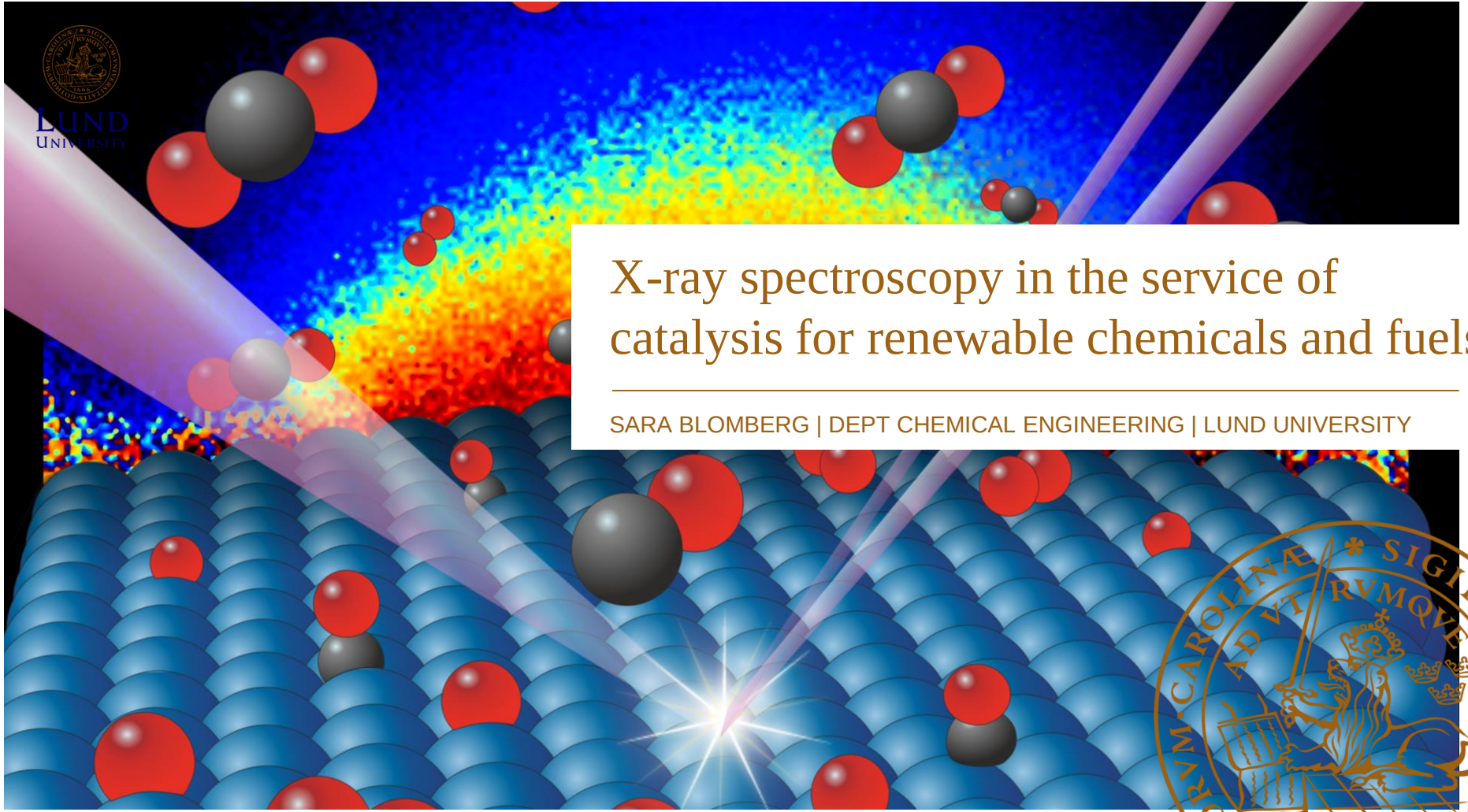

X-ray spectroscopy in the service of catalysis for renewable chemicals and fuels

SARA BLOMBERG | DEPT CHEMICAL ENGINEERING | LUND UNIVERSITY

Outline

- *Operando* experiments using XPS
- *Lignin* – a potential renewable feedstock
- *In situ* characterization of industrial NiMo catalyst
- Nanoparticles as model system
- Conclusions

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What is a catalyst?

- Swedish chemist Jöns Jakob Berzelius
- A substance that modify the reaction rate of a chemical process without being consumed.
- Powerplants, industries and cars.

Jöns Jakob Berzelius
1779-1848

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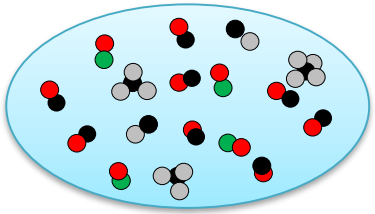
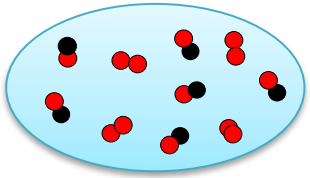
CO oxidation on simplified model systems

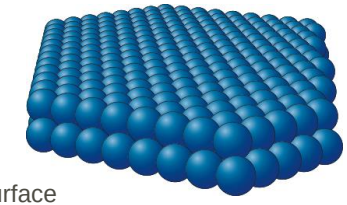
Complex gas phase



CO oxidation

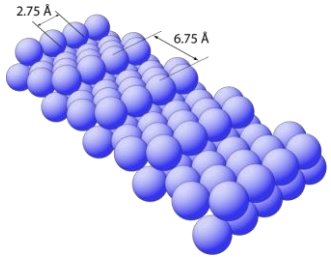


Low-index surface

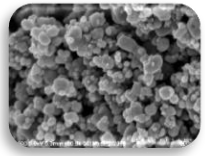


Three-way catalyst

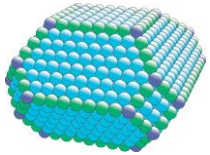
Vicinal surface



Porous material supporting catalytically active particles



nanoparticles



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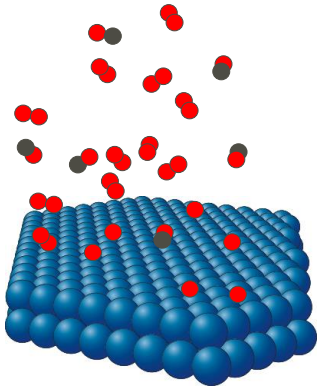
Ex situ vs ***In situ*** Studies

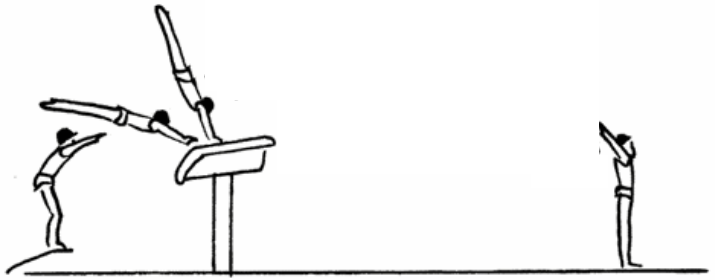
1. Expose ga

Study the surface ***during*** exposure of gases

2. Study the surface



Why in situ?



