Olga V. Safonova:: Operando Spectroscopy group :: Paul Scherrer Institute :: Switzerland

Catalysis research at SuperXAS beamline

CONEXS meeting, Newcastle University, UK, 18th February 2020

Operando spectroscopy group

joint project between **Energy and Environment** and **Photon Science Divisions**

Head:
Maarten Nachtegaal

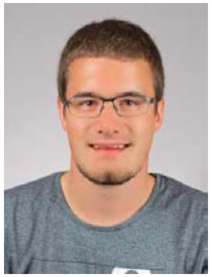
Senior scientists:

Olga Safonova

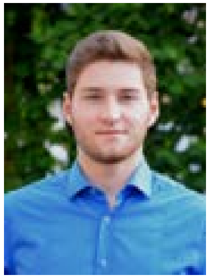
Grigory Smolentsev

Adam Clark

Technicians:



Stephan Hitz



Urs Vogelsang

Temporary staff: currently 1 postdoc and 5 PhD students

Outlook

- Catalysis and its importance
- X-ray spectroscopy for catalysis research
- SuperXAS beamline
- Research examples:

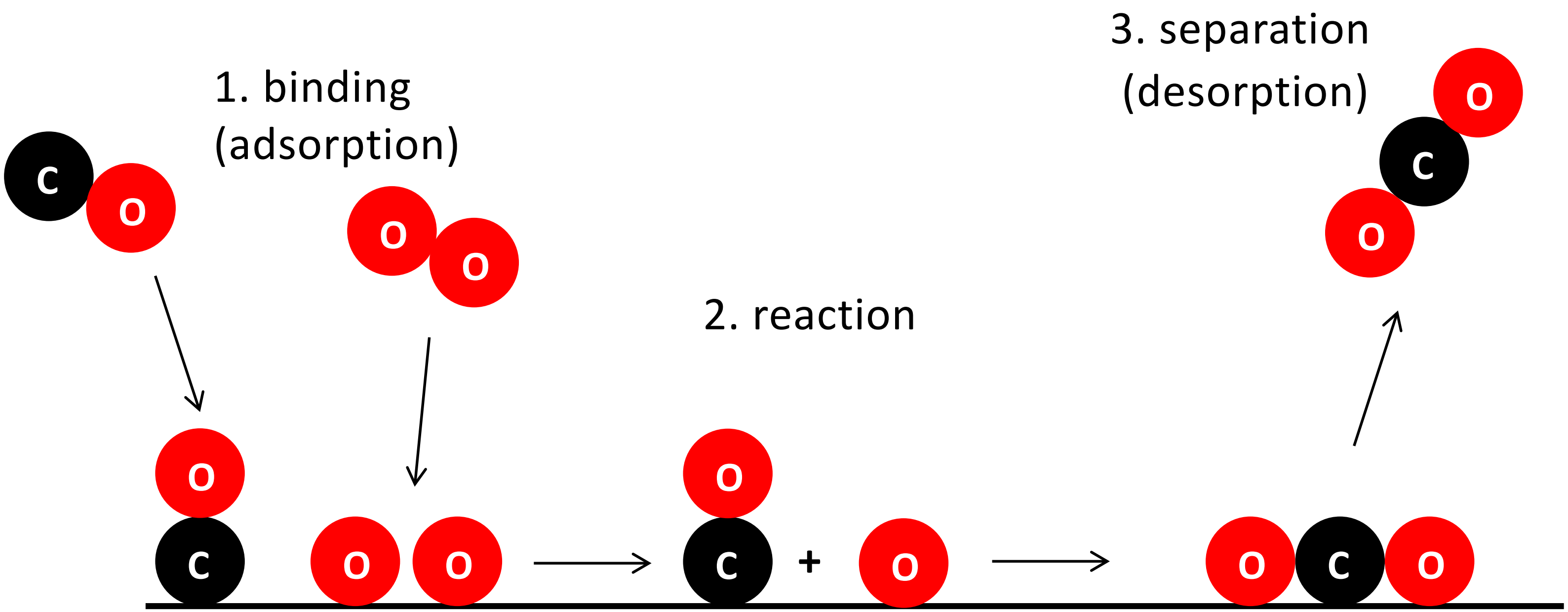
  Active phase in oxygen evolution electrocatalyst

  Selective catalytic reduction of NOx on Cu-species in zeolite

  Oxygen activation on Cu-CeO_2 catalyst

Catalysis

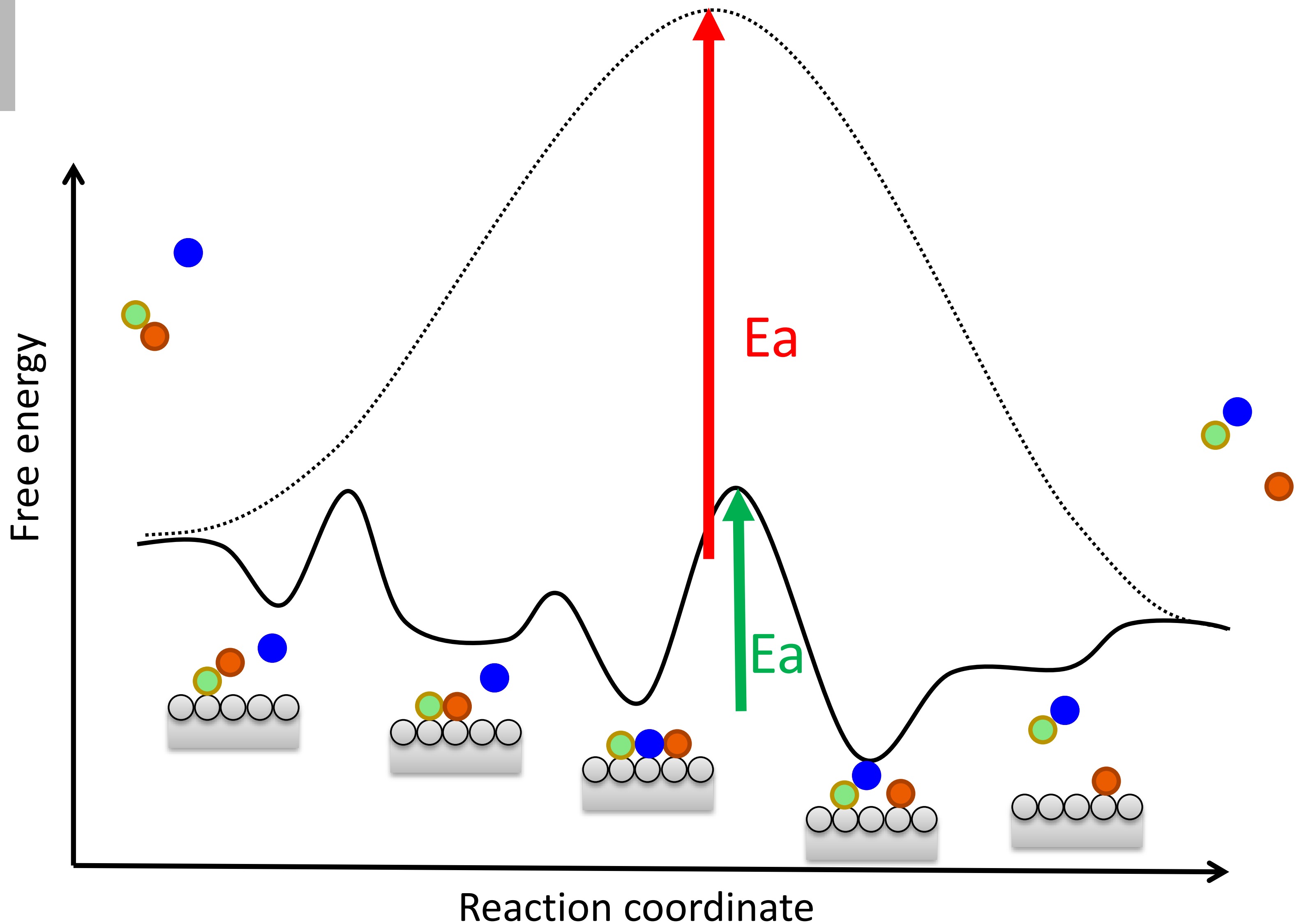
- Catalyst accelerates chemical reaction without being consumed



Pt surface = catalyst

Catalysis and energy

- Catalyst offers more energetically favorable reaction pathway



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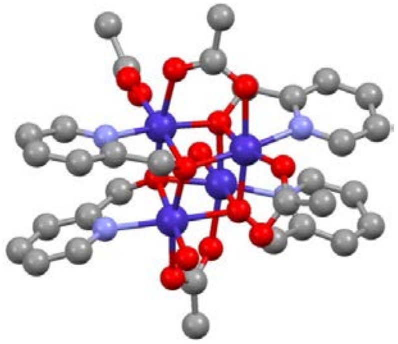
Application of catalysis

- More than 85 % of chemicals are produced with a help of catalysts
- Catalysts clean car and industry exhausts
- Electrocatalysts produce zero emission hydrogen fuel
- Catalysts are widely used in pharmaceutical industry

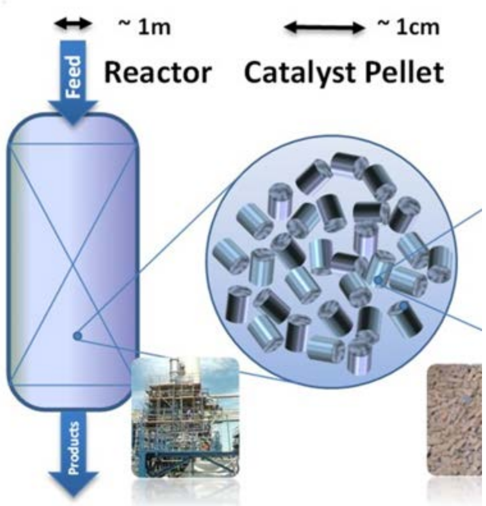
Structure of catalysts

- **Homogeneous catalysts:** molecules in solution



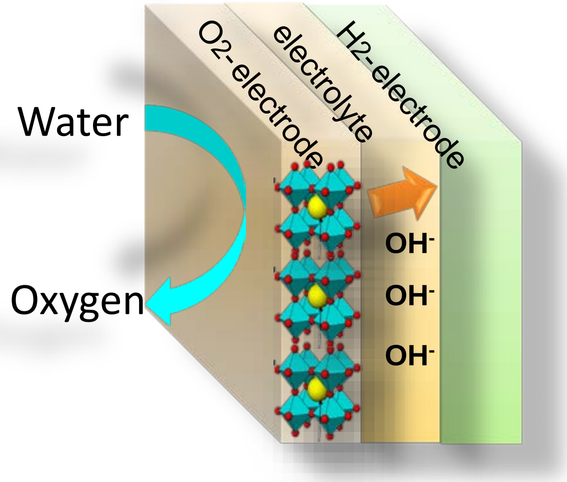
- **Heterogeneous catalysts:** active component

is dispersed on the surface of a high surface area support, pressed into pellets and filled into reactor



