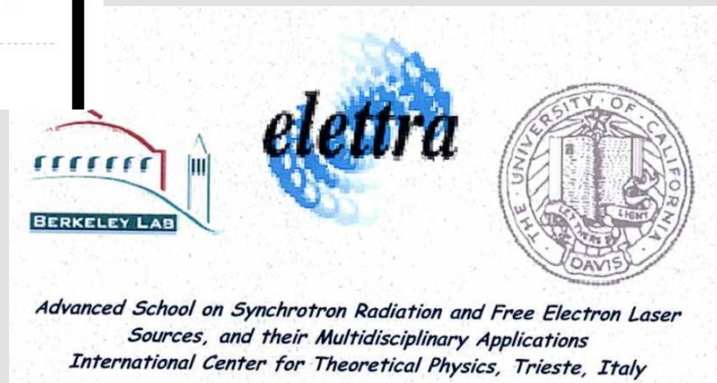
Abstract

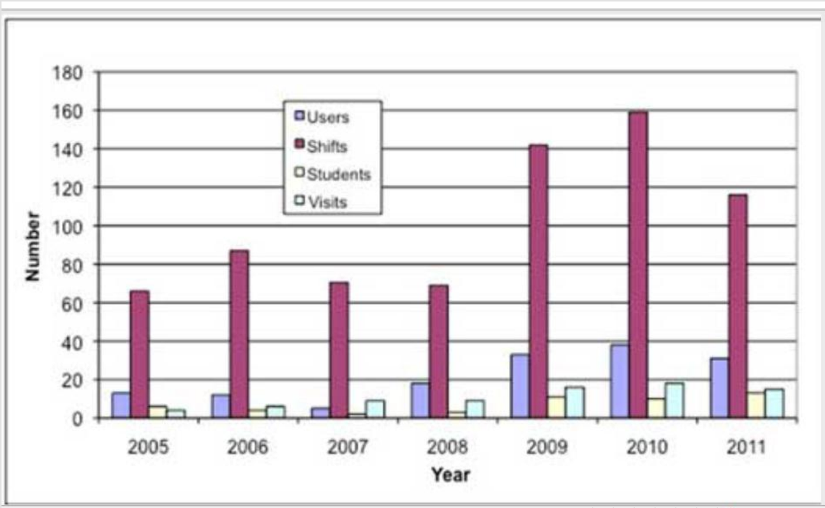
The oxidation of cobalt during Fischer–Tropsch synthesis (FTS) has long been postulated as a major deactivation mechanism. In this study, wax coated samples of a Co/Pt/Al2O3 catalyst were taken from a 100-barrel/day slurry bubble column reactor operated at commercially relevant FTS conditions, i.e. 230 °C, 20 bar, (H2 + CO) conversion between 50 and 70%, feed gas composition of ca. 50 vol.% H2 and 25 vol.% CO, PH2O/PH2=1–1.5, PH2O=4–6 bar and quantitatively characterised by X-ray absorption near edge spectroscopy (XANES). The cobalt catalyst samples, carefully removed from the reactor during the course of Fischer–Tropsch synthesis, were protected from air by the FTS wax. It is clear from the XANES measurements that during realistic FTS conditions cobalt crystallites of 6 nm supported on alumina were stable against oxidation to CoO/CoAl2O4 and a gradual reduction of residual cobalt oxide (i.e. following activation in pure hydrogen) was observed. This result is in line with recent thermodynamic analysis of the oxidation and re-reduction of nano-sized cobalt crystallites in water/hydrogen mixtures.

Saib, A.M., Borgna, A., Loosdrecht, J. van de, Berge, P.J. van & Niemantsverdriet, J.W. (2006). XANES study of the susceptibility of nano-sized cobalt crystallites to oxidation during realistic Fischer-Tropsch synthesis. *Applied Catalysis. A, General*, *312*, 12-19. *in Web of Science Cited 47 times*

How we build contact – International schools, NRF

Memoranda of Understanding:
Soleil
ESRF





Science and technology

SA, European scientists 'in synch'

Like 11
Tweet 4
+1 0

23 May 2013

South Africa's National Research Foundation (NRF) has signed an agreement with the European Synchrotron Radiation Facility (ESRF) in Grenoble, France to promote scientific collaboration and knowledge sharing.