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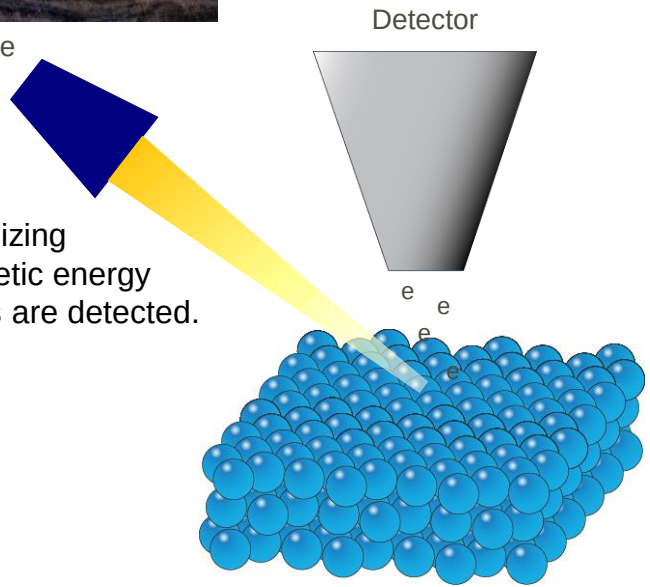
X-ray Photoelectron Spectroscopy

Light source

Detector

Incoming X-ray is ionizing
the atom and the kinetic energy
of the photoelectrons are detected.



$$E_b = h\nu - E_k$$

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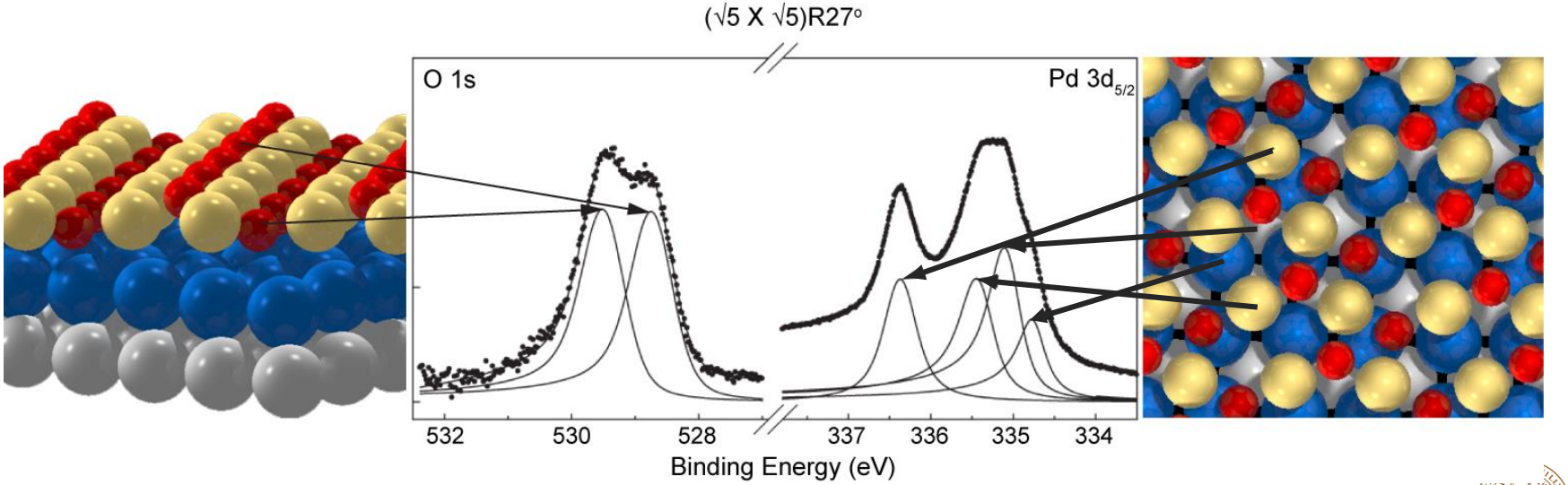
Surface sensitive and chemical information



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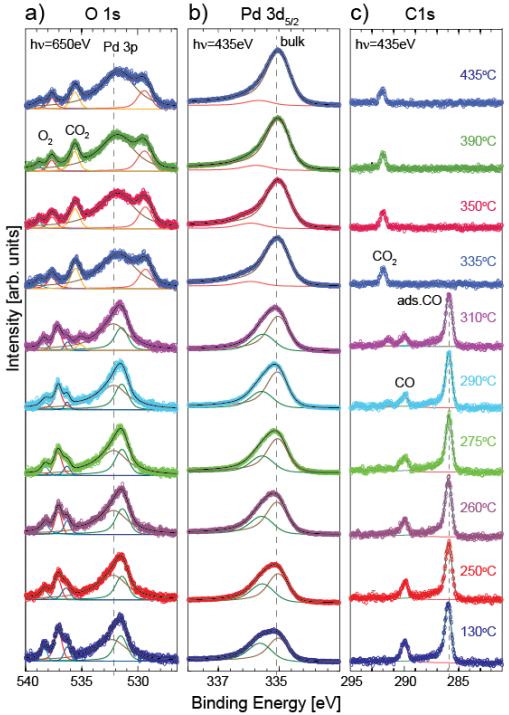
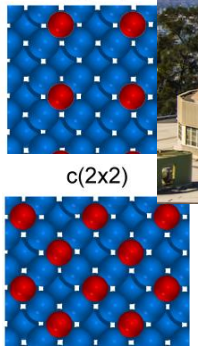
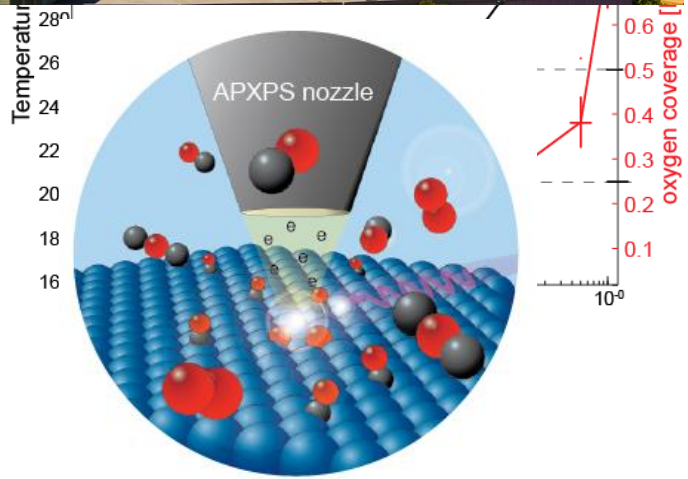
CO oxidation over Pd(100) < 1 mbar

9.3.2 ALS

0.25 Torr CO and 0.25 Torr O_2







"In Situ X-Ray Photoelectron Spectroscopy of Model Catalysts: At the Edge of the Gap"
S. Blomberg et al, Phys. Rev. Lett. ***110*** *117601 (2013)*