- **Electrocatalysts:**

high surface area materials deposited on an electrode



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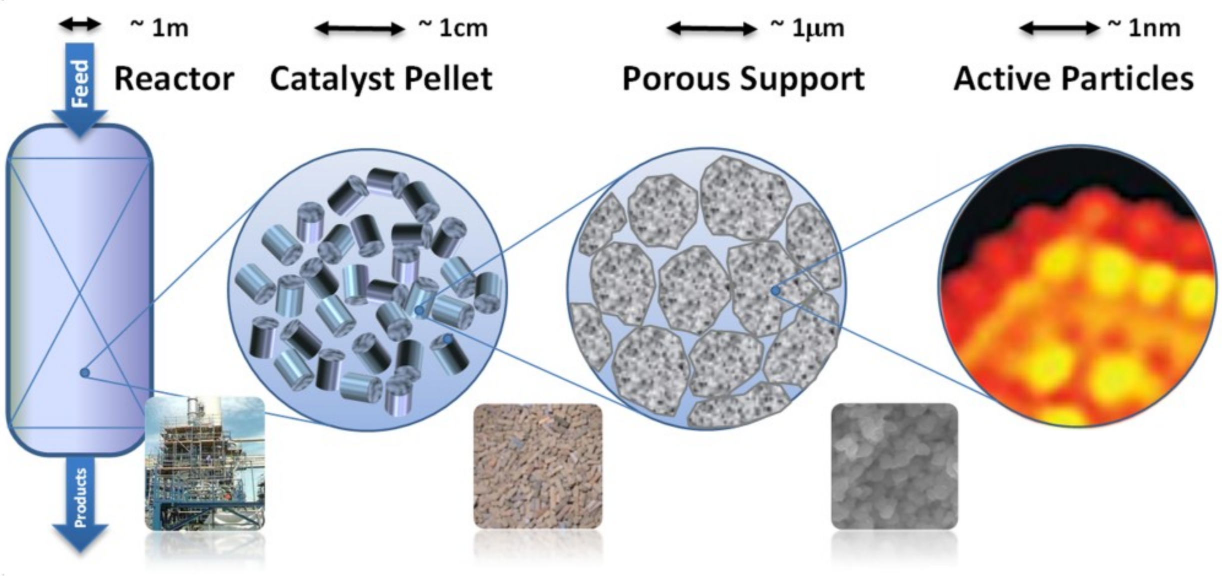
Relevant length scales in catalysis



X-ray absorption spectroscopy (XAS)

(structure of active site on the atomic scale)

Ex situ, in situ and operando spectroscopy

Ex situ
(catalyst removed from reactor)

In situ
(catalyst under specific conditions)

Operando (catalyst under working conditions)

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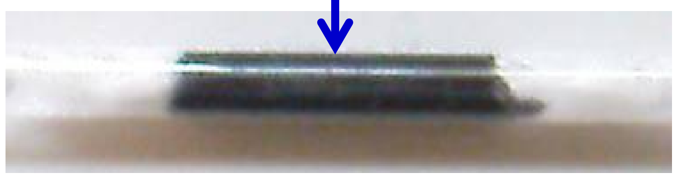
X-ray spectroscopy allows uncovering structure – activity relationships

Structure (XAS and XES)

Reactants



Operando reactor

Products

Activity

(MS,GC, IR..)

- no material and pressure gaps
- quantitative information about activity
- quantitative/element specific structural information

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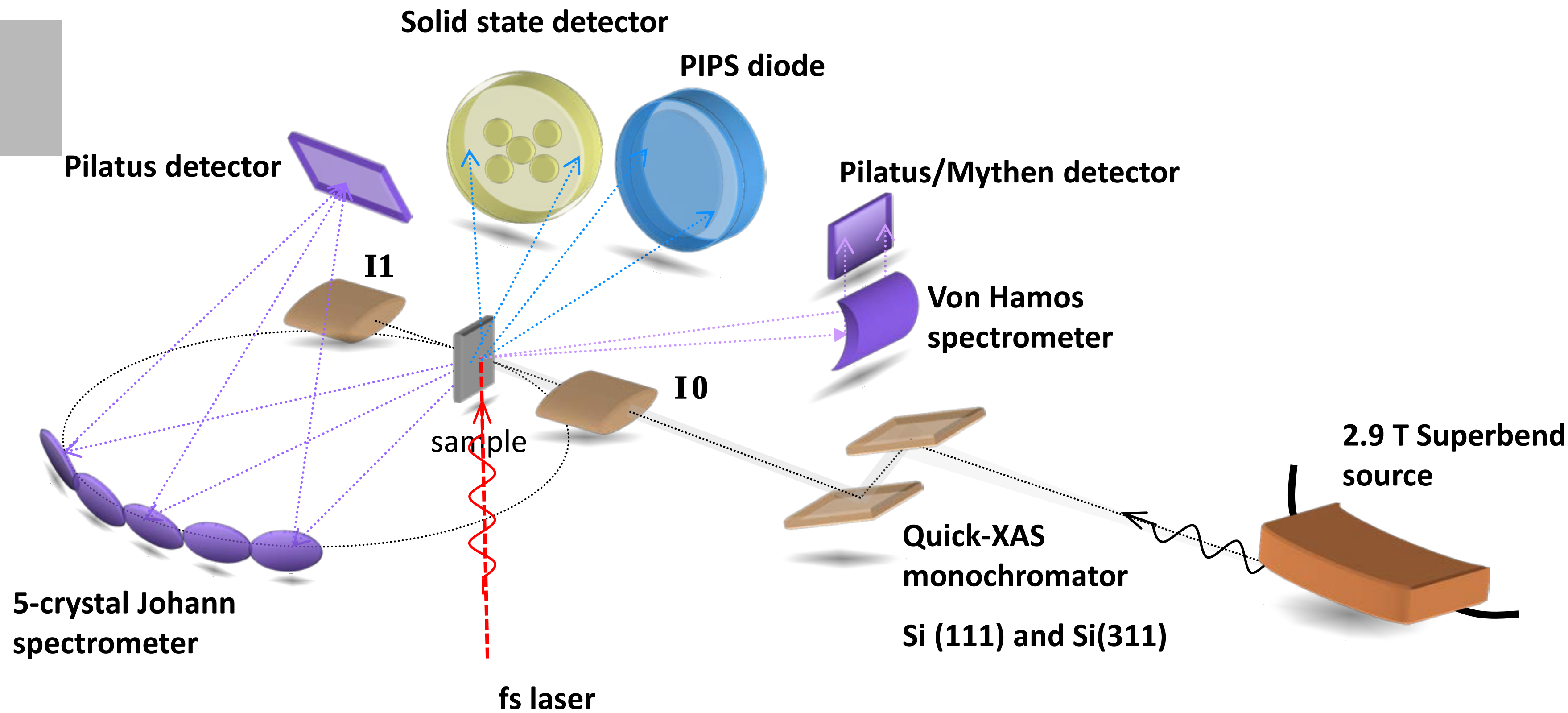
SuperXAS beamline

SuperXAS beamline



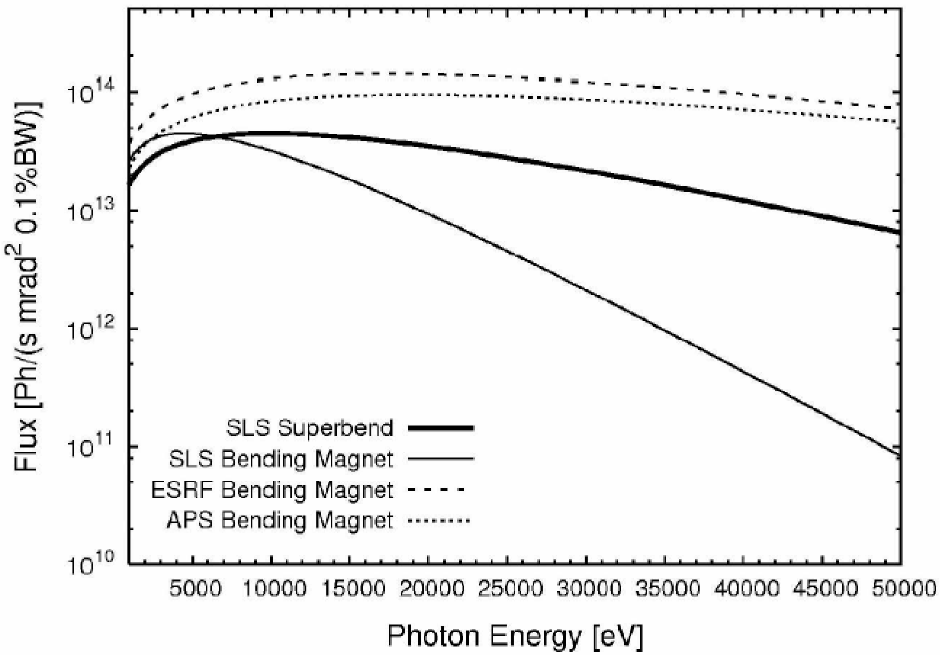
Energy range: 4.5-35 keV

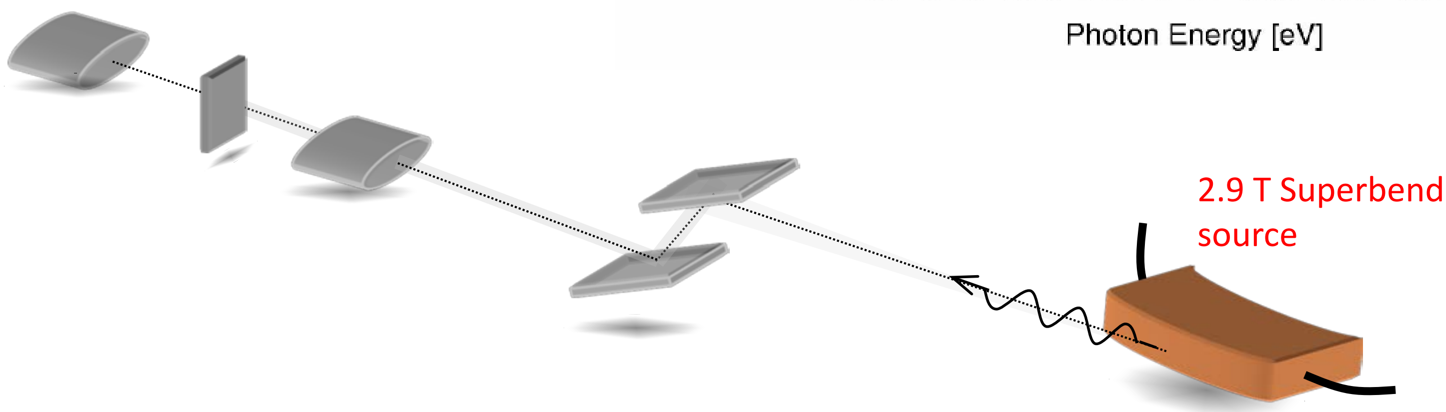
Flux : up to 1×10^{12} ph/s (@ 12 keV)

