ETH zürich

From spectator species to catalytically active site

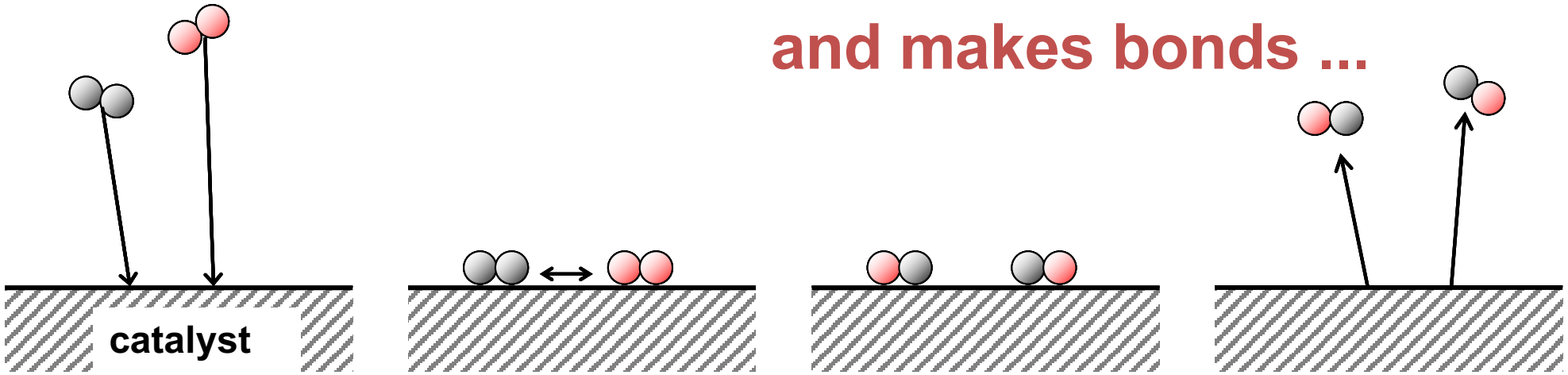
Jeroen A. van Bokhoven

ETH Zurich, Paul Scherrer Institute Villigen

What does a catalyst do?

A catalyst breaks bonds ...

and makes bonds ...

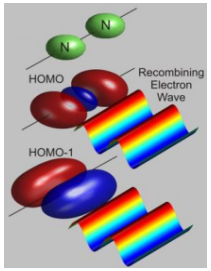


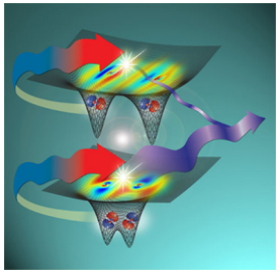
1. Adsorption 2. Reaction 3. Desorption

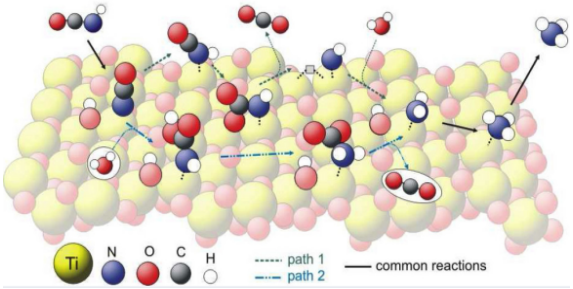
What is an active site?

... ...

Catalysis: time and length scales







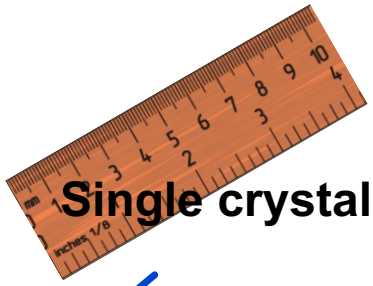
Fundamental **Applied**

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

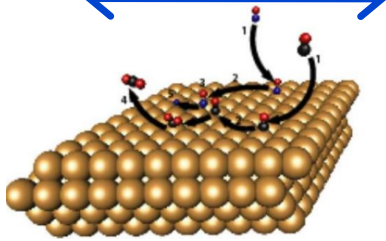
Bond breaking/ formation

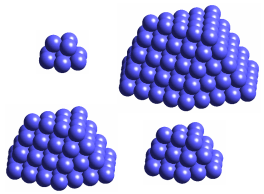
Reaction kinetics

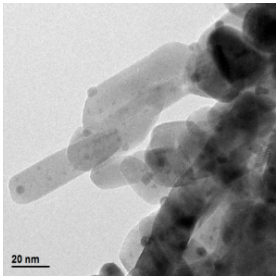
Stability, deactivation

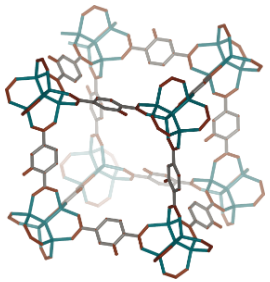


Single crystals · · · clusters · · · supported metals · · · single site catalysts · · · reactors