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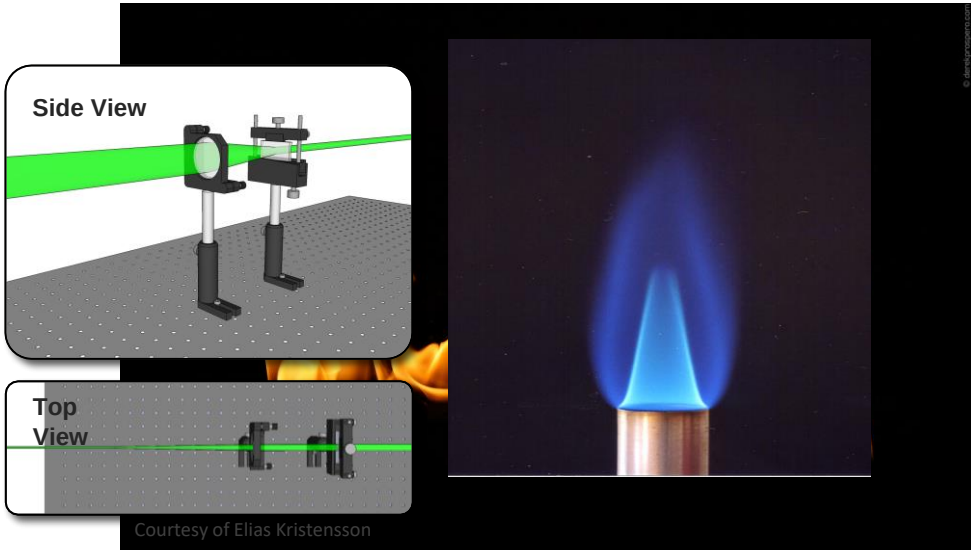
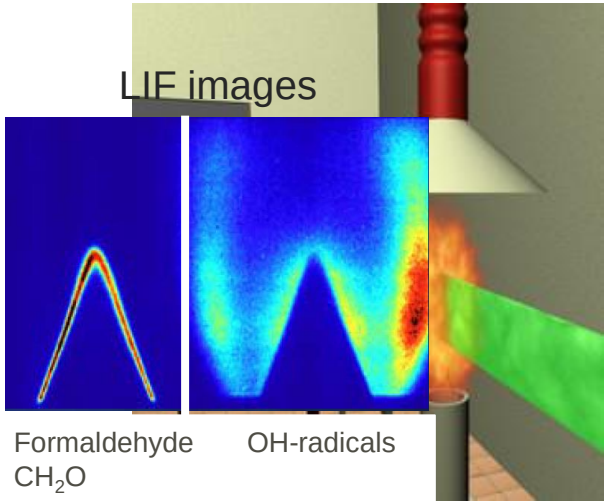
Laser-induced Fluorescence

Common technique used in combustion physics



Probe the flame with laser to achieve information about the chemical composition.



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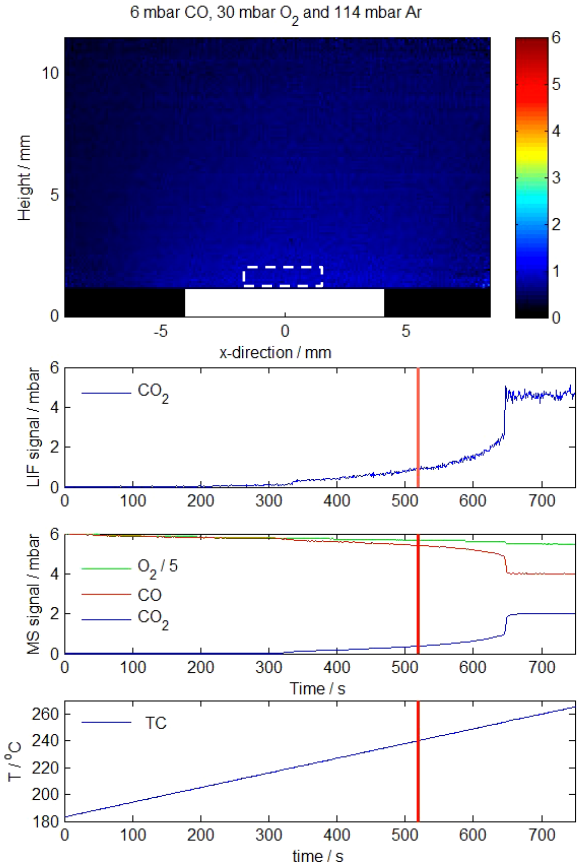
CO oxidation over Pd(100), detecting CO_2



LIF signal 0.5 mm above surface

MS signal
- average gas signal

Sample temperature

S. Matera, S. Blomberg et al, ACS Catal. 5 4514 (2015)

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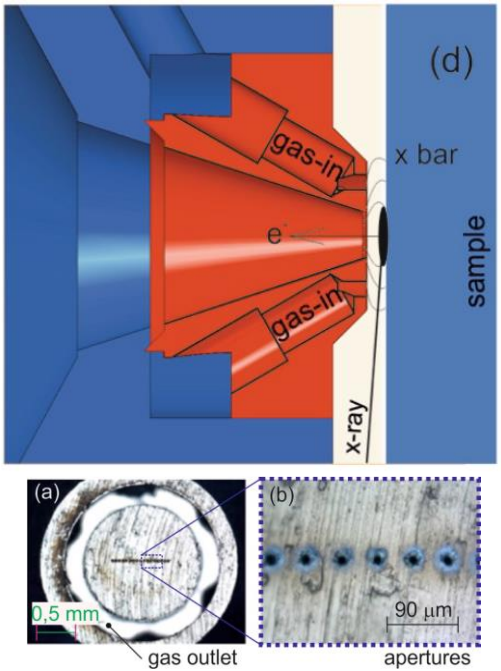
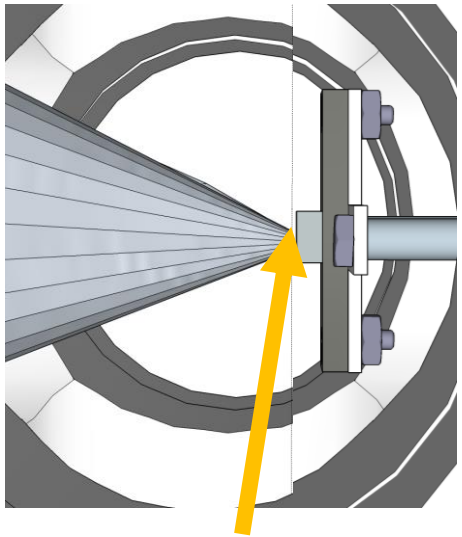
POLARIS endstation P22, DESY

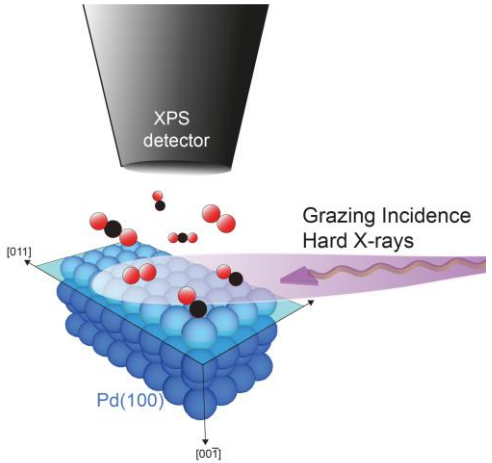
New design
Peter Amann - Stockholm University



Tot gas flow : 3.5-5 l/min - 1bar



0.6 degrees
hv = 4600 eV



"A high-pressure x-ray photoelectron spectroscopy instrument for studies of industrially relevant catalytic reactions at pressures of several bars"
P. Amann et al, Rev Sci Instrum, 90 (2019)

"Bridging the Pressure Gap in CO Oxidation"
S.Blomberg et al, ACS Catalysis, ***11,*** *(2021)*