Spot size: from 100 x 100 μm^2 to 5000 x 500 μm^2

Quick XAS at SuperXAS

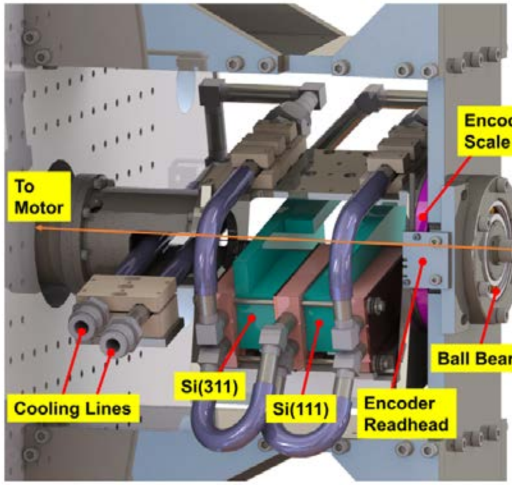
Flux at SLS Superbend source (2.9 T)

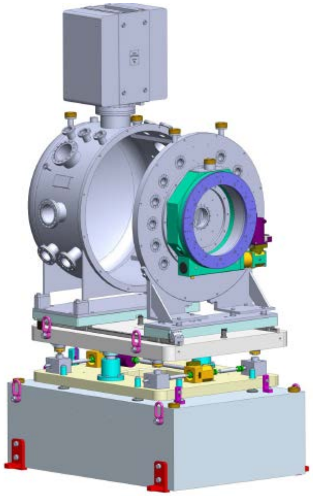


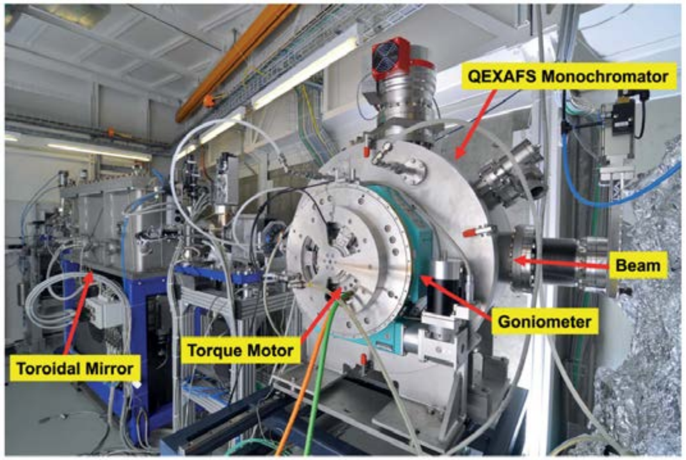


Quick XAS monochromator

Direct drive torque motor oscillating channel-cut monochromator

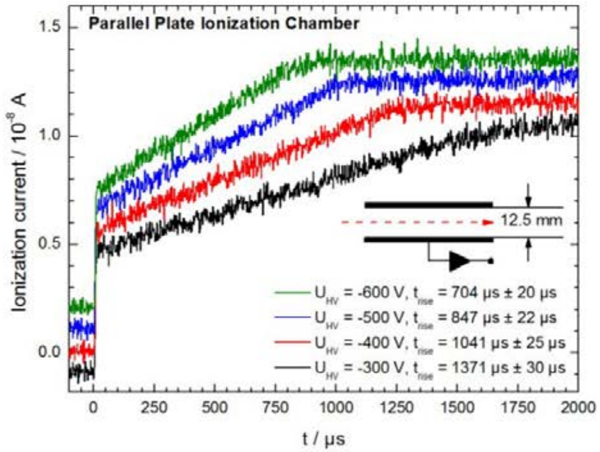


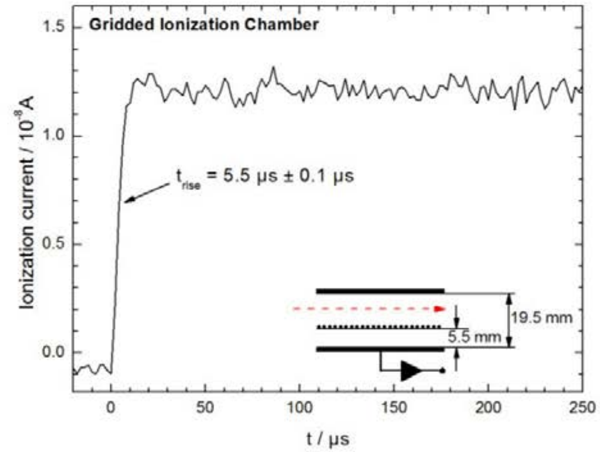


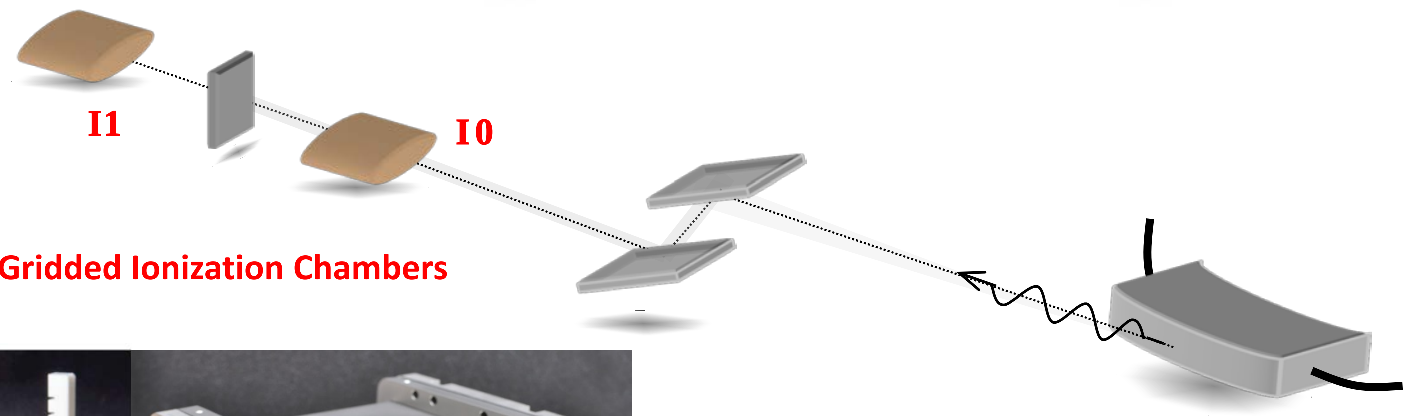


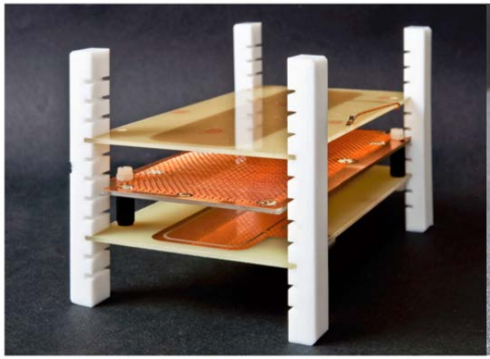
O. Muller et al. REVIEW OF SCIENTIFIC INSTRUMENTS 86, 093905 (2015)

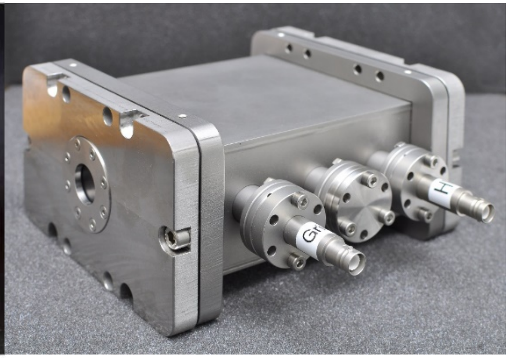
How is Time-Resolution Achieved?











O. Muller et al. Journal of Physics: Conference Series 2013 vol: 425 (9) pp: 092010

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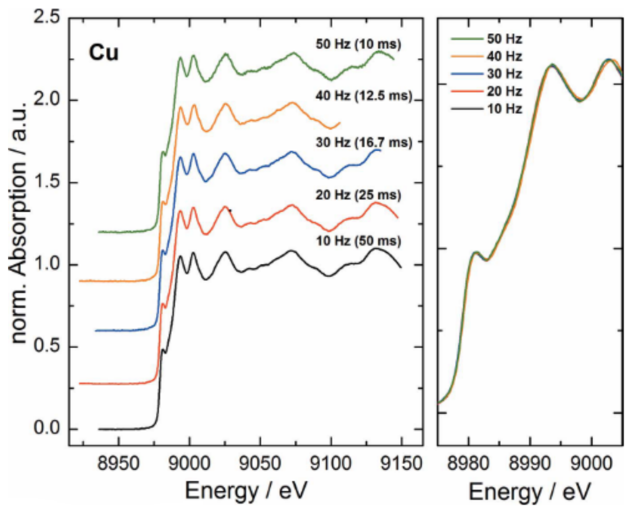
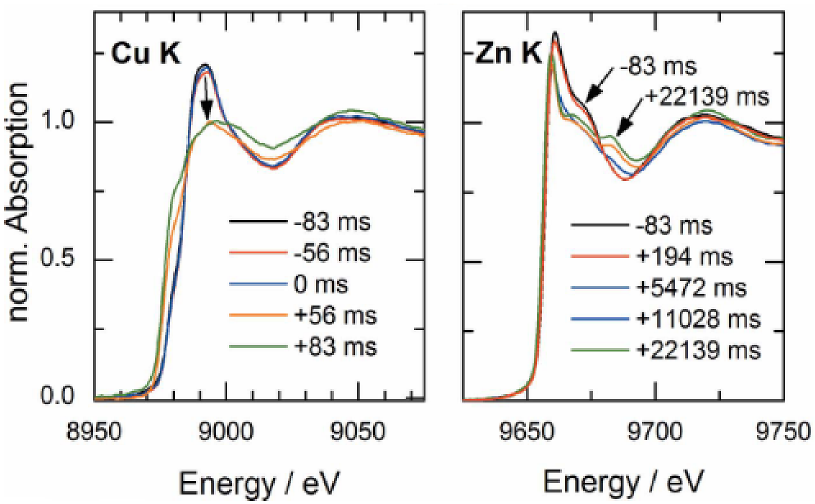
Time resolution

Where does this leave us?

10ms achievable time-resolution





Follow chemistry in action

Chemical reaction is triggered at t = 0 s by fast injection of a chalcogene source.

