Non X-ray analytical methods at P64/65

Potential contributions to and from VIA

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Non X-ray analytical methods at P64/65

Some thoughts

Not a topic of this talk:

Ionisation chambers, SDDs or **HPGe detectors** because they are part of the beamline's core business that is detecting X-rays after their interaction with matter.

Offline analytical techniques are not part of my talk but might be of interest for VIA if we agree that the *nano-lab* is – for whatever reason - not the right place for this.

Equipment needed for **in-house research**

Topic of this talk is:

How and with which analytical methods do we currently support the users of P64/65 **during their measurement** and which additional analytical methods might benefit the users in the future

Users at P64/65

- Come to do X-ray (absorption) spectroscopy experiments

- Characterise their samples and procedures in advance in their home laboratories

=> Usually don’t need offline analytical techniques

- Do a lot of in-situ experiments in catalysis and related fields and are interested in structure/function relations

=> Need to analyse the products of their reactions

- Are usually **experts** in the analytical methods they use

- Do most of their in-situ experiments in the gas phase

=> Need methods for gas analysis

- Almost **never** ask for additional analytical tools for **ex-situ** experiments

=> Probably because they have all the time in the world to this stuff at their home laboratory

Multi modal measurements at P64/65

In-situ experiments

“A capillary microreactor heated by a hot air gas blower (Oxford) was used as the in situ cell. Gases were dosed using mass flow controllers (Bronkhorst). The gas concentration in the product flow was monitored online using a **mass spectrometer** (Omnistar, Pfeiffer Vacuum) and an **FTIR spectrometer** (MultiGas 2030 FTIR Continuous Gas Analyzer, MKS”

From: Maurer, F., Jelic, J., Wang, J. et al. T*racking the formation, fate and consequence for catalytic activity of Pt single sites on* CeO_2. **Nat Catal** 3, 824–833 (2020). https://doi.org/10.1038/s41929-020-00508-7

“Note that this sequence may contain other (short-lived) intermediates, such as the reactive thiol (CHB-SH) shown in Fig. 4A, which we directly observed via **mass spectrometry**. “

From: M. F. Wagenhofer, H. Shi, O. Y. Gutiérrez, A. Jentys, J. A. Lercher, *Enhancing hydrogenation activity of Ni-Mo sulfide hydrodesulfurization catalysts* **Science Advances** 08 May 2020 : eaax5331

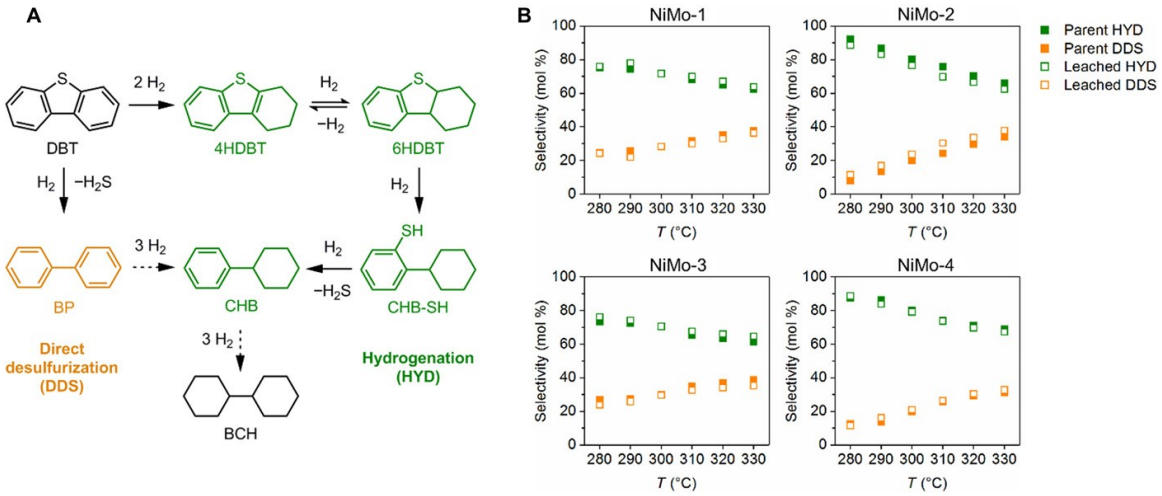


Fig. 4 DBT HDS network and measured selectivities.
(A) Reaction network. (B) Selectivity for DDS and HYD of DBT on Ni-Mo sulfide catalysts before and after acid treatment as a function of temperature [trickle-bed reactor, 280° to 330°C, 5.0 MPa total pressure (H2), 1 weight % DBT in decalin, gas/liquid = 500 Nm3/Nm3, weight hourly space velocity = 1]. mol %, mole percent.

Our mass spectrometer

The Swiss knife in catalysis...

- Predecessor available since ~2005 (DORIS XAFS beamlines)
- Hiden ExQ available since ~ 2 years, replaced the old Pfeiffer MS
- 0 – 200 AU
- Detectors: Faraday cup and Channeltron Electron Multiplier
- Part of our in-situ cell set-up, shared control computer for gas flow controllers, hot air blower and MS
- Regularly used at both beamlines
- Co-ordinated scheduling for the 2 beamlines
- Experts: Marcel Goerlitz and Claudia Schwan.