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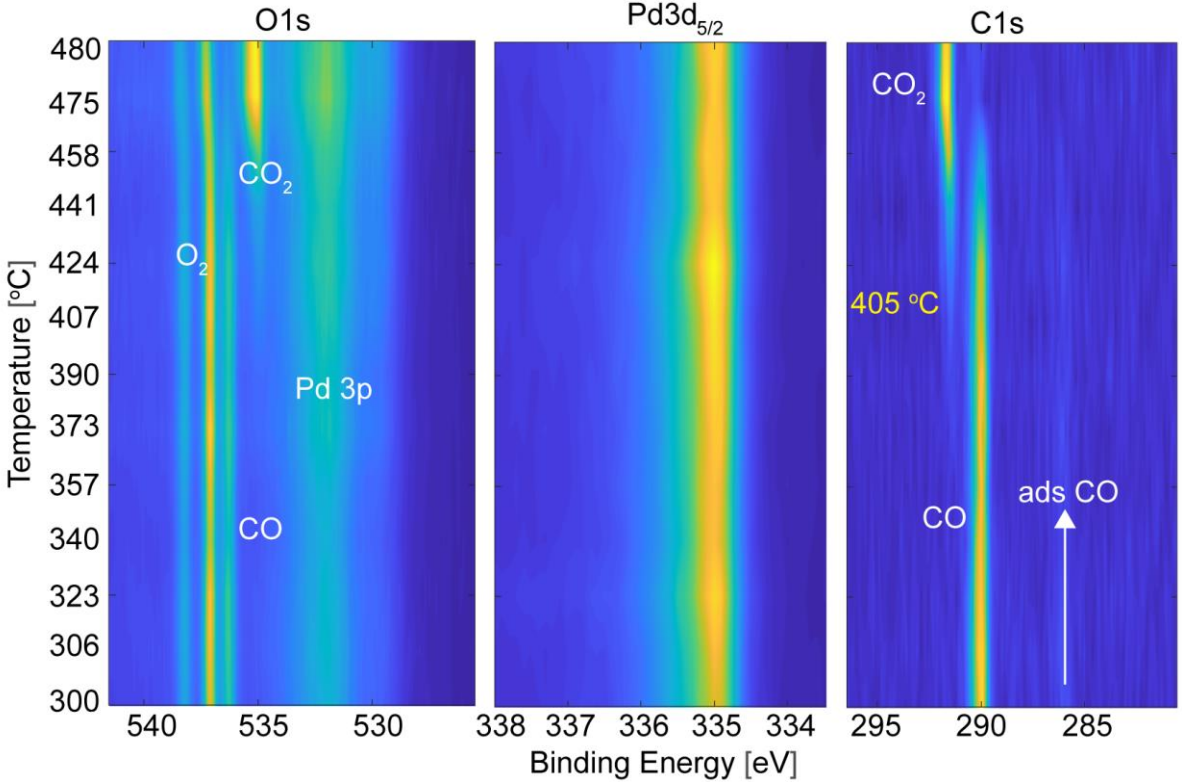
CO oxidation Pd(100) @1 bar

- 1:1 $CO:O_2$ - 6% CO and O_2 each in He, tot flow 5.18 l/min with



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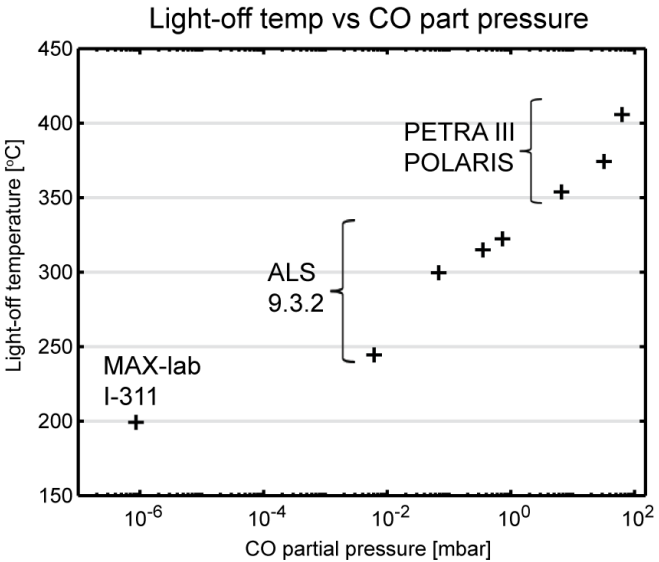
Pressure dependent light off

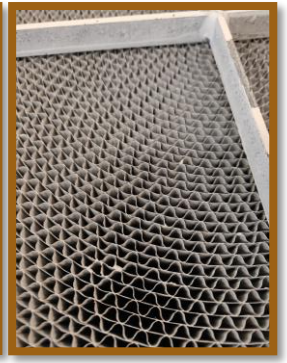


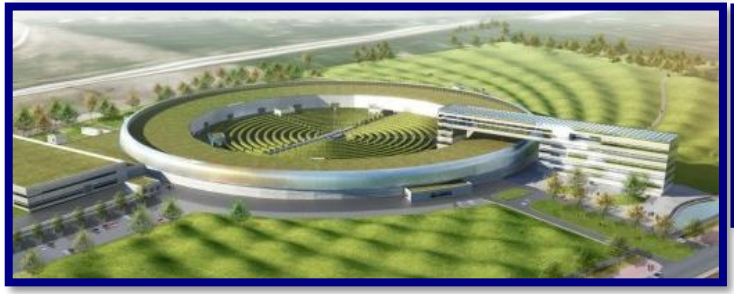
Szanyi, J.; Goodman, D. W., Co Oxidation on Palladium .1. A Combined Kinetic-Infrared Reflection-Absorption Spectroscopic Study of Pd(100). J Phys Chem-Us 1994, 98 (11), 2972-2977

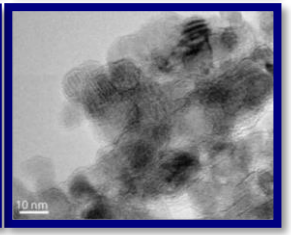
Gabasch, H.; Knop-Gericke, A.; Schlogl, R. et al., Comparison of the reactivity of different Pd-O species in CO oxidation. Phys Chem Chem Phys 2007, 9 (4), 533-540.

From meter to nanometer and back

12 reactors – Ø 0.6m X 1.8 m catalyst bed







Reactor- Ø 1.5 mm X 2 cm catalyst bed

-*In situ* X-ray techniques for characterization

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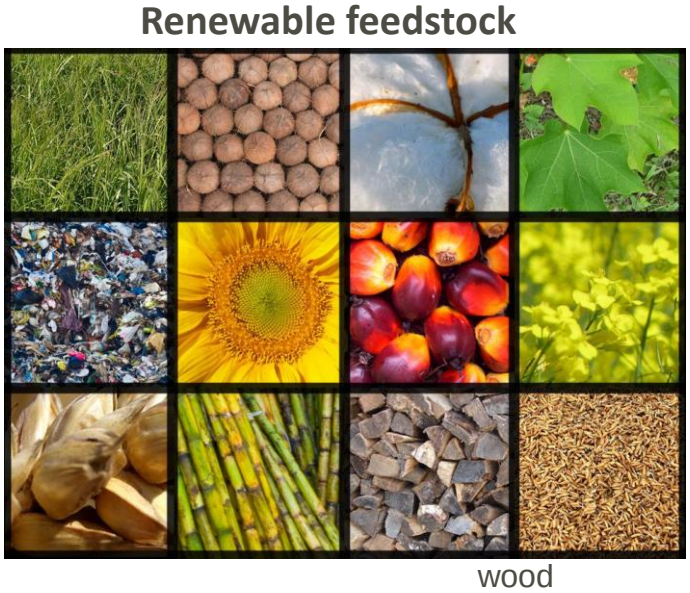
Transition to sustainable aviation fuel