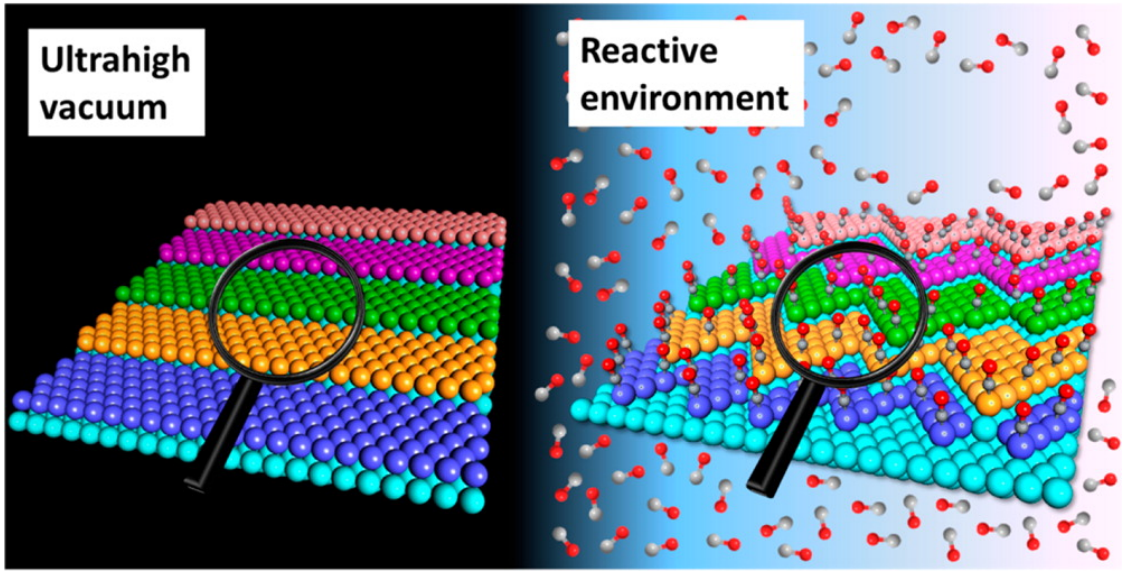






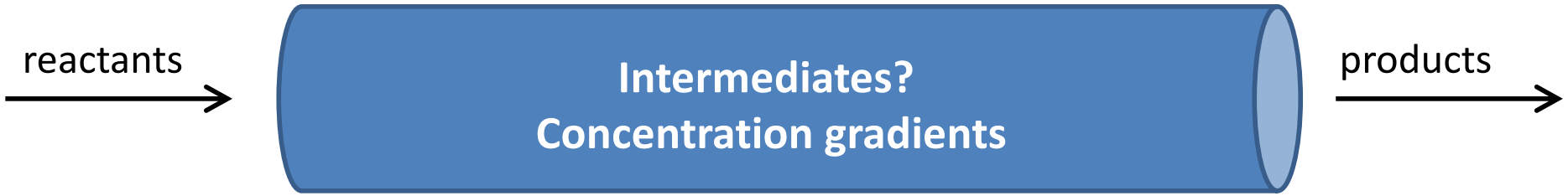
In situ spectroscopy

- Catalyst structure is a function of its environment
- Only structure measured under reaction conditions can give insight into activity
- Conversion changes the gas environment



Shiran Zhang; Luan Nguyen; Yuan Zhu; Sihui Zhan; Chia-Kuang (Frank) Tsung; Franklin (Feng) Tao; *Acc. Chem. Res.* **2013,** 46, 1731-1739.

What about a plug-flow reactor?



Catalyst structure is not necessarily the same everywhere in a reactor!!