The NRF has become a full international scientific partner to the ESRF through the agreement, which will facilitate the access of South African scientists to the ESRF and of

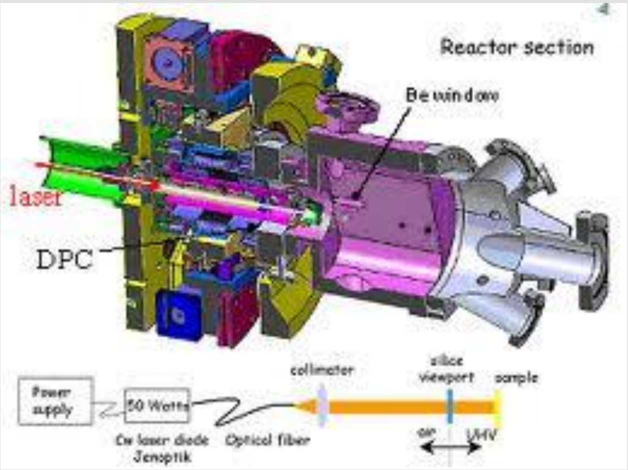
The European Synchrotron Radiation Facility in Grenoble, France has partnered with South Africa's National Research Foundation on scientific collaboration *(Photo: National Research Foundation)*

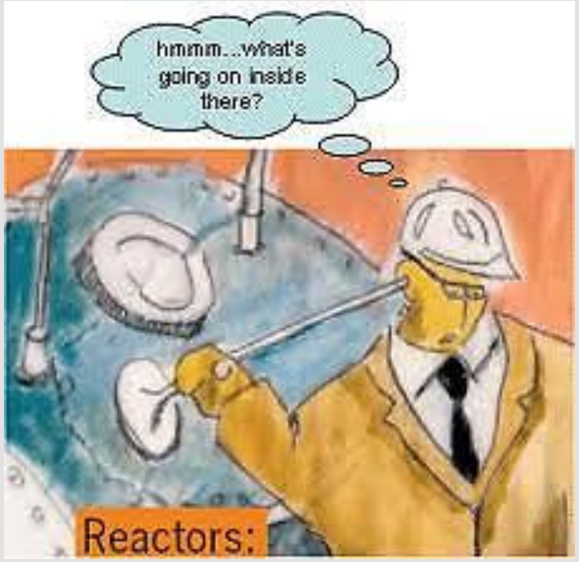
How we build contact

Consulting

Reading

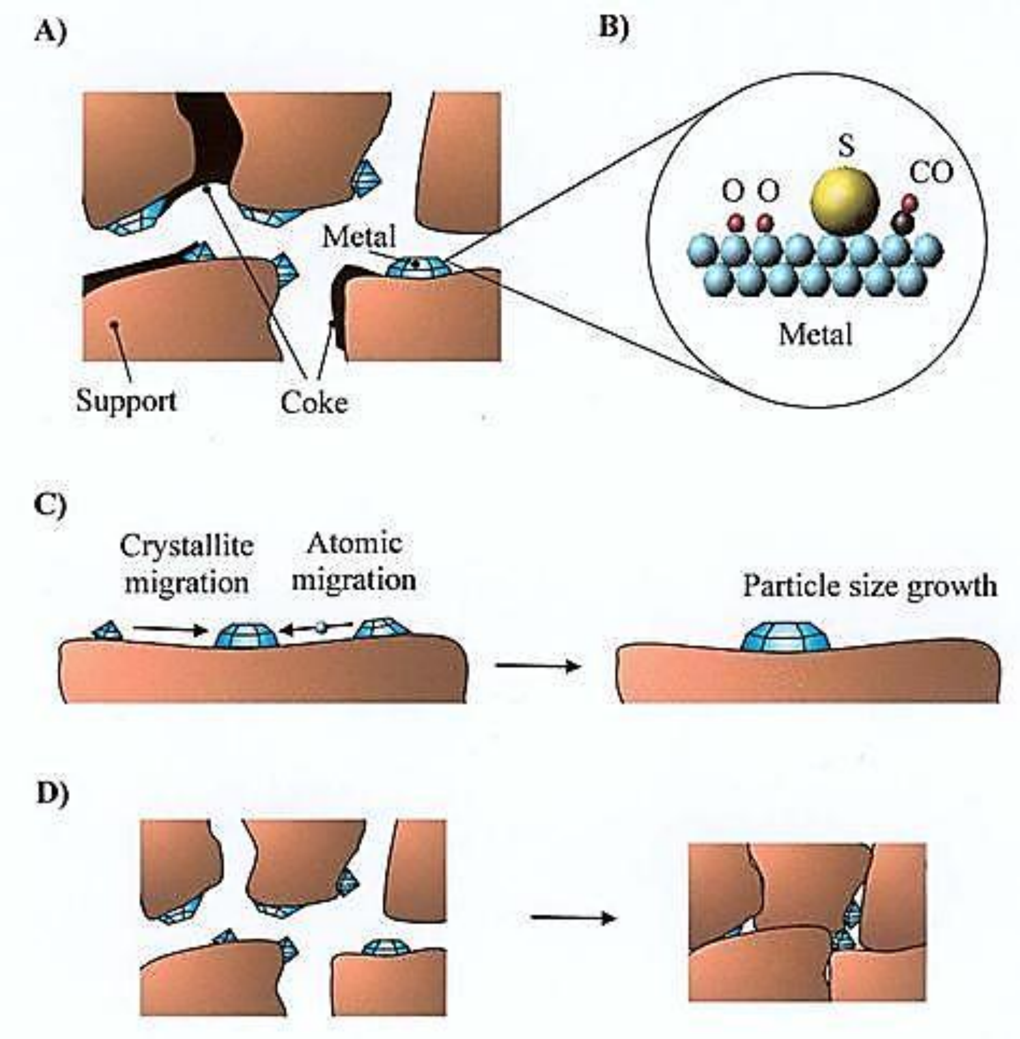
In situ catalyst characterization





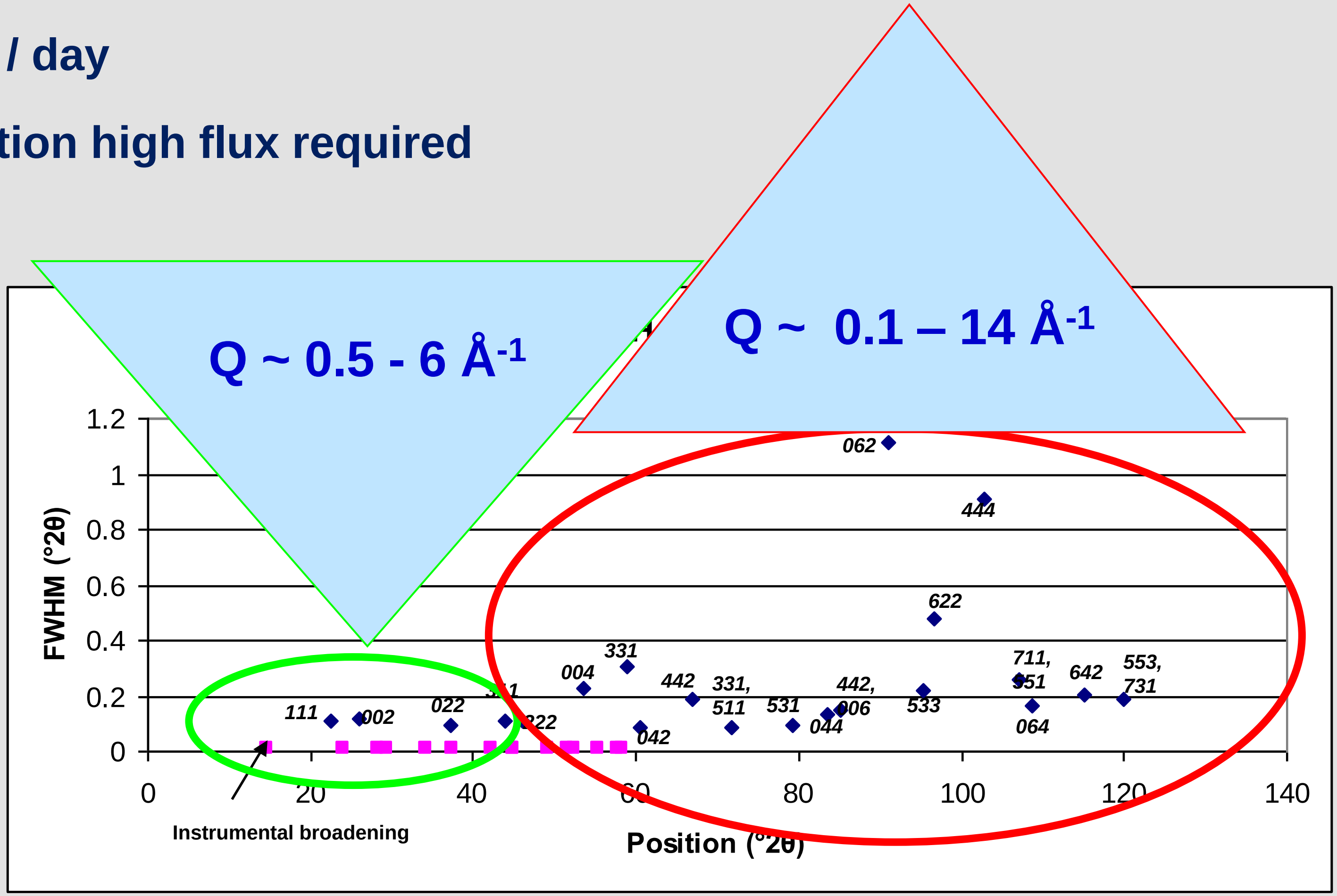
Catalysis Materials Characterization?