O. Muller et al. J. Synchrotron Rad. (2016). 23, 260–266

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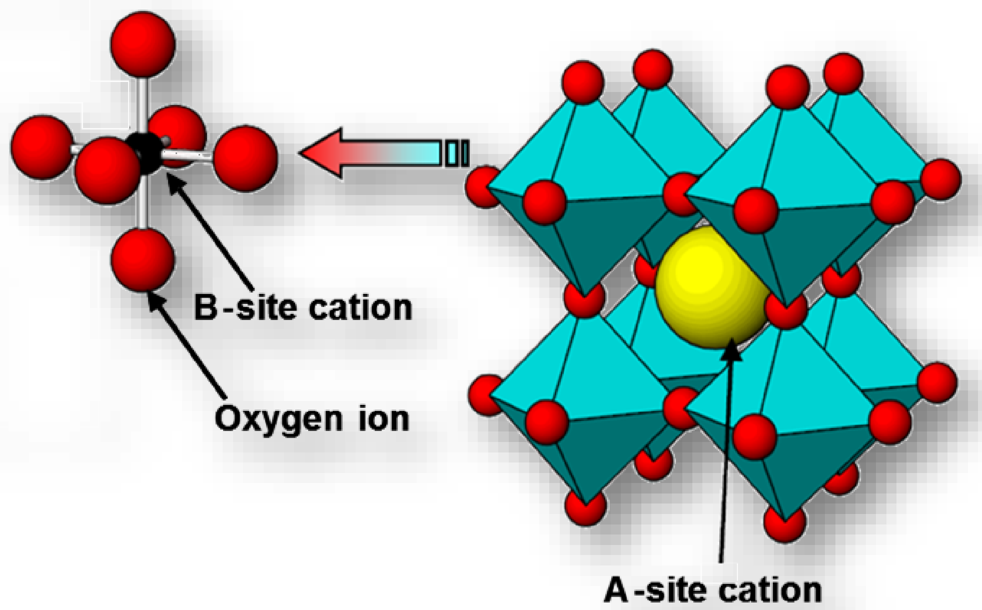
Research example 1:

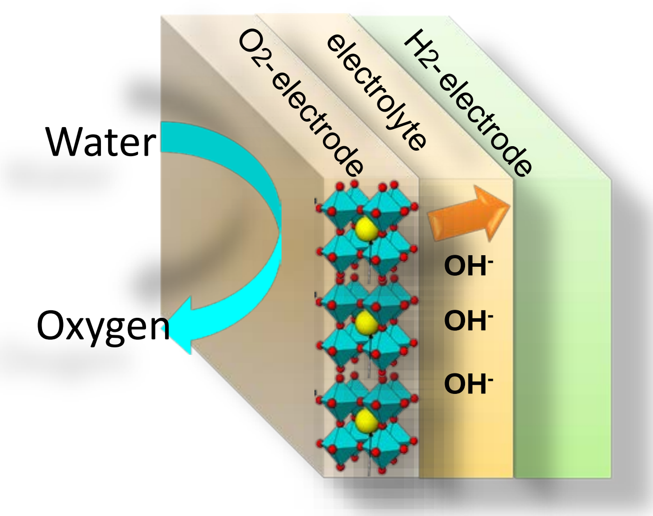
Structure of active phase in oxygen evolution electrocatalyst

Oxygen evolution electrocatalyst

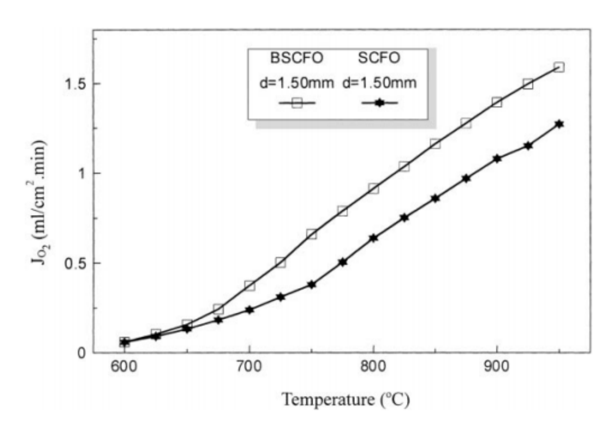
- $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-d}$ perovskite



- Alkaline fuel cell



Why $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-d}$ was chosen?



An oxygen permeation membrane material

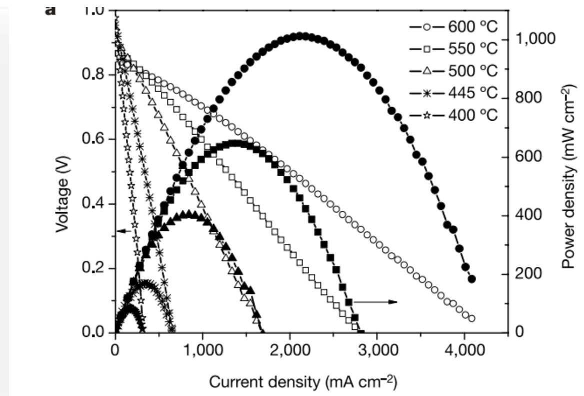
Journal of Membrane Science 172 (2000) 177–188

NATURE | VOL 431 | 9 SEPTEMBER 2004 |

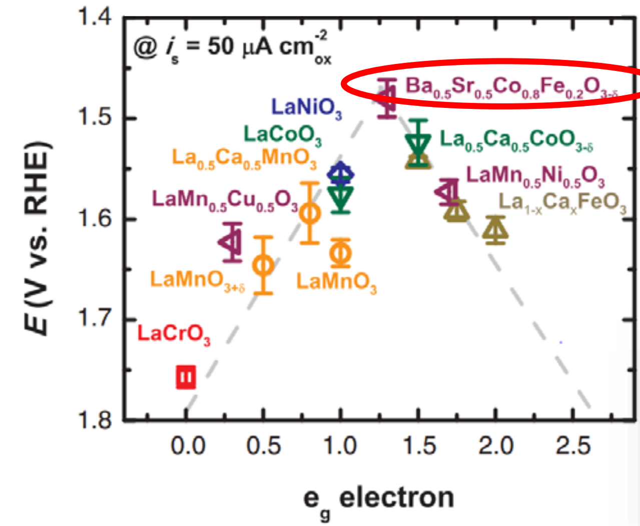
A high-performance cathode for the next generation of solid-oxide fuel cells

Zongping Shao & Sossina M. Haile

Materials Science, California Institute of Technology, Pasadena, California 91125, USA



SCIENCE VOL 334 9 DECEMBER 2011

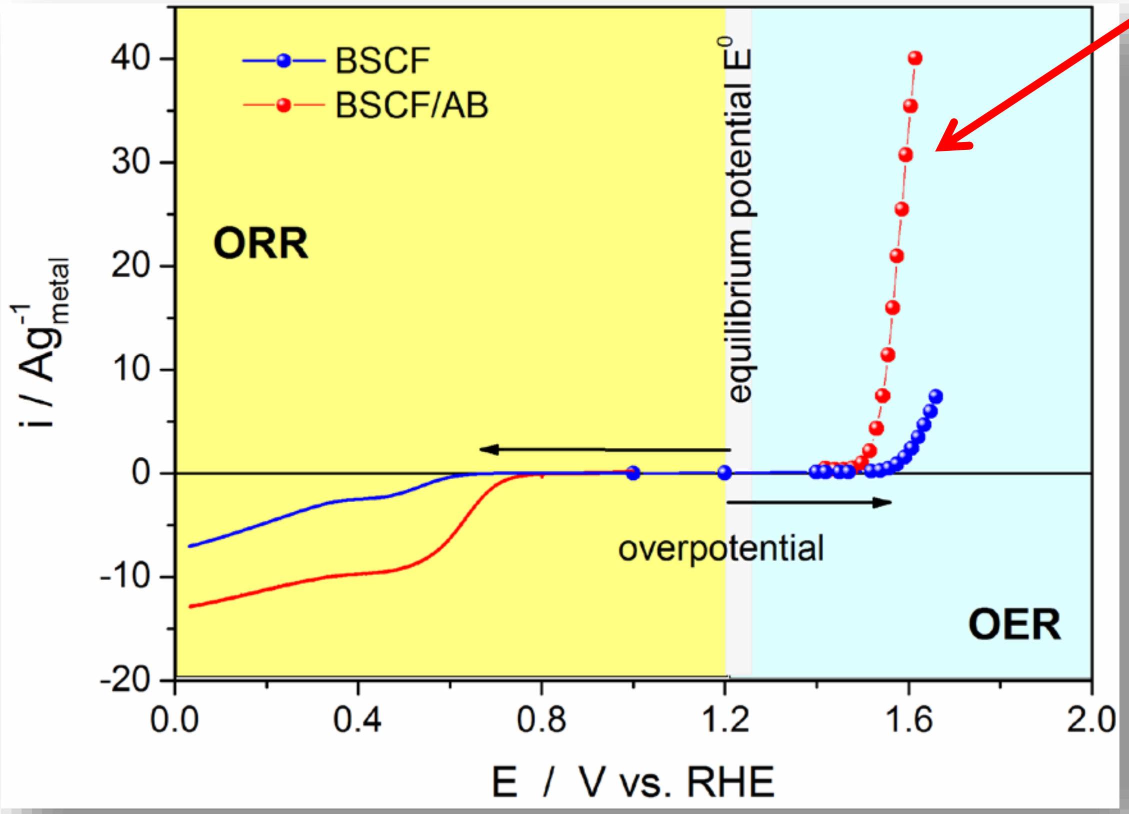


A Perovskite Oxide Optimized for Oxygen Evolution Catalysis from Molecular Orbital Principles

Jin Suntivich,[1,2] Kevin J. May,[2,3] Hubert A. Gasteiger,[2,3]* John B. Goodenough,[4] Yang Shao-Horn[1,2,3]†

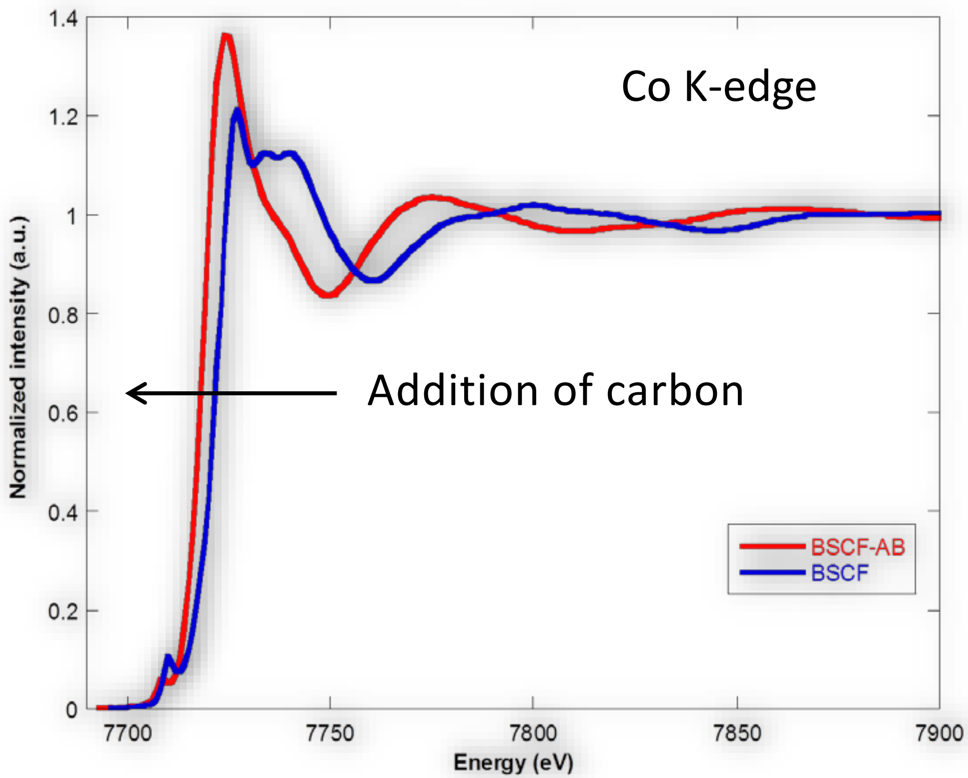
Addition of carbon improves oxygen evolution activity of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-d}$

with carbon
more active



Fabbri et al. ACS Catalysis , 2014, 4 ,1061,
Fabbri et al., Adv. Energy Mater. 2015, 5, 1402033