Grundwaldt (2007) ; van Bokhoven (2010)

Some definitions

- In situ:

  measuring under specific conditions, such as during heating, during synthesis, and under catalytic conditions

- Operando:

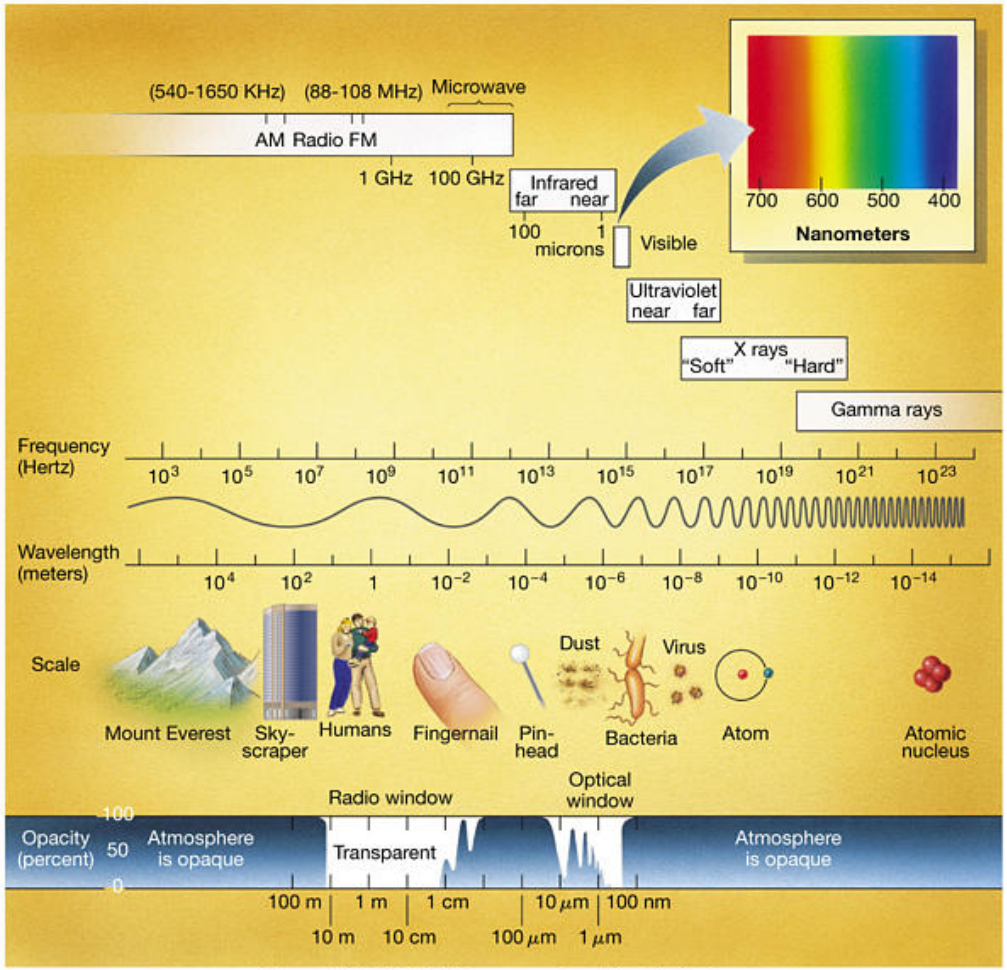
  measuring catalyst structure and its performance simultaneously