- Catalyst preparation
  - › Precipitation
  - › Calcination optimization
- Catalyst activation
  - › Optimization
  - › Promoter
- Working catalyst
  - › Phase ↔ activity ↔ selectivity
  - › Deactivation
    - Mechanism
    - Rate
    - Regeneration
- Fundamental understanding
  - › Catalyst design
  - › Characterization method development



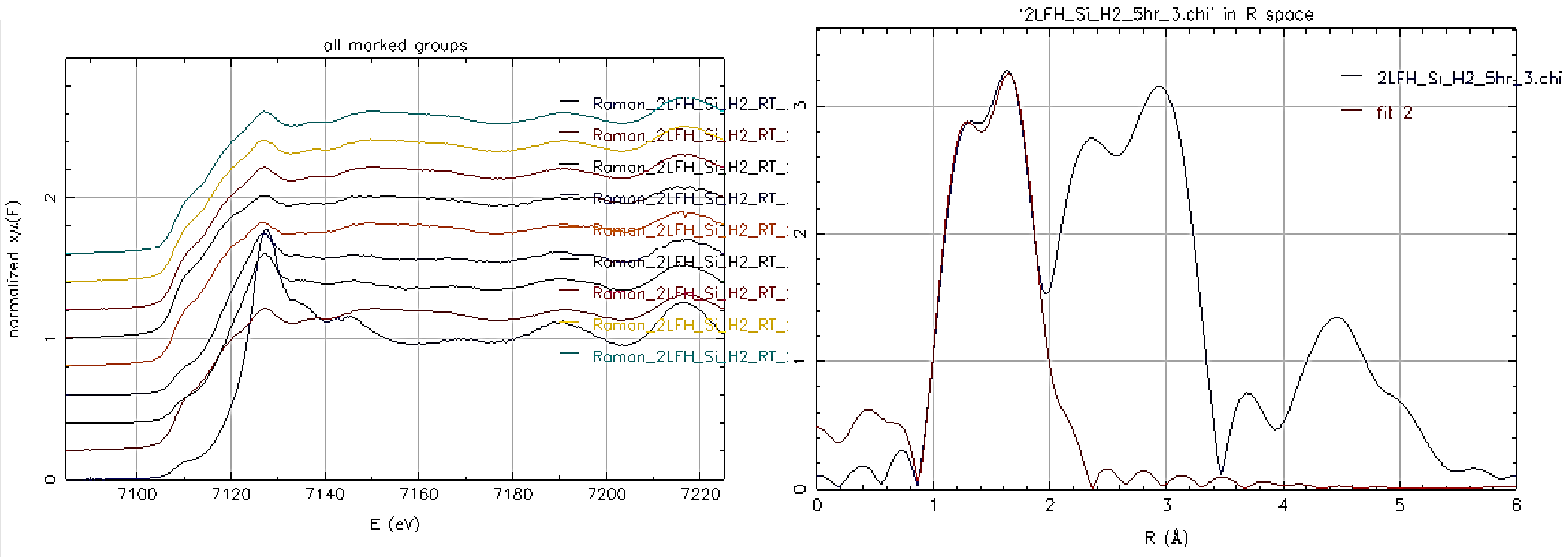
Synchrotron XRD: cost vs. benefit?