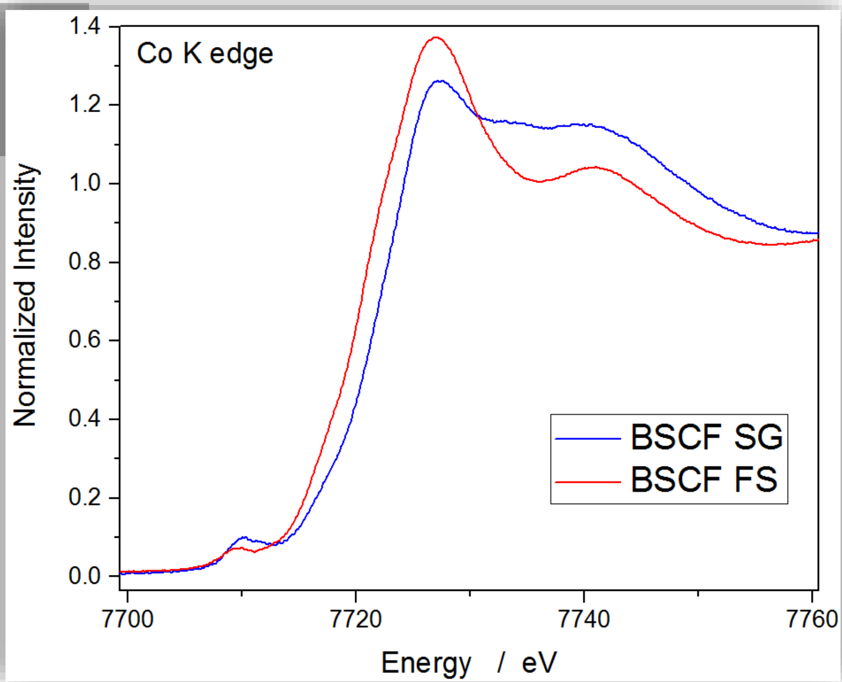
Ex situ Co K-edge XANES

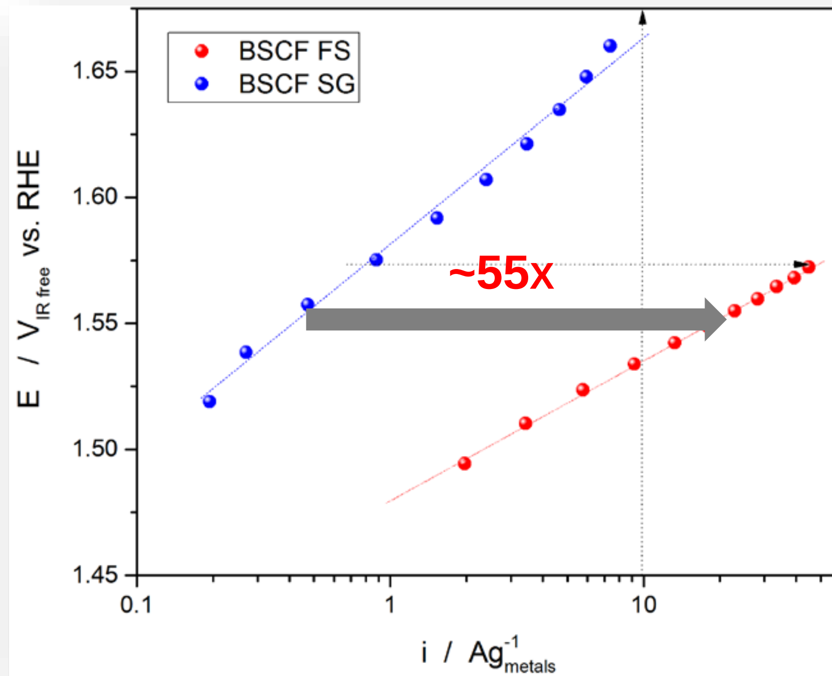


Co^{2+} is the active state?

Fabbri et al. ACS Catalysis , 2014, 4 ,1061,
Fabbri et al., Adv. Energy Mater. 2015, 5, 1402033

Ex situ Co K-edge XANES: higher Co^{2+} fraction makes better catalyst





SG: sol gel method

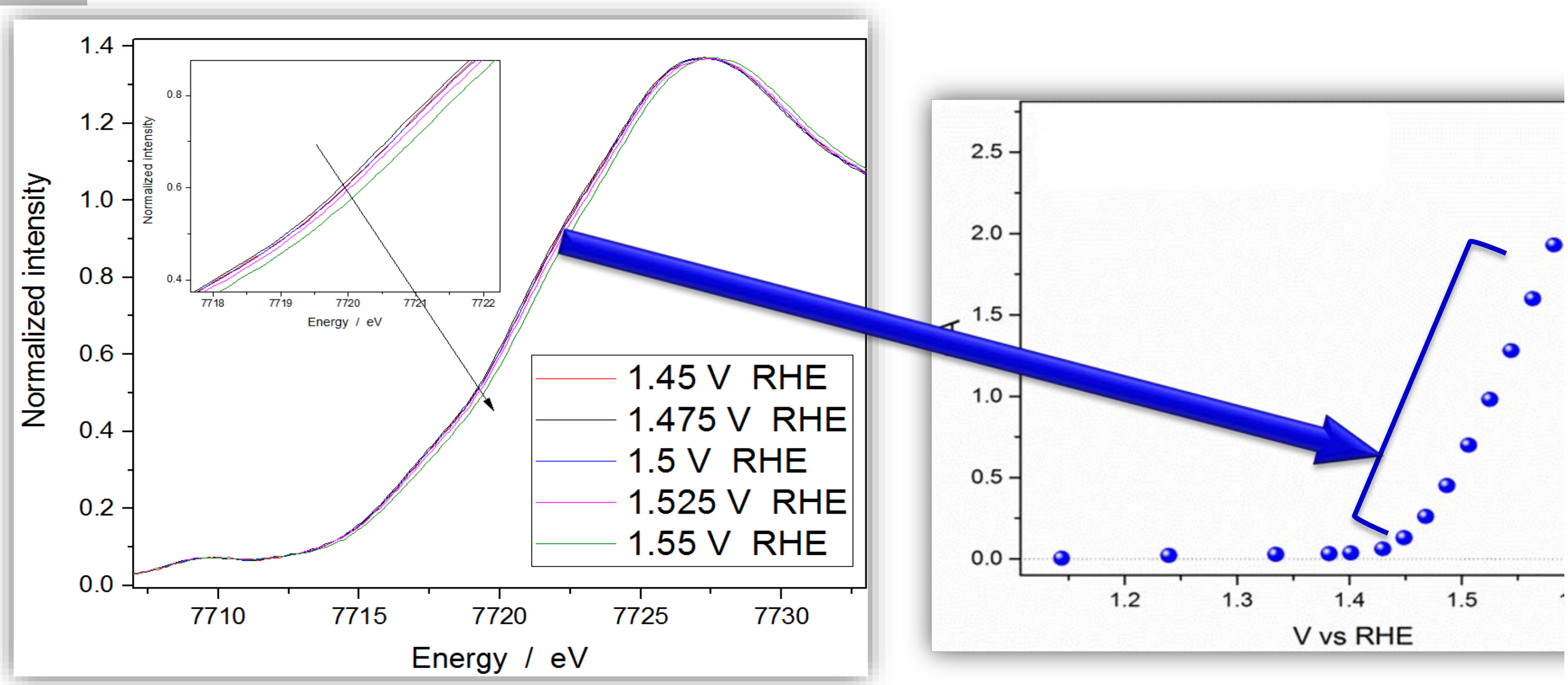
FS: flame spray method

Fabbri et al. Nature Materials, 2017, 16, 925

Operando cell for XAS

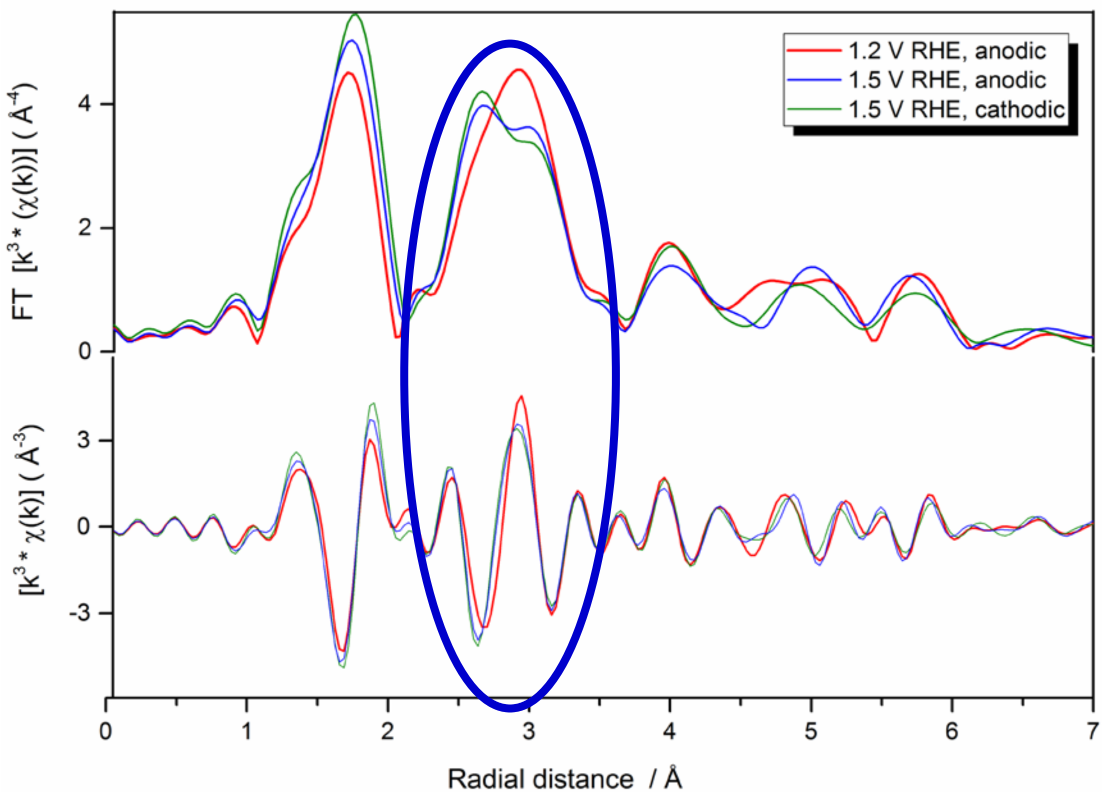
Binninger et al., J. Electrochem. Soc. 2016

Operando Co K-edge XANES: Co^{2+} oxidizes into Co^{3+} under operation conditions and activity increases