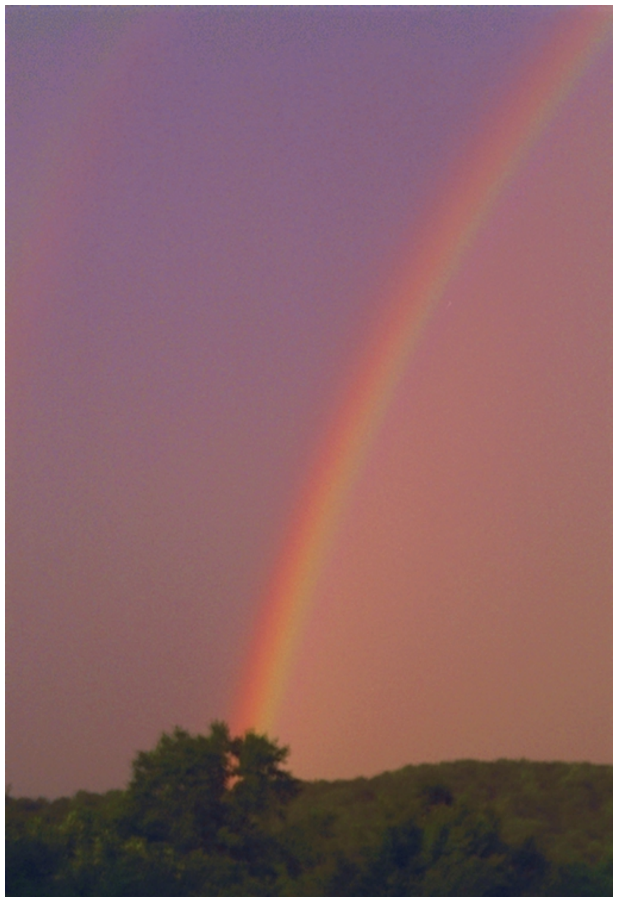
Operando is more narrowly defined

Shining light on catalysts

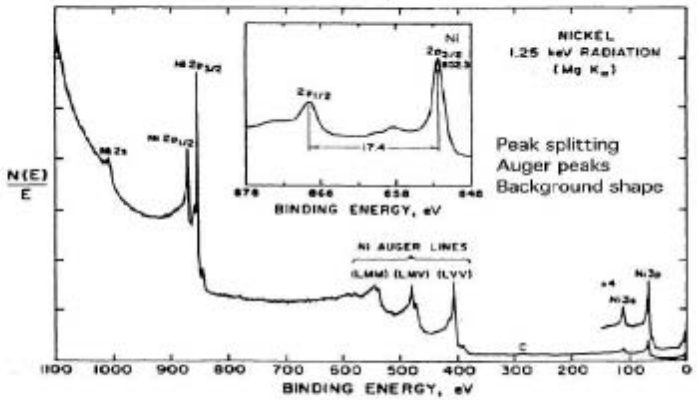
Catalyst characterization:

UVvis, infrared, XRD, TGA, TPD-MS, TPR/O, NMR, XPS, XSW, XAS, XES … …



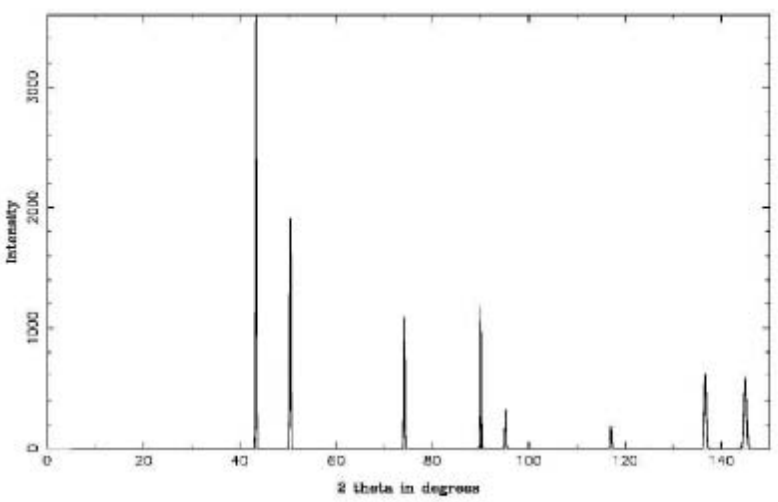


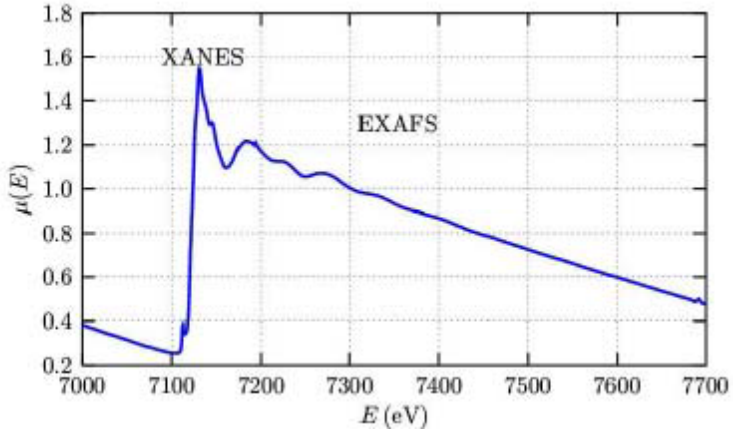
Comparison: XPS, XRD, XAS



- Yields electronic information
- Surface sensitive
- In-situ application difficult
- Needs UHV