- **Pay per 8 hr shift for data acquisition**
- **> € 10 000 / day**
- **3rd generation high flux required**



Williamson-Hall plot

EXAFS/XANES: cost vs. benefit?



$$\gamma\text{-}Fe_2O_3 + H_2 \rightarrow Fe_3O_4 + Fe_xO + \alpha\text{-}Fe + H_2 \rightarrow \alpha\text{-}Fe$$

- **Flux requirements**
- **Academic beam time application to test with students**
- **Develop gas-rig, reactor configuration, network of specialists & data interpretation speciality**
- **Infrastructure established for industrial beam time**
- **Commercial beam time successful**

Academic or commercial beam time?

Academic

- New methodology/technique
- Have time to prove concept
- Want to probe possibilities of technique
- Development of infrastructure
- Can publish within a year
- Data can be made available to other users after a year
- A high impact, relevant research topic that can compete to thousands others

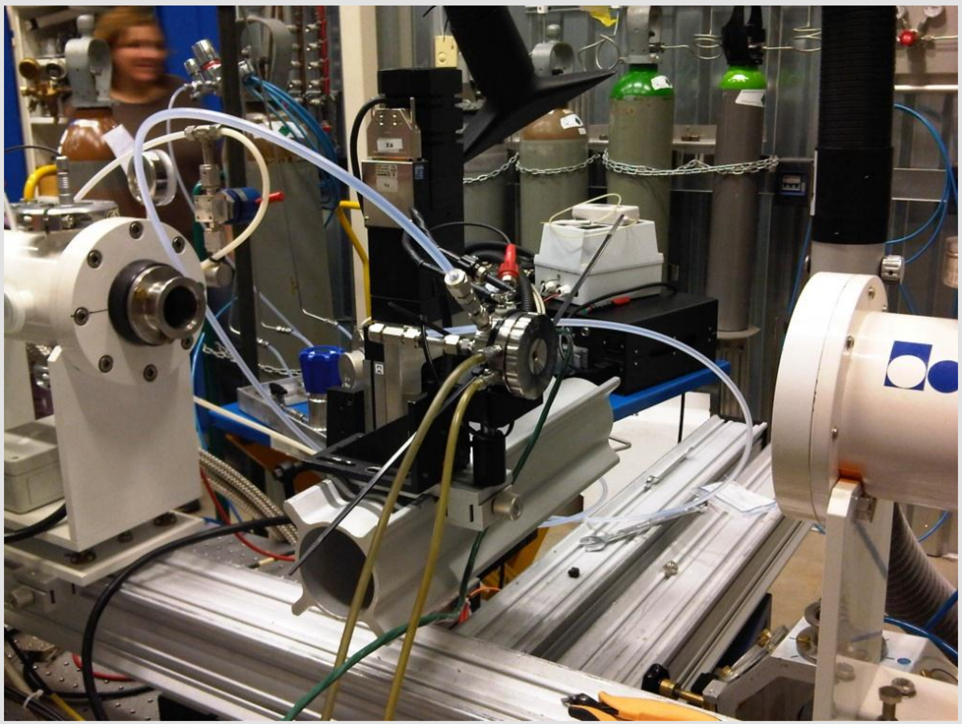
Commercial

- Have budget
- Analytical concept already proven
- Infrastructure available & reliable
- To compare to previous synchrotron results
- Data cannot be made available to competitors
- IP sensitive research
- *Ex situ* – the right sample for maximum measurement time
- *In situ* – absolutely worth the waiting time (3 hrs holding time)?