Fabbri et al. Nature Materials, 2017, 16, 925

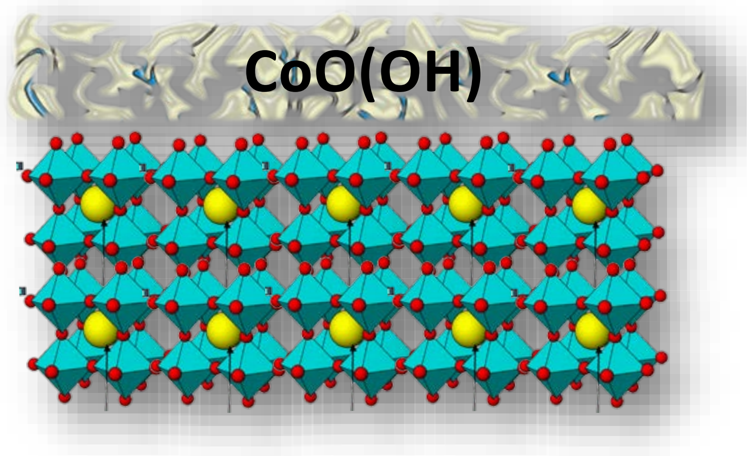
Operando Co K-edge EXAFS



- For highly oxygen deficient perovskites, a Co-Co scattering peaks appears at 2.8-3.2 Å
- Under operando conditions Co-Co contribution at 3.2 Å decreases and at 2.85 Å typical of the CoO(OH) structure increases

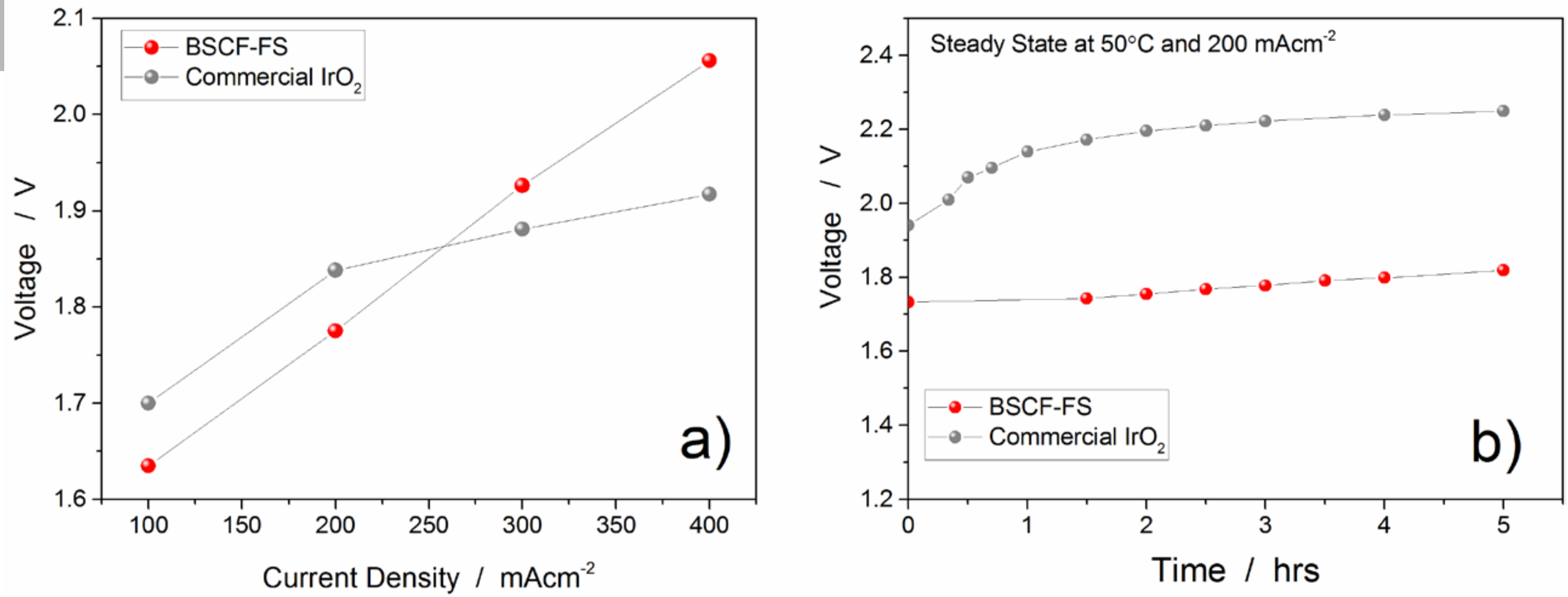
Fabbri et al. Nature Materials, 2017, 16, 925

CoO(OH) is active phase



Fabbri et al. Nature Materials, 2017, 16, 925

This catalyst is more active than the benchmark IrO2 catalyst and is very stable



Performance comparison of BSCF-FS and IrOx under operating conditions. Polarization curves (**A**) and voltage vs. time at the steady state current density of 200 $mAcm^{-2}$ (**B**) obtained for membrane electrode assemblies (MEAs) MEAs having BSCF-FS and IrOx as anodic electrode.

Fabbri et al. Nature Materials, 2017, 16, 925

Research example 2:

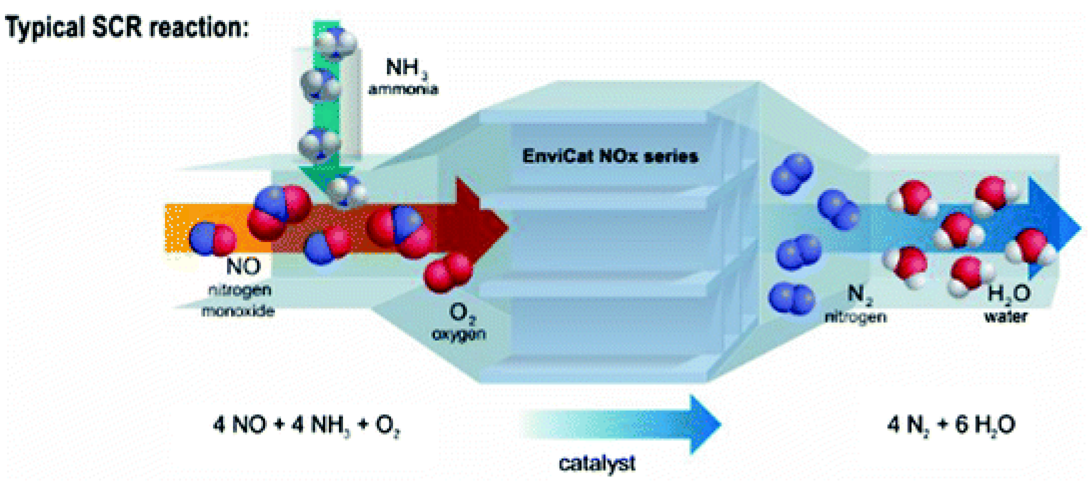
Selective catalytic reduction of NOx on Cu-species in zeolite

Research example 2:

Selective catalytic reduction of NOx on Cu-species in zeolite

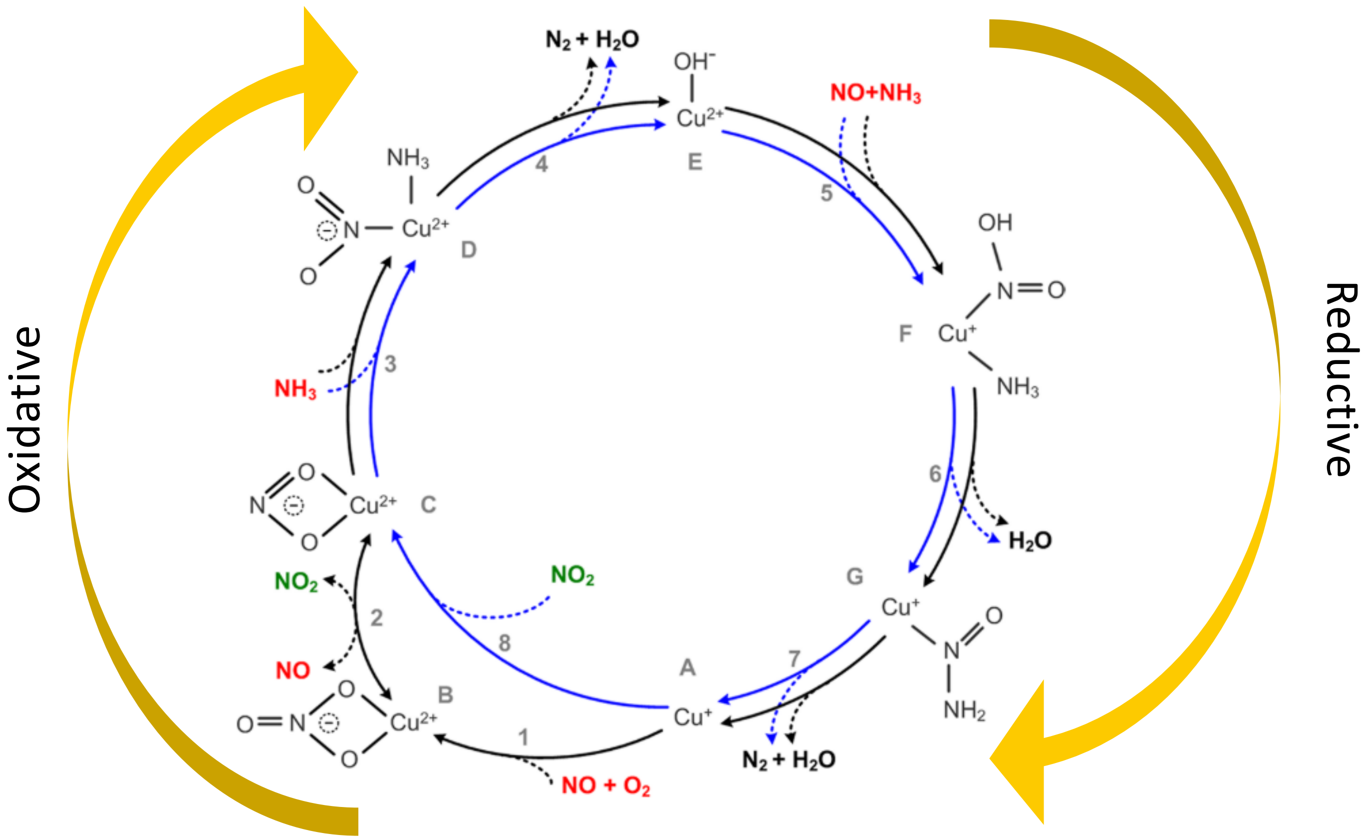
Selective Catalytic Reduction (SCR) of Nitrogen Oxides with Ammonia

$$4NO + NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$



Selective catalytic reduction of NOx on Cu-species in zeolite

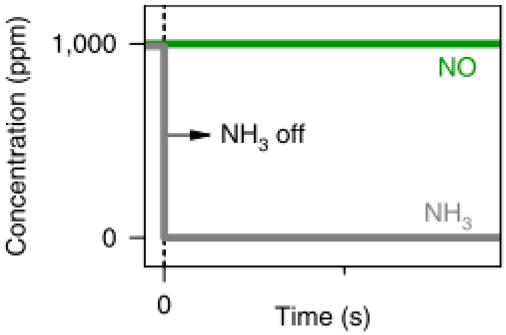
A Consistent Reaction Scheme for the Selective Catalytic Reduction of Nitrogen Oxides with Ammonia