- Transition from fossil feedstock to renewable feedstock is urgent!
- Net-zero carbon emissions from air transport industry by 2050.
- Competence centre CESTAP – sustainable aviation biofuel

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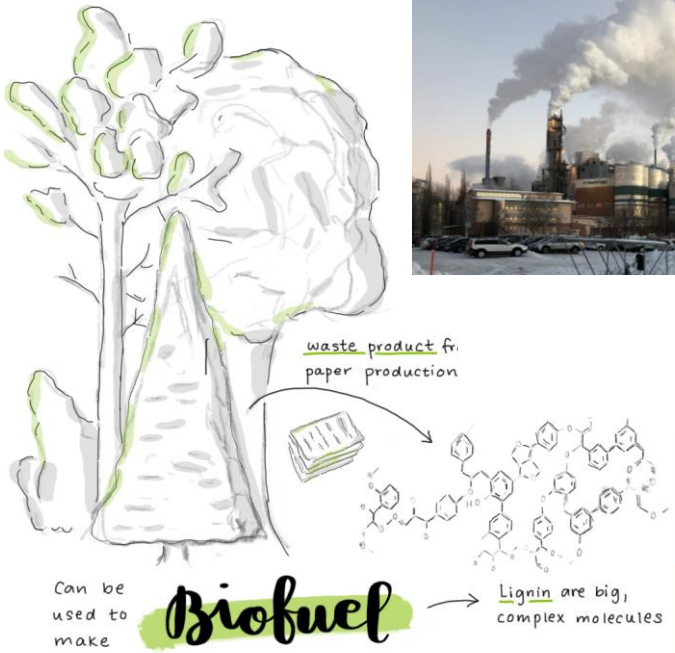
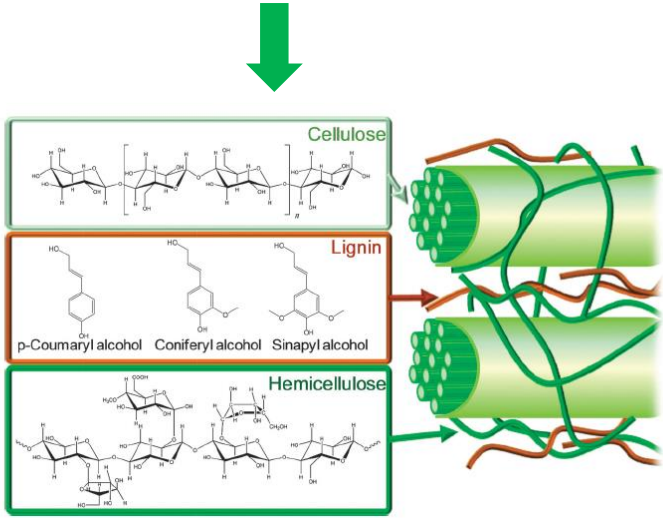
www.ec.europa.eu

Valorization of lignin, a byproduct from papermills



Courtesy of Emilie Hillner

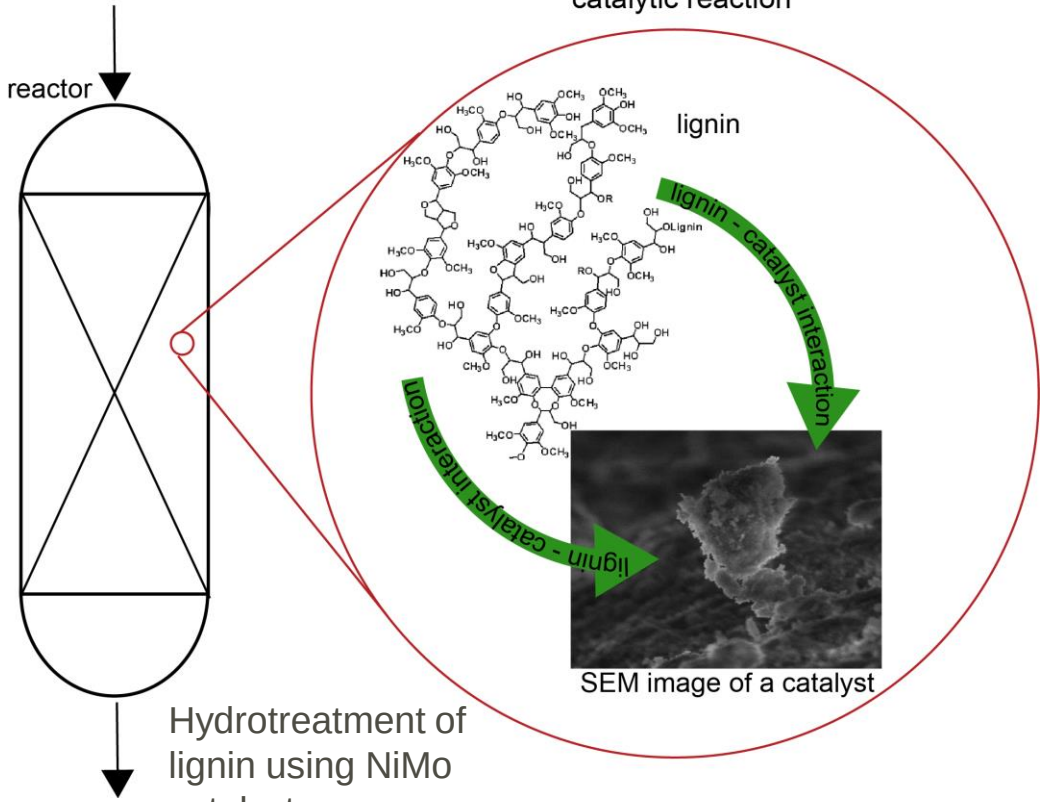
Smurfit Kappa



Sweden is the 3rd largest exporter of pulp and paper in the world

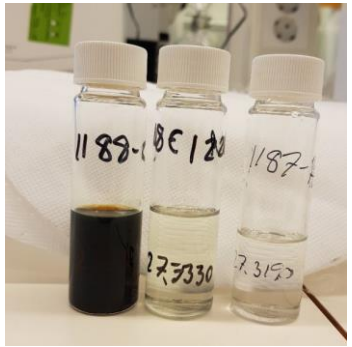
Hydrotreatment of lignin

Ligninbased feedstock



Hydrotreatment of lignin using NiMo catalysts

Biofuel



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Chemical reactions

Feedstock

Chemical reaction

Products

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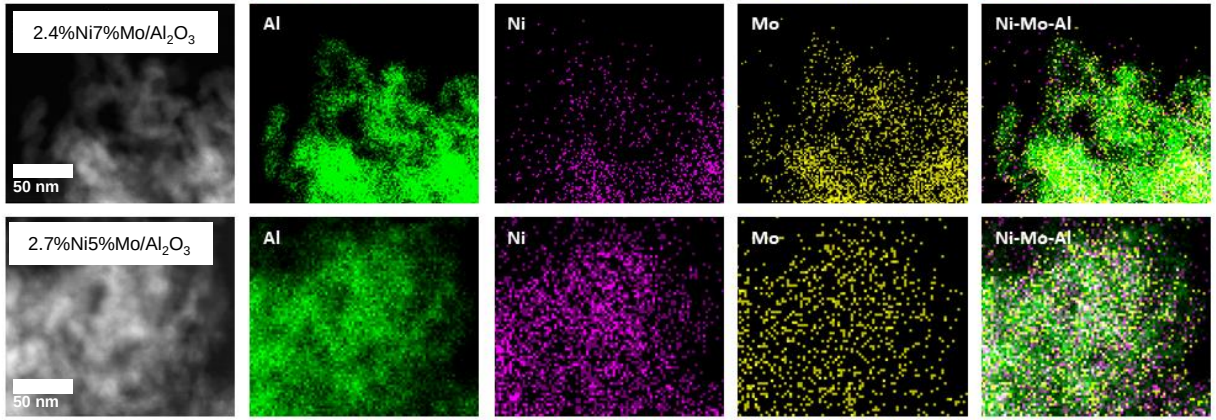
Characterization of Alumina supported NiMo