Stakeholders



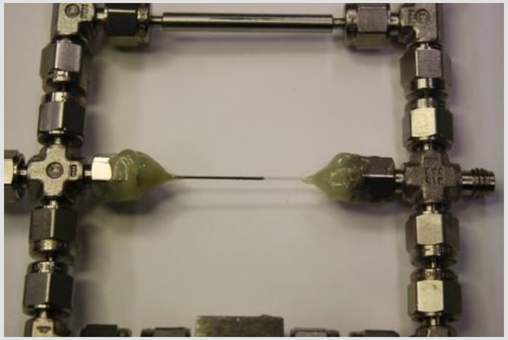


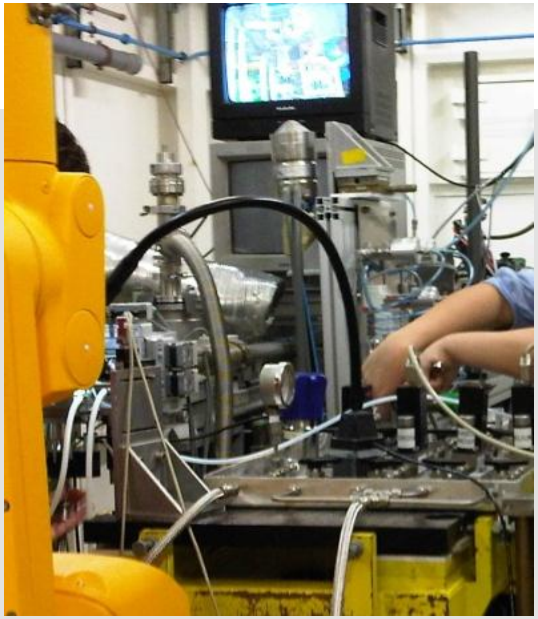


Research - coffee & little sleep
Safety first
Operate & know reactor
Know exact goal of each measurement
Can solve challenges
Know what the spectra should look like
Mobile
Networking skills
Laboratory skills
Teamwork

Lessons learnt

- Reaction chamber and gas supply





- Check each method with lab XRD prior to measurement to optimize time allocation
- Appropriate standard materials available
- Courier service functioning
- Back up reaction chamber(s)
- Start commercial process 6 months in advance
- *In situ* experiments require minimum of 4 people per 24 hrs
- Each team member must know the reaction chamber control software and limits
- Additional equipment (chiller); access to glove box/chemistry laboratory

Business & Strategic Success

sasol
reaching new frontiers

Dedicated strategy

Development of scientists & students

Building and understanding business case

Select & combine appropriate characterization techniques

Business gain

Maintain networks

Hunger for knowledge

Disordered cobalt aluminate?

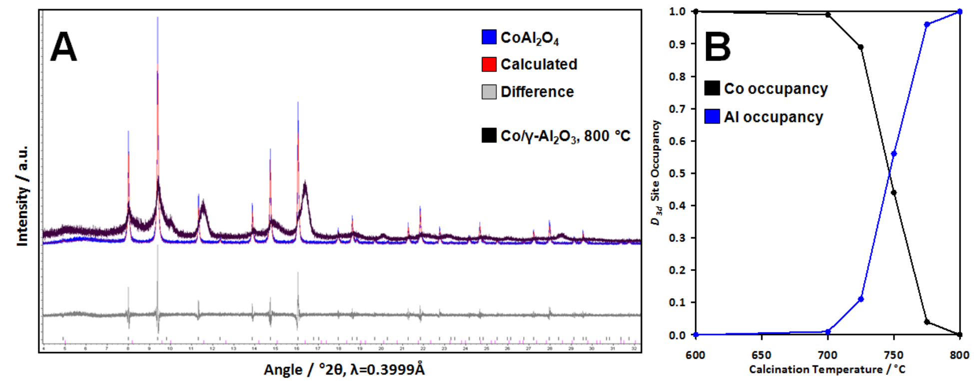


Figure 2A. Comparative synchrotron X-ray diffractograms of ordered $CoAl_2O_4$ and Co/γ-Al_2O_3 and 2B. The average D_{3d} site occupancy of Co and Al in the defect $Co_xAl_yO_4$ as determined using

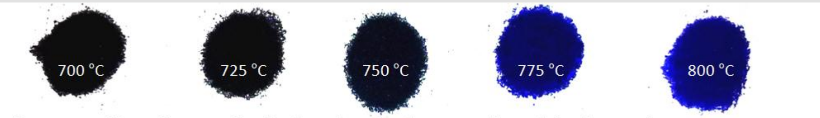


Figure 1. Colour photograph of selected Co/γ-Al_2O_3 samples calcined at various temperatures showing the formation of blue $Co_{3-x}Al_xO_4$ ($0 \le x \le 2$)

M(T) curves in the remanent mode (Figure 6) show gradual phase change from Co_3O_4 to $CoAl_2O_4$ via $Co_xAl_yO_4$ as intermediate phase with increasing calcination temperature. Fits of the Curie-Weiss model to the temperature dependence of the reciprocal susceptibility show that in both Co_3O_4 and $CoAl_2O_4$ the Co^{2+} ions are subjected to strong antiferromagnetic coupling.