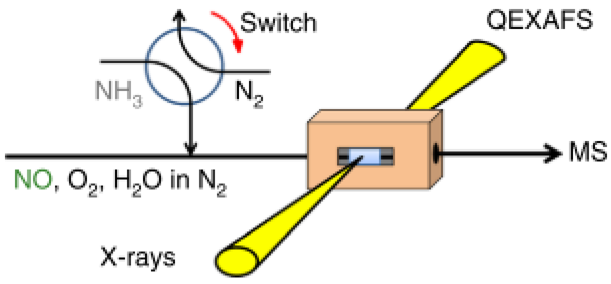


Ton V. W. Janssens et al. ACS Catal. 2015, 5, 2832–2845

Dynamic copper speciation

Time-resolved copper speciation during selective catalytic reduction of NO on Cu-SSZ-13





A. Marberger et al. Nature catalysis, 1, 2018, 221–227

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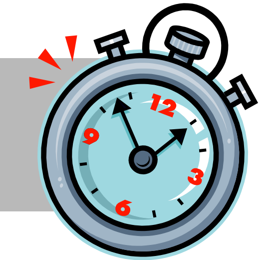
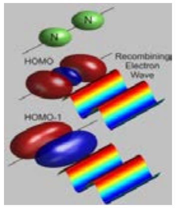
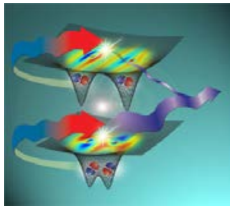
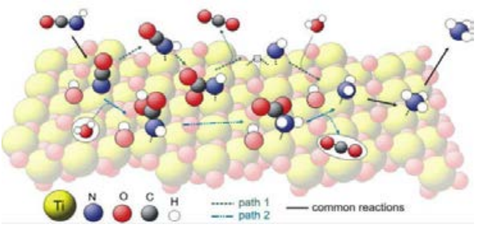
Relevant time scales in chemistry and catalysis









Fundamental — **Applied**

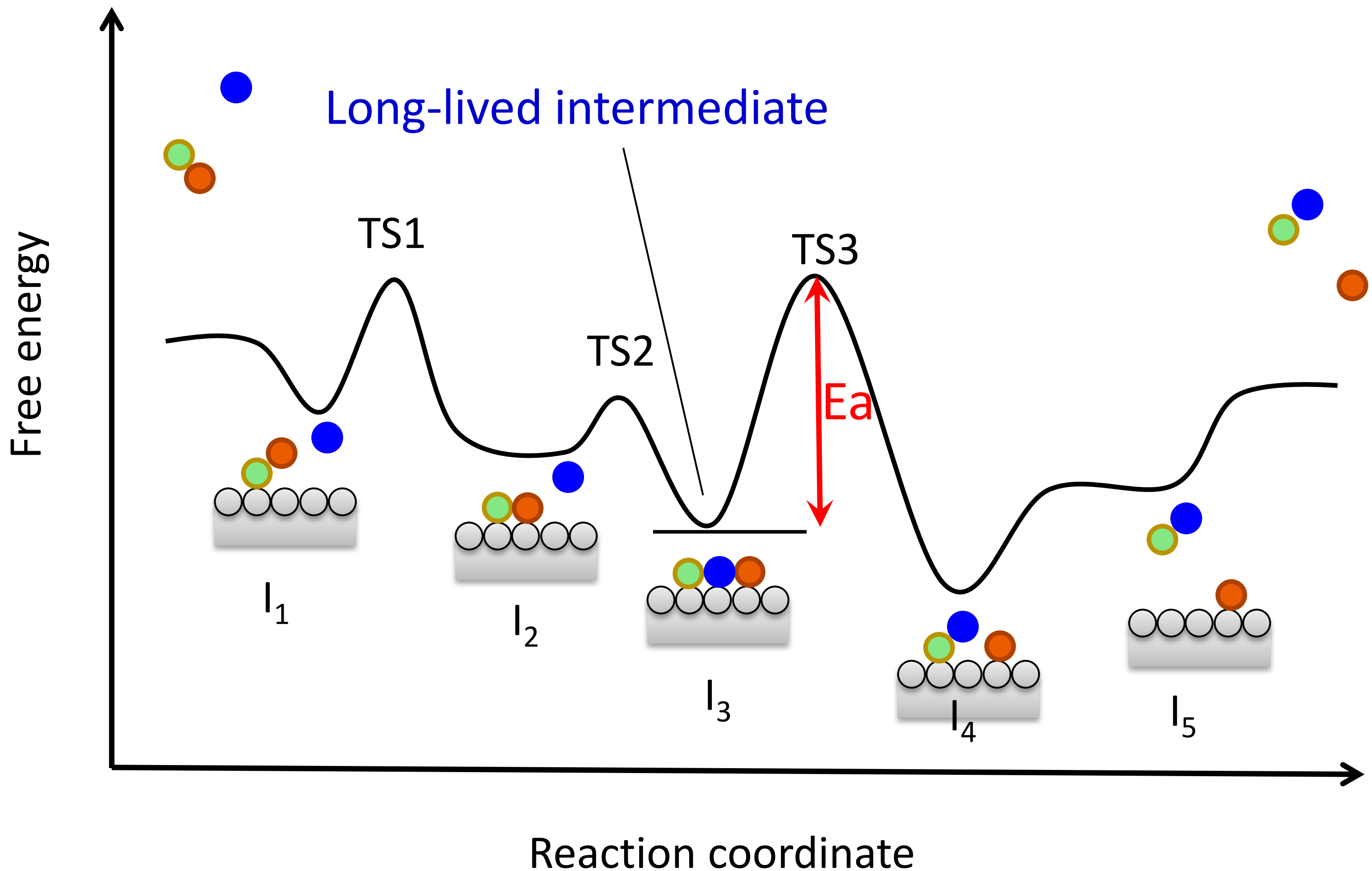
10^{-18} 10^{-15} 10^{-12} 10^{-9} 10^{-6} 10^{-3} 1 10^{3} s

Bond breaking/ formation

Reaction kinetics

Stability, deactivation

Active site structure during catalytic cycle



Relevant time scales based on turn-over frequencies (TOF)

Ethylene hydrogenation

$C_2H_4 + H_2 \rightarrow C_2H_6$

Pt nanoparticles , 60 °C [5]

Selective alcohol oxidation

$ROH + O_2 \rightarrow RHO$

AuPd/TiO2, 160 °C [2]

Alkene metathesis

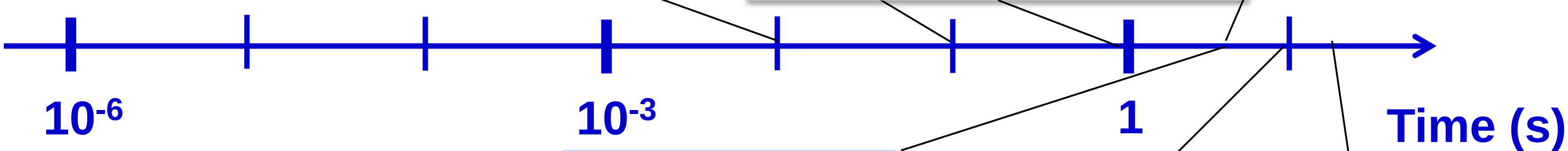
$R_1\,C = C\,R_2 \rightarrow R_{1(2)}\,C = C\,R_{1(2)}$

W/SiO$_2$, 70 °C [7]

Ammonia synthesis

$3H_2 + N_2 \rightarrow 3\,NH_3$

Ru surface, 450 °C, 100 bar [6]



CO oxidation

$CO + O_2 \rightarrow CO_2$

Pt/CeO$_2$, 80 °C [1]

Fischer-Tropsch synthesis

$CO + 2H_2 \rightarrow (CH_2)n + H_2O$

Co/Al$_2$O$_3$, 210 °C , 35 bar [3]

Methanol synthesis

$CO/CO_2 + H_2 \rightarrow CH_3OH$

CuZn/Al$_2$O$_3$, 260 °C , 25 bar [4]

[1] Science, 2012, 341,771

[2] Science, 2006, 311, 696

[3] JACS, 2006, 128, 3956

[4] Nature Comm., 2016, 7, 13057

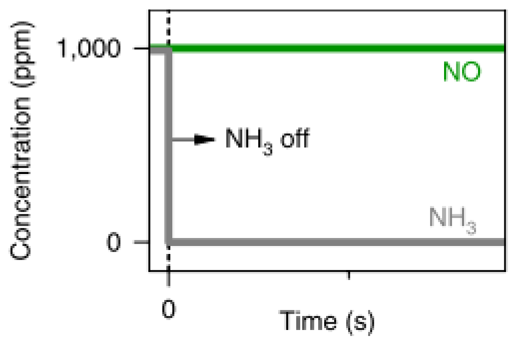
[5] J. Catal., 127, 342

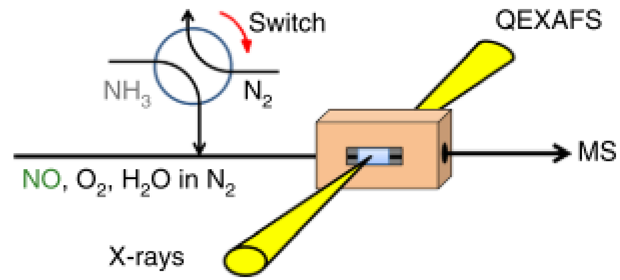
[6] Nature Chem., 2009, 1, 37

[7] Central Sci., 2016, 2, 569

Dynamic copper speciation

Time-resolved copper speciation during selective catalytic reduction of NO on Cu-SSZ-13