STEM

STEM / EDX

Wt% on δ-Al_2O_3



2.4wt%Ni 7.0wt% Mo

2.7wt%Ni 5.0wt%Mo

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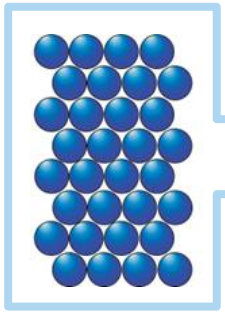
Simplified systems

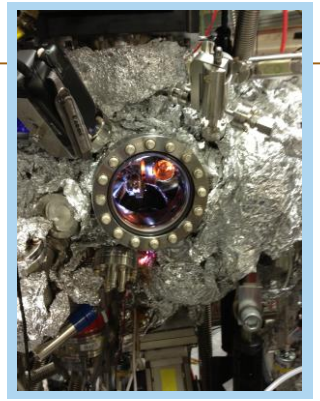


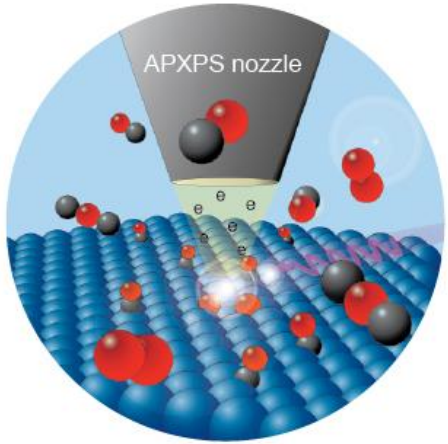
Simplified model system

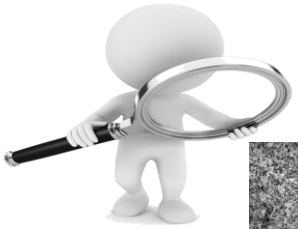
Pressure (mbar)

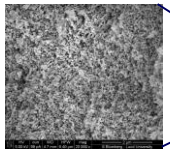
10^{-11}
10^{-10}
10^{-9}
10^{-8}
10^{-7}
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
1
10
100
1000

UHV

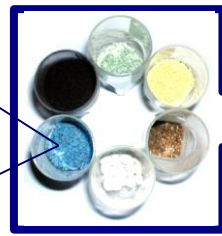








Industrial catalysts



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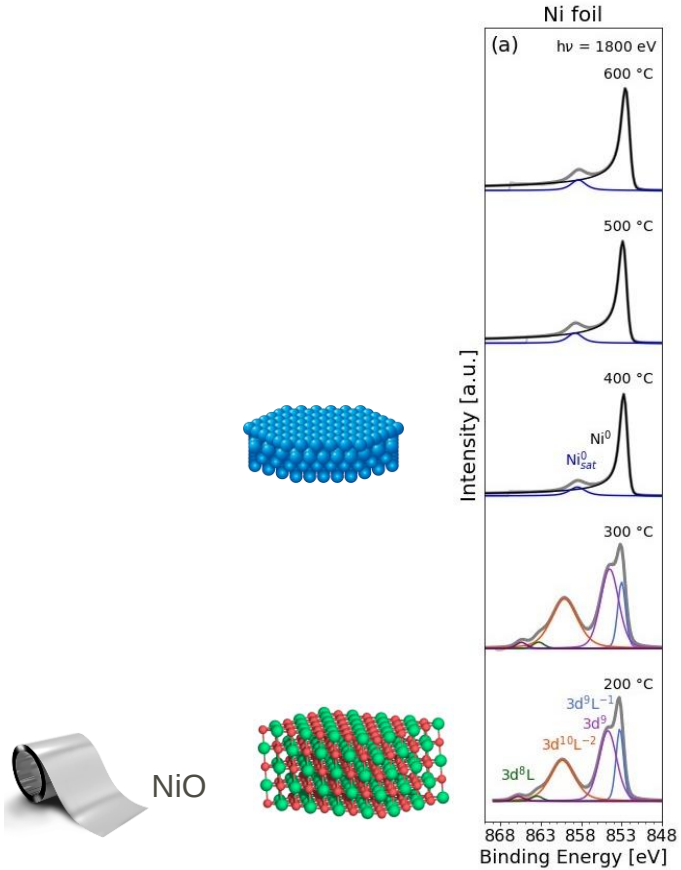
APXPS *In situ* reduction –1 mbar H_2

Beamline: Hippie



Foil as model for an industrial catalysts

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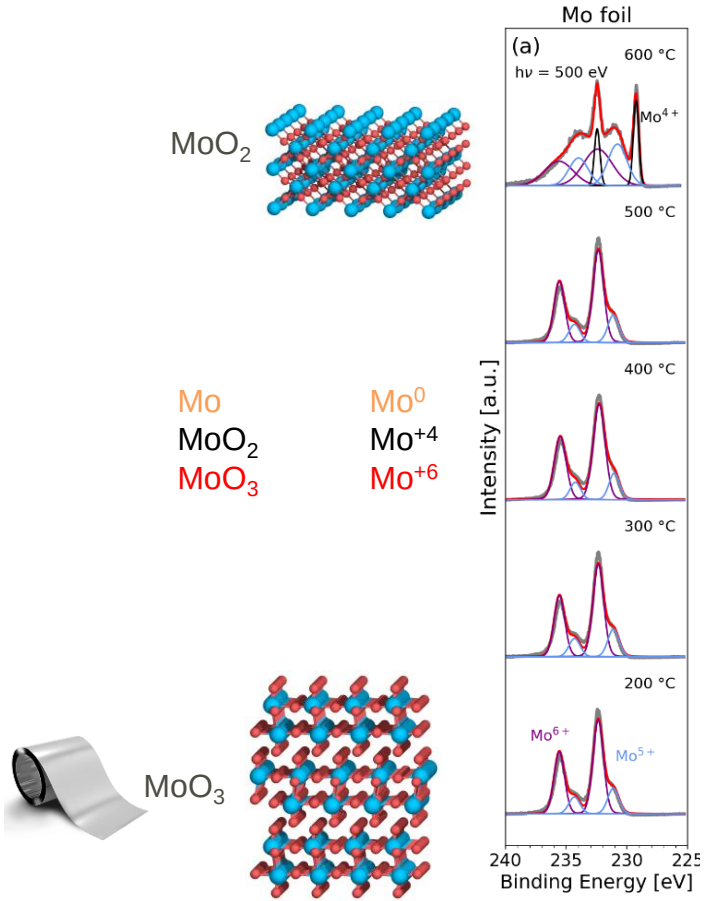
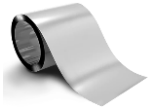
APXPS *In situ* reduction –1 mbar H_2