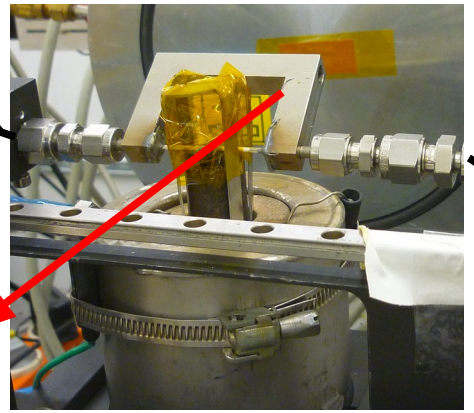
Hiden ExQ at the beamline

P64/65 in-situ set-up

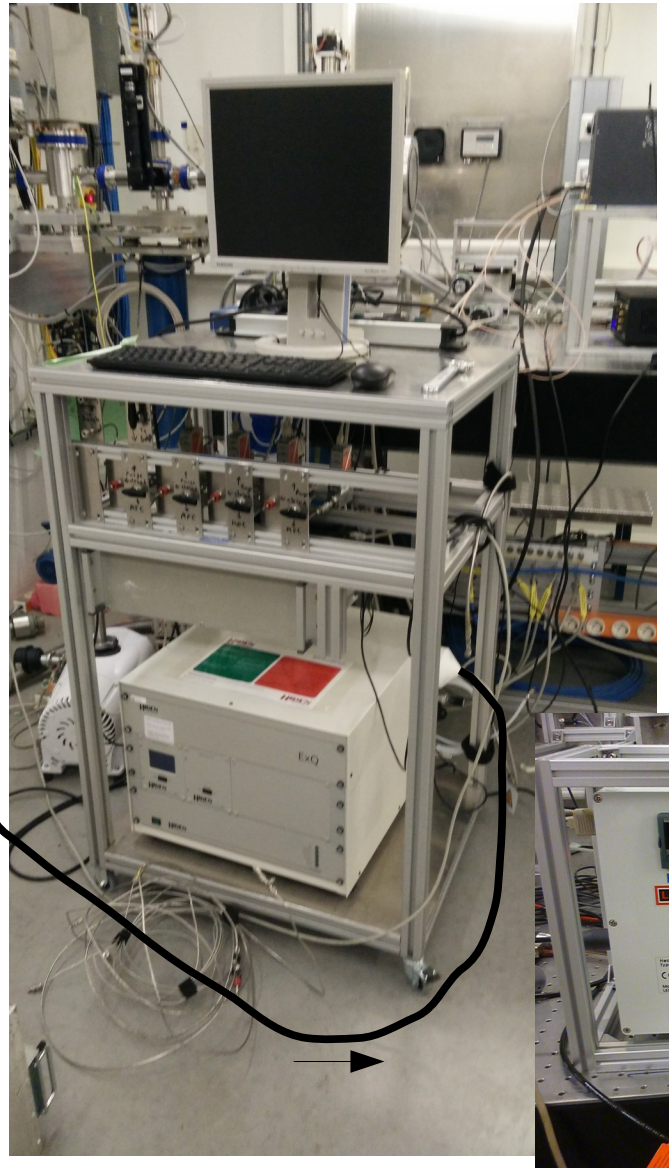
The MS as part of a complete experiment

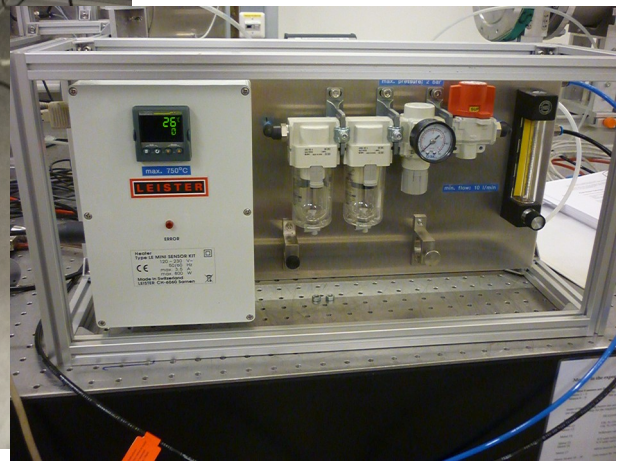
- Main components were designed and build in the group of A. Jentys (TU-Munich) as part of a BMBF Verbund-forschungs project

- MS integration by us



Quartz capillary cell with hot air blower





Gas flow controller and temperature / air flow controller for hot air blower

Observations

From our user's perspective or Why do many groups bring their own MS?

Own equipment	Beamline/VIA
Control about contamination	Unknown history (contamination)
Bespoke design	One size fits all
Familiar with operation	Unfamiliar with operation, comparability with results from home lab
Transport of delicate equipment	No tranport
Costs of own equipment	Non regular users safe expenses for seldom used equipment
	Mandatory for full service experiments (Industry, mail-in)

Methods used so far

- **Mass spectrometry**
- **Mass spectrometry**
- **…**
- **Mass spectrometry**
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- GC-MS
- GC-FTIR
- FT-IR
- HPLC - UV/Vis

In all cases non x-ray analytical methods served to analyse the products of in-situ/operando experiments in the gas stream

Future additions / wish list

Product analysis:
- Different flavours of spectrocopy (UV/Vis, IR, Raman…)

- Coupled methods **GC**-MS, **HPLC**-MS, GC-IR…

Direct view on the sample:
- **XEOL** (in principle also an – indirect - detector for X-rays), currently set-up as part of a BMBF project (Uni-Leipzig, C. Schnohr)

- Fast online detection of **radiation damage** with (non X-ray) spectroscopic methods (Finally an ex-situ application)

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Summary

- Many user experiments at P64/65 use non X-ray analytical methods in parallel to their (XAFS) spectroscopy experiment

- Most experimental set-ups are very special and it will be hard to implement a *one size fits all* solution for for use by all/many user groups

- However, some analytical methods like MS are so popular that they should be or are already part of the beamline equipment even so experienced users often prefer to use their own equipment

- VIA should focus on support for the less often used analytical methods which are only occasionally used at one beamline