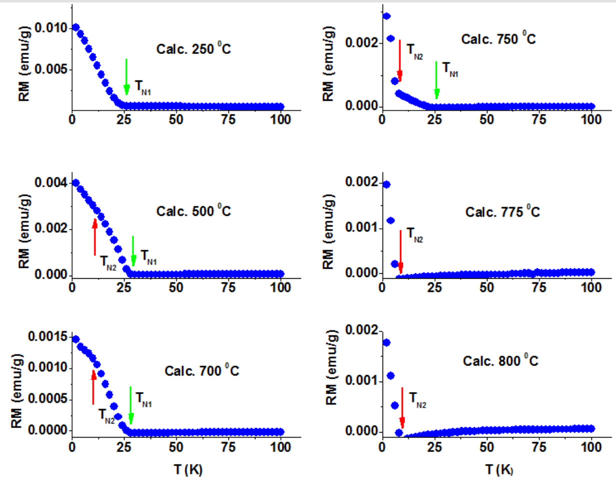


Figure 6. Temperature dependence of the magnetization in the remanent mode (RM) (i.e. zero applied magnetic field). $T_{N1} \approx 28$ K is the magnetic phase transition temperature for Co_3O_4 and $T_{N2} \approx 8$ K is the transition temperature for $CoAl_2O_4$.

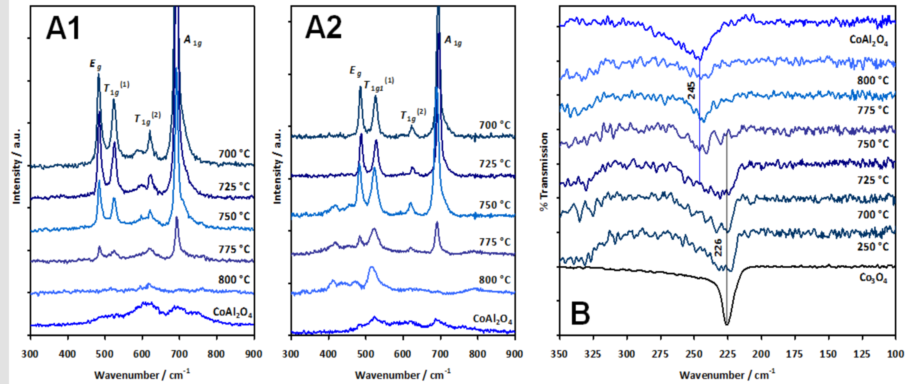


Figure 5A. Raman spectra of the samples calcined at 700 – 800 °C, measured using 1. 488 nm and 2. 514 nm radiation, 5B. ATR-FIR spectra of samples calcined from 250 – 800 °C

Broad bands in the $CoAl_2O_4$ spectrum shows that Co/Al site disorder is present. Factor group analysis for a spinel gives the following; with brackets indicating extra modes when metal site exchange occurs:

$$\Gamma_{cryst.\ vib.} = A_{1g}^{R} + E_g^{R} + 3T_{2g}^{R} + 4T_{1u}^{IR} [+ T_{2g}^{R} + 2T_{1u}^{IR}]$$

Epdic13 poster – W. Barnard, R. Forbes, E. du Plessis

The Crystal Structure of δ-Al_2O_3

Esna du Plessis, D.R.G. Mitchell, W. Barnard, J.P.R. de Villiers, A. Steuwer, A. Tuling

Sasol Technology (Pty) Ltd., R & D Division, Sasolburg, 1947, South Africa

E-mail: esna.duplessis@sasol.com

Powder Diffraction

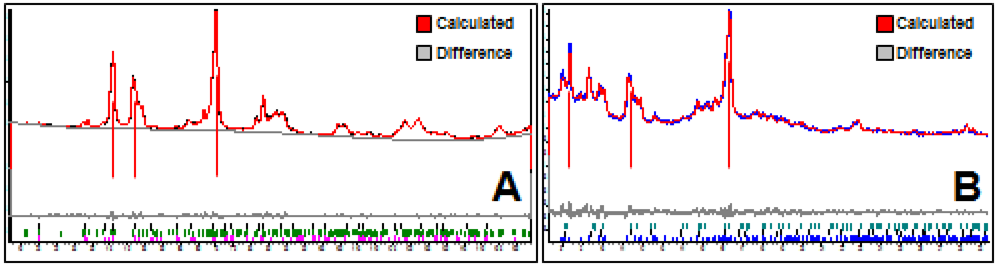
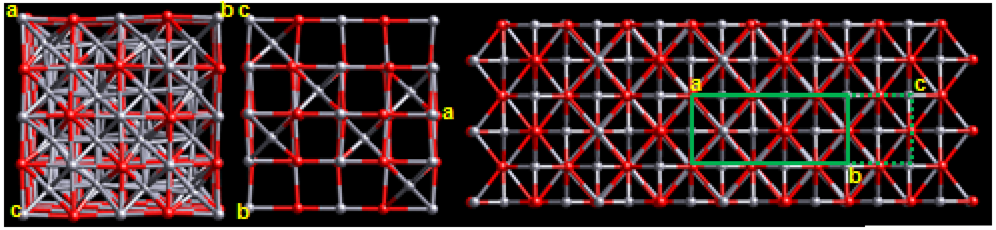
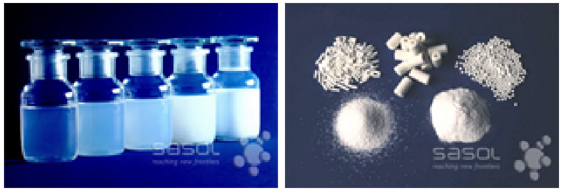