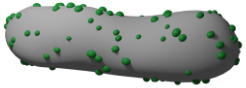
Foil vs supported catalyst

Mo foil



≠

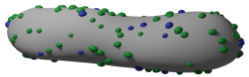
Mo/Al_2O_3



Foil reduce at higher temp

≠

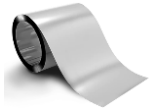
$NiMo/Al_2O_3$



Bimetallic cat reduce at lower temp

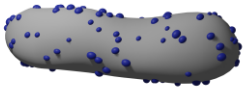
≠

Ni foil



≠

Ni/Al_2O_3



Foil reduce at lower temp

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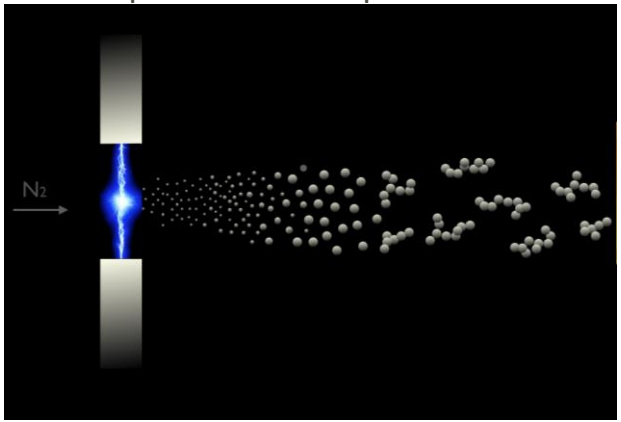
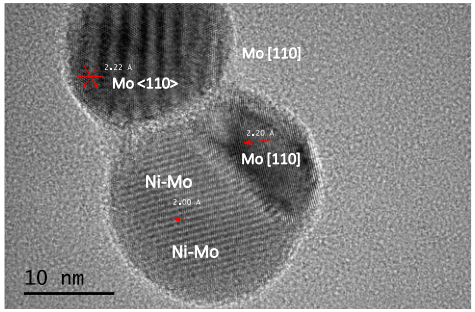
Design model system

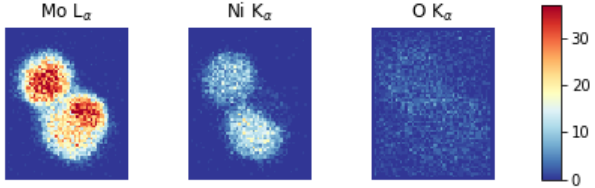
Ni (atomic %)	Mo (atomic %)
66	34
29	71

Nanoparticles from spark ablation

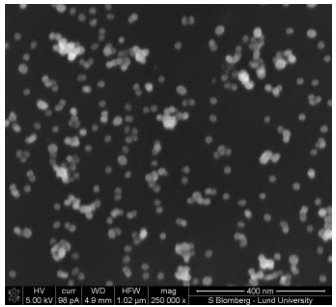


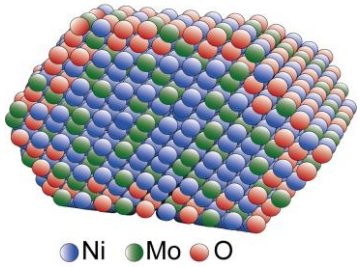
TEM- XEDS mapping





SEM





"Bimetallic nanoparticles as a model system for an industrial NiMo catalyst"
S. Blomberg et al, Materials. ***12*** *3727 (2019)*

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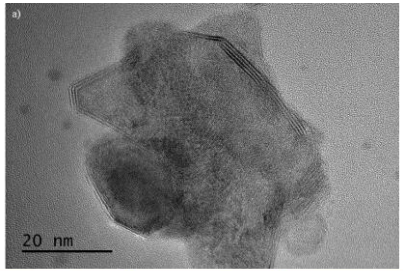
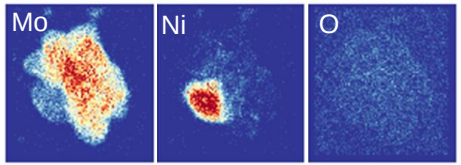
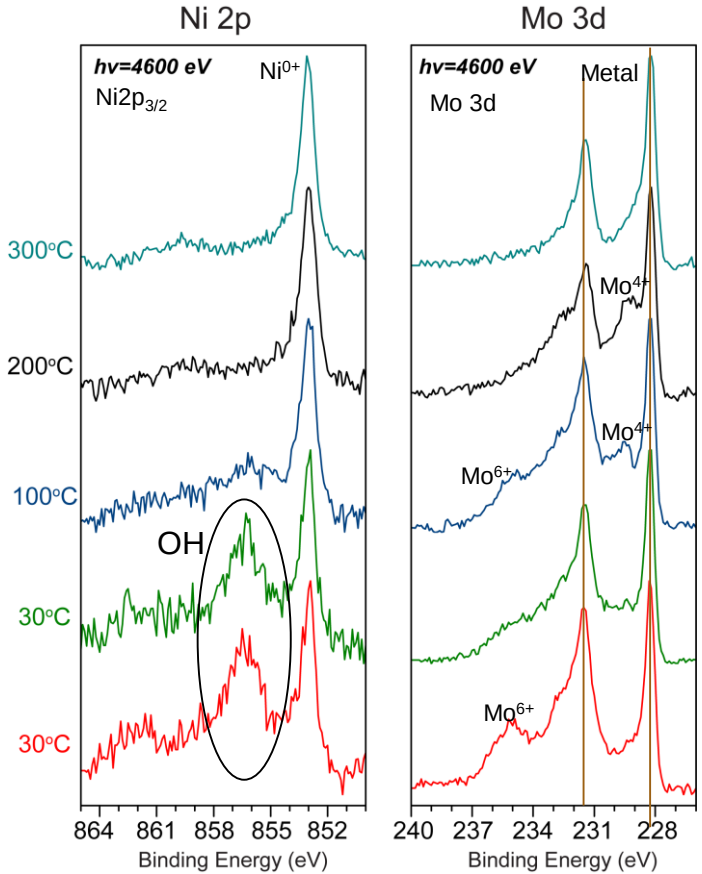
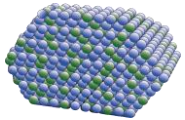
In situ 140 mbar reduction