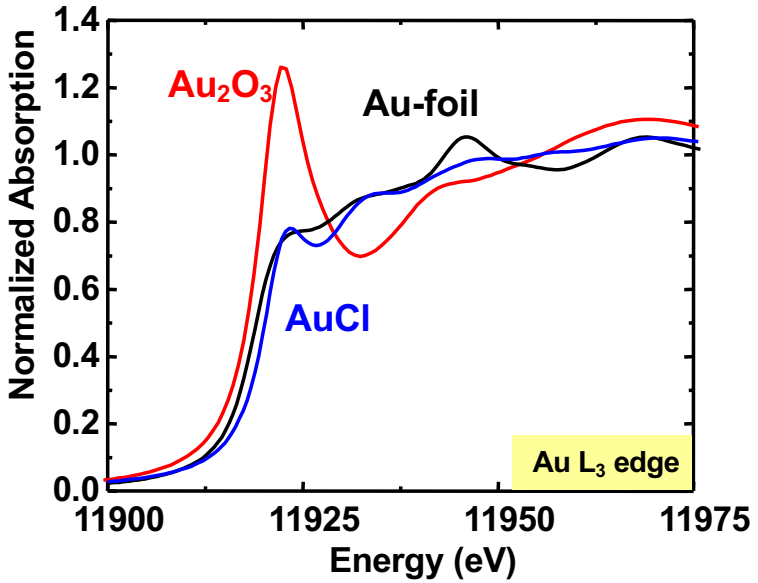
- Yields structural information
- Bulk technique
- In-situ applications realizable
- Needs long range order to work





- Yields electronic and structural information
- In-situ application easy to realize
- Needs a synchrotron
- Data interpretation difficult

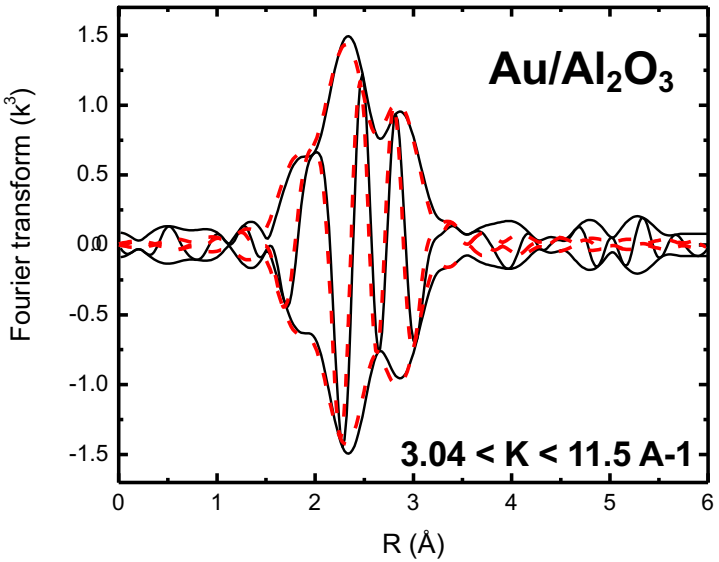
X-ray Absorption Spectroscopy



XANES: geometry
oxidation state
density of states

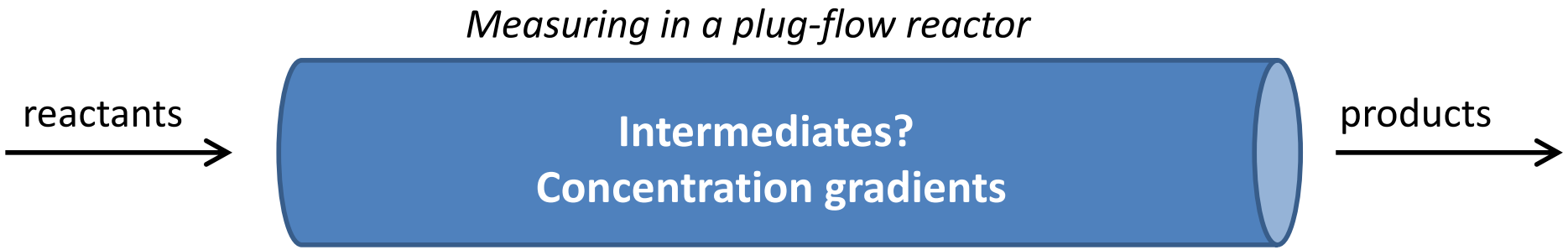
EXAFS: local structure
(particles size)

in situ / operando conditions



Coordination number	6.8
Au-Au distance	2.76 Å
ΔDWF	0.0058
C3	9 E-6
C4	3E-6

does the structure measured under reaction conditions relate to catalysis?