Figure 2. Match of theoretical and experimental diffractograms for (A) Neutron °2θ, λ=1.00Å and (B) Synchrotron X-rays °2θ, λ=0.40Å (| reflections originating from oxygen lattice).



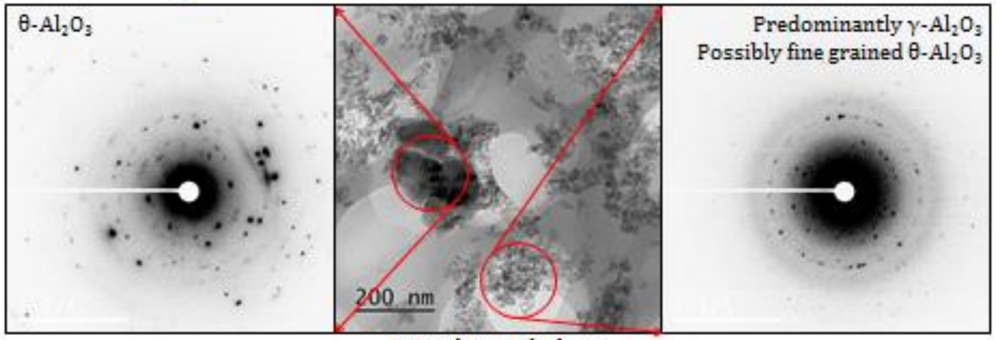
Cubic γ-Al_2O_3[9] **Tetragonal γ-Al_2O_3[10]** **Monoclinic θ-Al_2O_3[11]**

Experimental



- A sample of δ-Al_2O_3 was obtained from Sasol Germany. The sample contained no promoters and is therefore a model catalyst support.

TEM Analysis



Mixed morphology
Fine & coarse

BUSINESS BENEFIT

Industry & patents & strategies – need the results by yesterday.

Work in a catalysis/characterization/engineering **team**.

Budget challenges.

Long- and short-term perspective.

Business case!

- Analysis beyond laboratory facilities
- Catalyst lifetime
- Deactivation mechanisms
- Explain results, put into context

Photon/neutron team & Industry

- Commercial beam time → results in (un)reasonable time.
- Planning: small oversights → cost implications.
- Confidentiality and legal agreements - paperwork.
- Corporate governance, due diligence for financial process.
- In situ, flow through, pressure, realistic operation conditions.
- Design and adapt longer term strategy to fit business needs.
- Translator between characterization techniques at facility & questions industry needs answering.

How to improve value obtained from industrial access to light & neutron sources:

- Industrial research questions can seem simple.
- Yet challenging/time consuming.
- Expensive beam time → tough questions.
- Photons & neutrons: resolution / time / flux.
- Photon & neutron results fit into characterization puzzle owned by industry.
- Trust, reliability, accessibility, deliver on promises.
- Experienced beam line scientist.
- Technical backup – 24 hr.
- Inexperienced users intimidated by facility and physicists, need an opportunity to ask stupid questions. Local conferences, workshops, follow up workshops.
- Train good students that can provide solutions in future.
- Model catalyst systems for academic beam times a good basis to develop expertise for commercial beam time.

Feedback

- Commercial beam time → IP sensitive.
- Feedback to photon & neutron facilities vague.
- Requests important, feedback important.
- Academic beam time: travel & access for students important to SA users.
- Sasol mentors support & drive photon & neutron techniques.
- Assist students with sample preparation, training on leading an excursion, planning & data interpretation.
- Maintain and expand current network.
- Enjoy the science!

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Dr Werner Barnard

S@S committee

Thank you