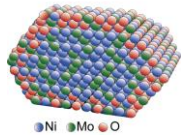




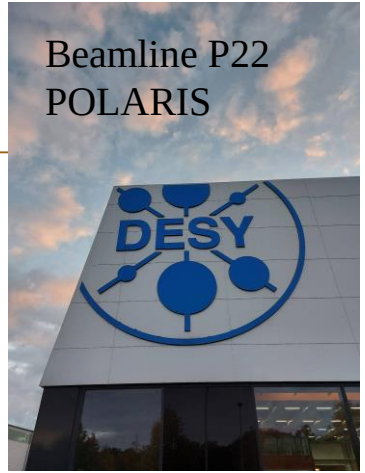


Pressure: **140 mbar**
0.32 l/min H_2
1.3 l/min He





$NiMoO_4$



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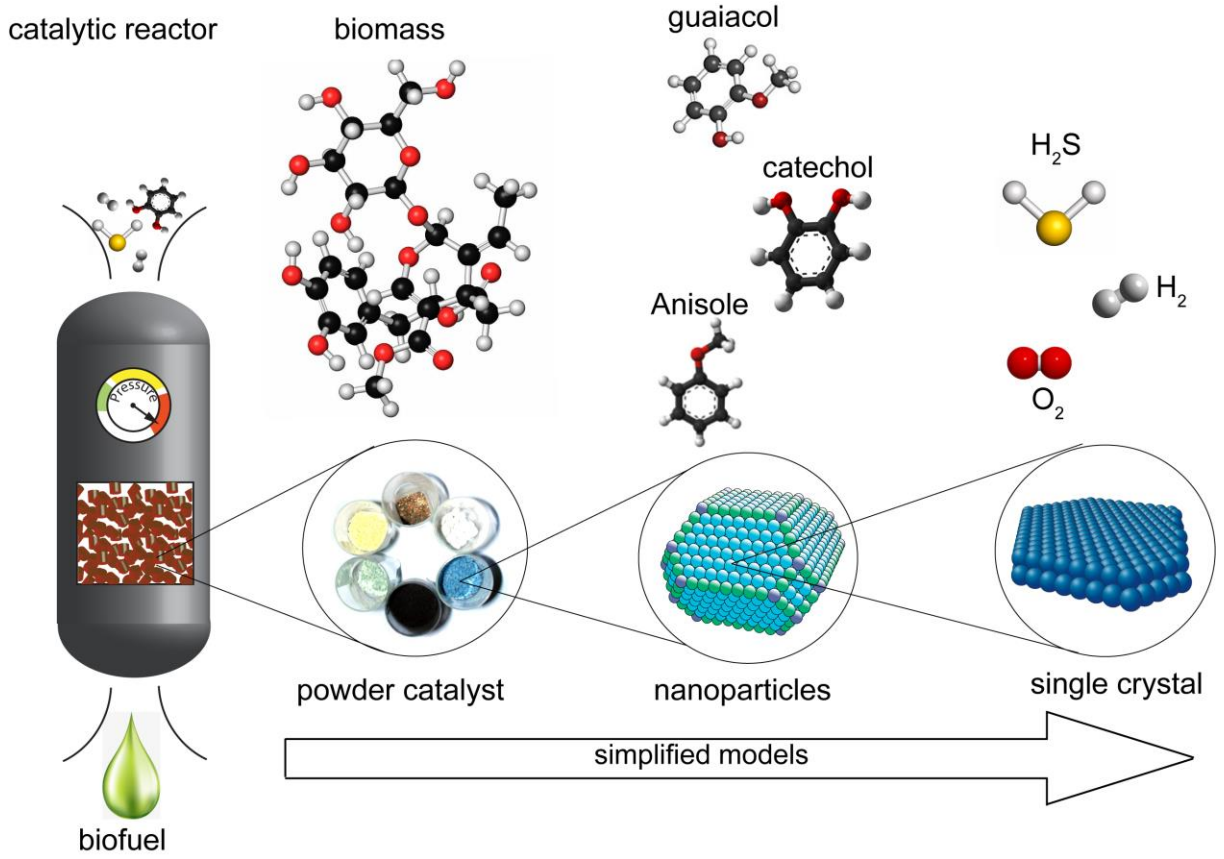
From complex to simplified systems



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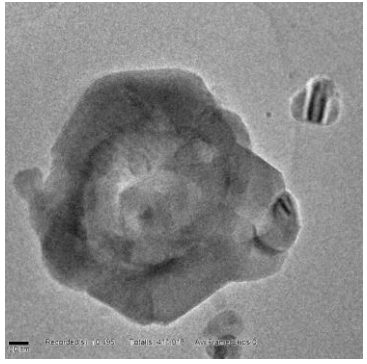
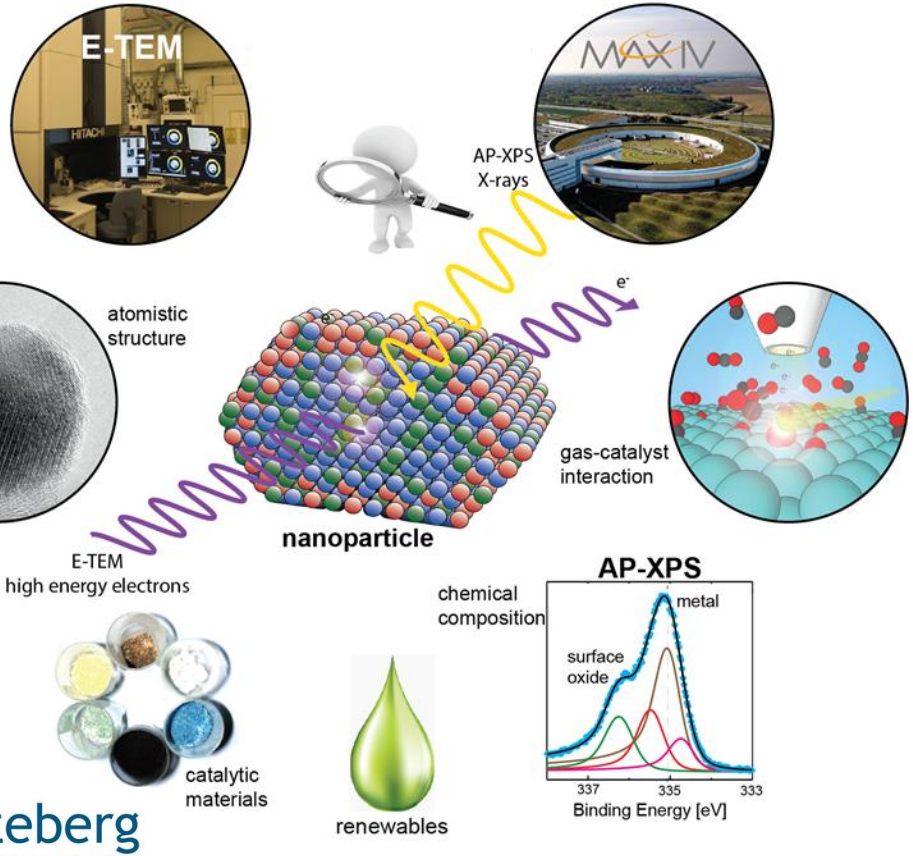
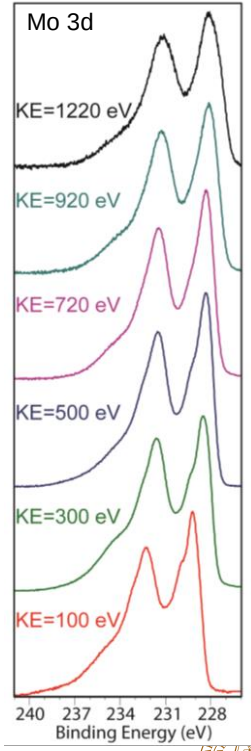
Combine Imaging and Spectroscopy

TEM





X-ray spectroscopy



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CHEMISTRY & ENGINEERING

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Acknowledgements

Division of Combustion Physics
- Sabrina Gericke
- Johan Zetterberg

Division of Solid State Physics
- Marie Bermeo Vargas
- Maria Messing

Stockholm University and DESY
- Patrick Lömker
- Mikhail Shipilin
- Christopher Goodwin
- Peter Amann
- Anders Nilsson

Dept Chemical Engineering
- Tove Kristensen
- Christian Hulteberg

Div Synchrotron Radiation Research
- Edvin Lundgren
- Johan Gustafson

MAX IV
- Andrey Shavorskiy
- Robert Temperton
- Mattia Scardamaglia
- Suyun Zhu
- Esko Kokkonen

Dept Chemistry
- Martin EK
- Jonas Nordlander
- David Wahlqvist

Malmö University
- Dorotea Gajdek
- Lindsay Merte

Brookhaven National Laboratory
- Tianhao Hu
- Ashley Head

Vetenskapsrådet

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