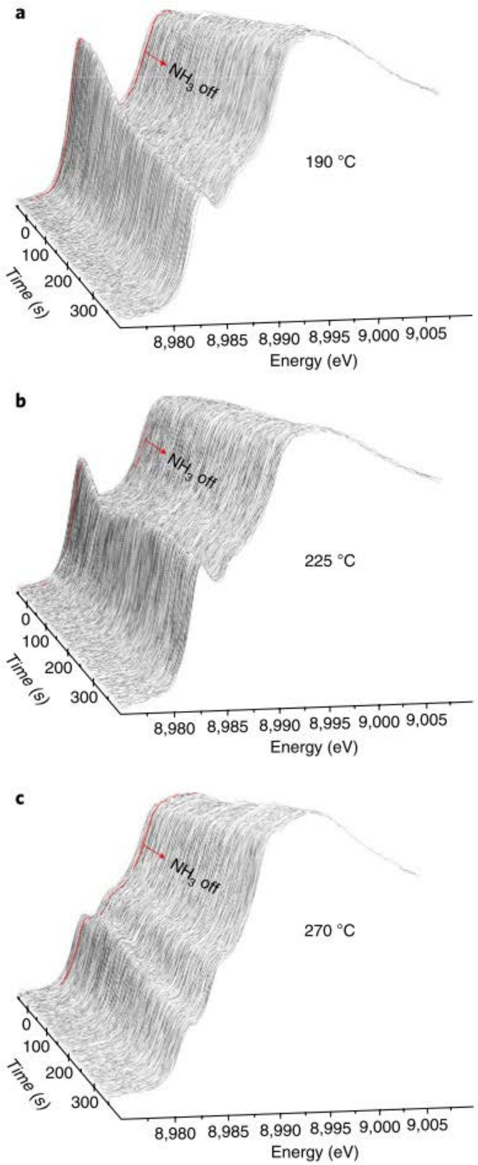


XAS probes the oxidation state and coordination geometry of Cu

1 Hz monochromator oscillation frequency
(500 ms per full XAS spectrum)

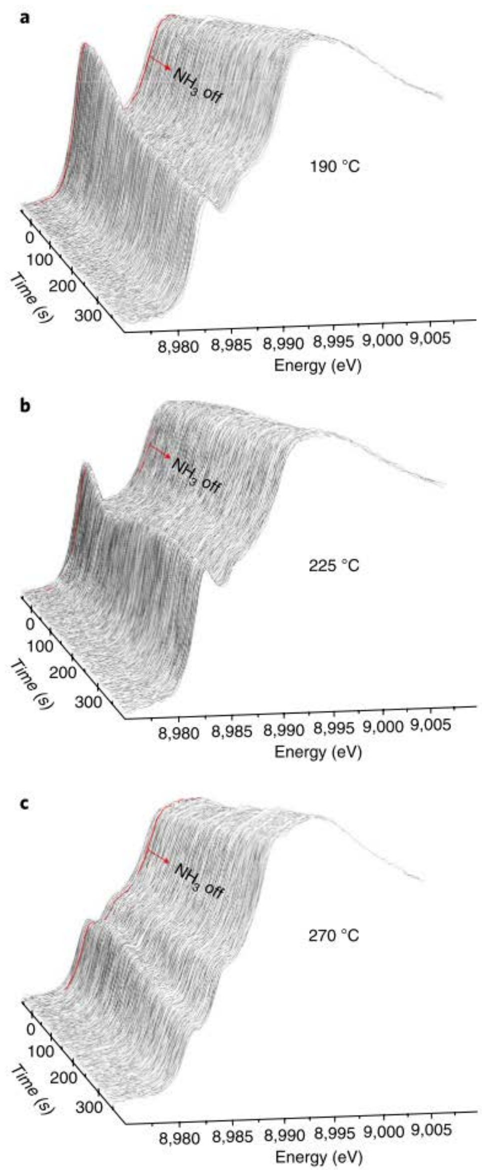
A. Marberger et al. Nature catalysis, 1, 2018, 221–227

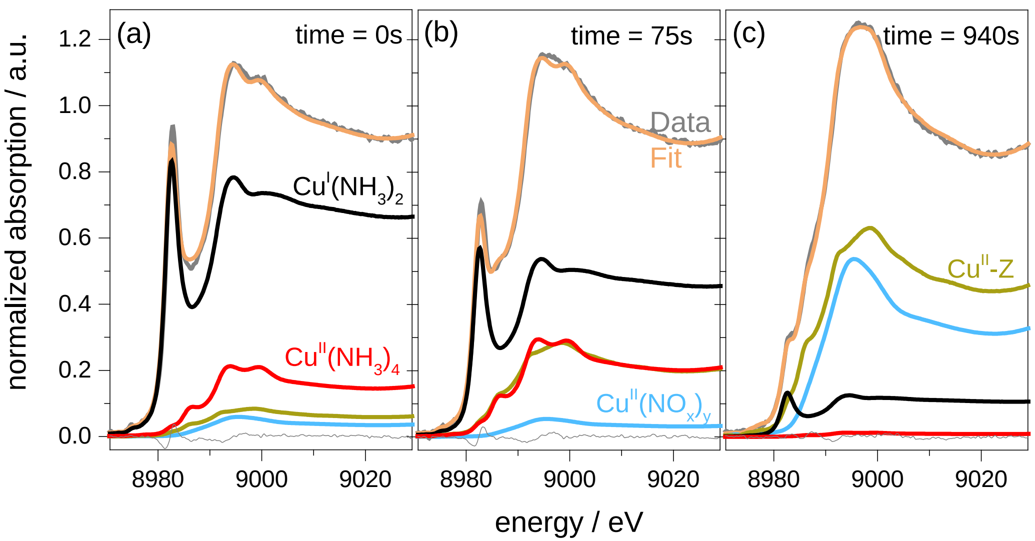
Dynamic copper speciation



A. Marberger et al. Nature catalysis, 1, 2018, 221–227

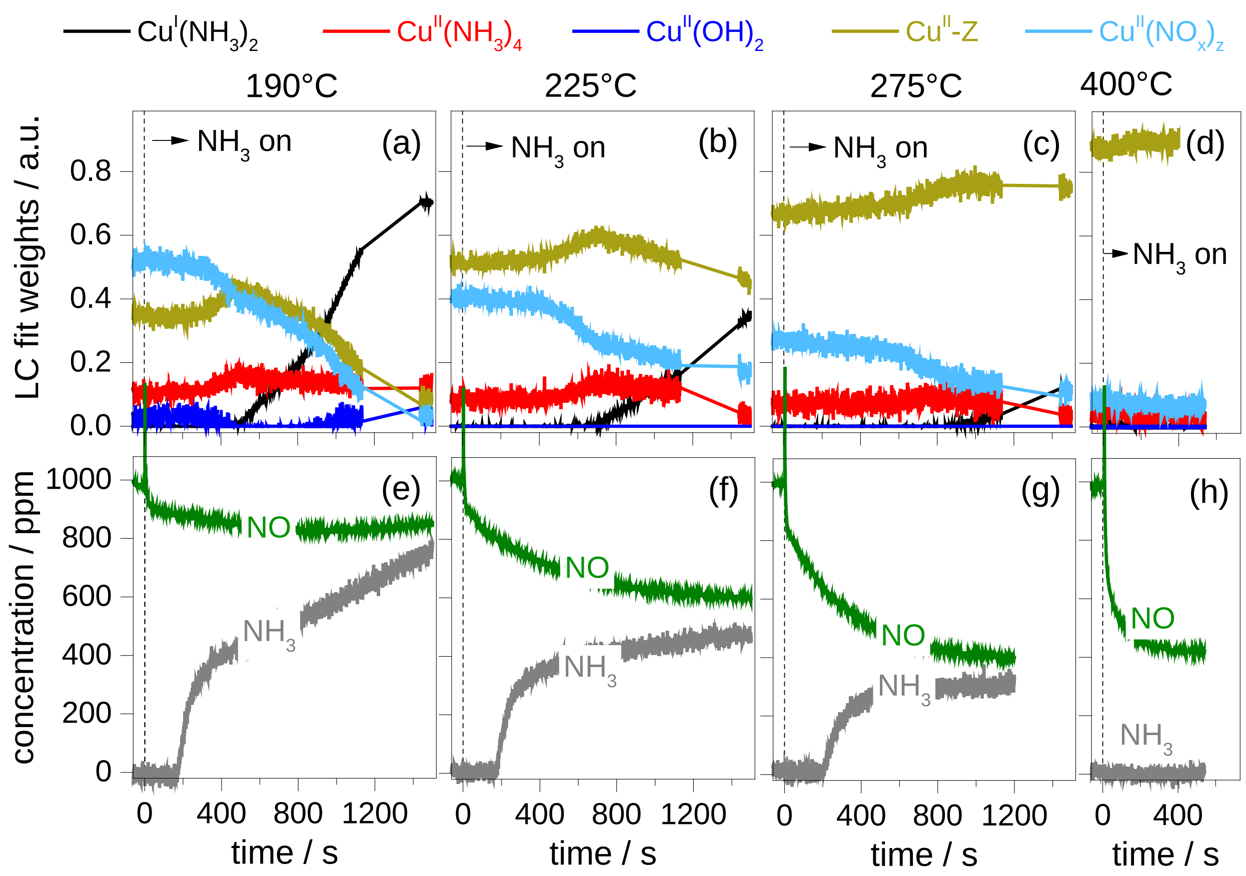
Dynamic copper speciation





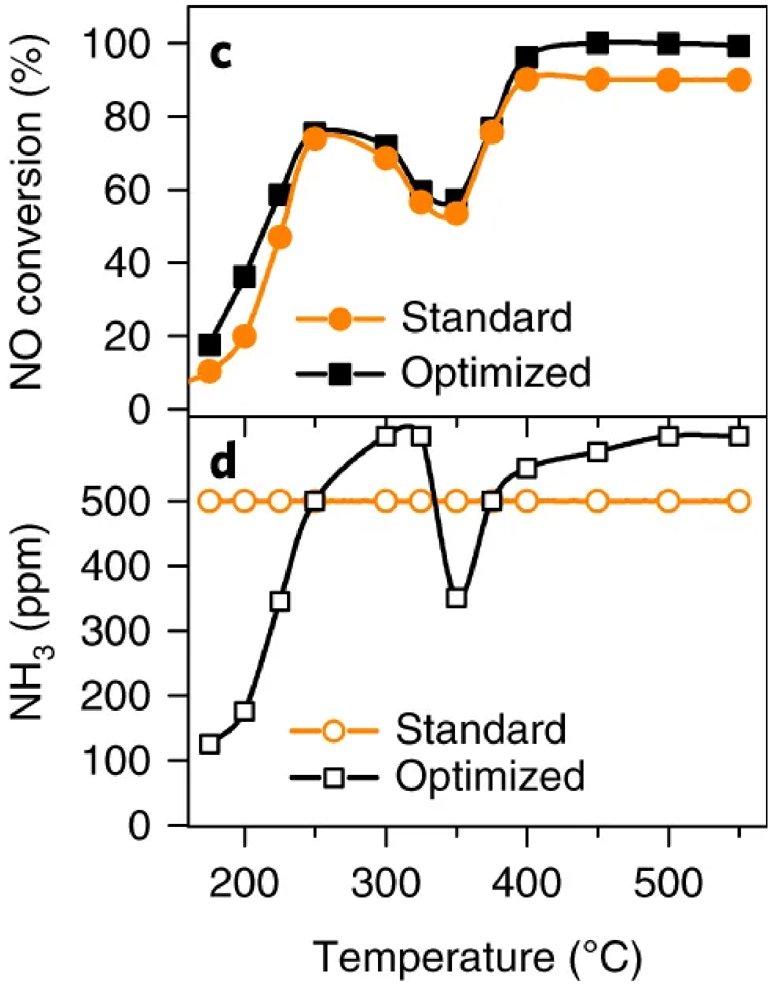
A. Marberger et al. Nature catalysis, 1, 2018, 221–227

Dynamic copper speciation



A. Marberger et al. Nature catalysis, 1, 2018, 221–227

Increased NO conversion and reduced NH3 slip with controlled feeding of ammonia



A. Marberger et al. Nature catalysis, 1, 2018, 221–227

Take home messages

- Operando methodology allows identifying active sites structure
- Time-resolved XAS methods help to uncover true reaction intermediates and distinguish them from spectators
- XAS methods uniquely allow for quantitative correlations between catalytic rates and the reactivity of true active sites