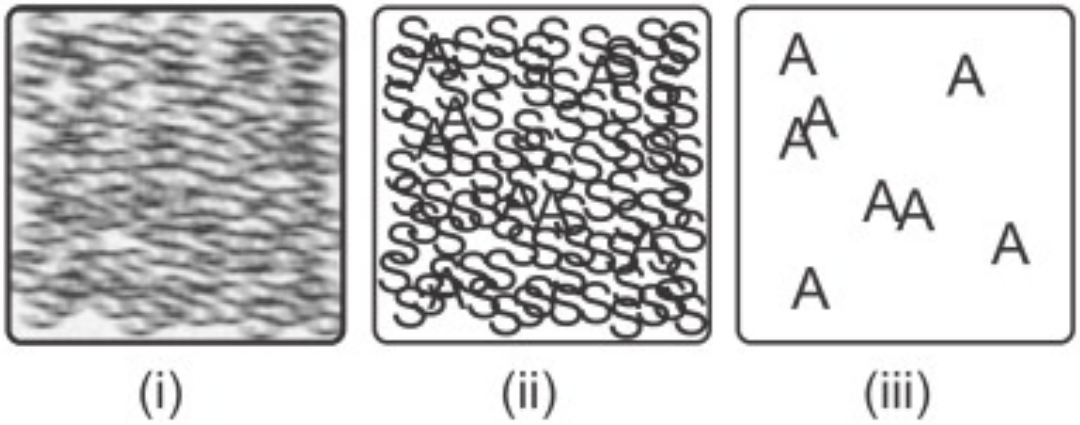


Catalyst structure is not necessarily the same everywhere in a reactor!!

Grundwaldt (2007) ; van Bokhoven (2010)

Spectator species

- Spectator problem: Most abundant is not most active
- Transient methods select for changing (active) species



Realistic

Sensitive

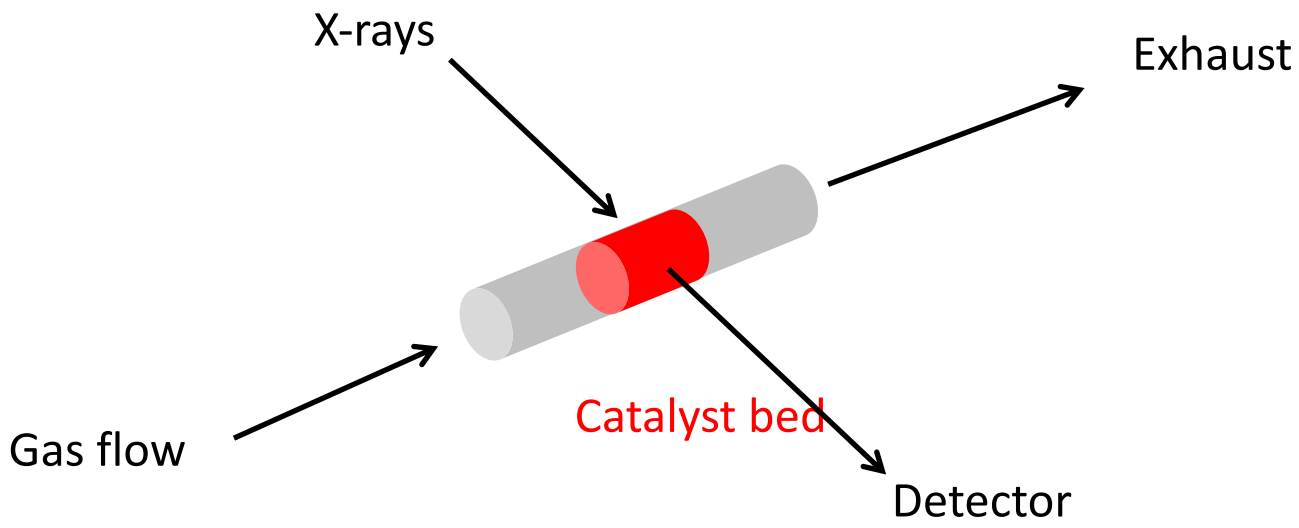
Sensitive and selective

Atsushi Urakawa , Thomas Bürgi , Alfons Baiker

Chemical Engineering Science, **63** (2008) 4902 - 4909

ingredients

- catalyst structure adapts to gas environment
- catalytic conversion changes gas environment
- in situ / operando measurement is essential
- active sites may be minority species



Measure catalyst structure operando
Time-resolved change to jump in gas environment

Role of ceria in catalysis

Ceria is an effective dopant in catalysis

- TWC, soot oxidation, FCC additive, oxidation and hydrogenation reactions
- Oxygen storage capacity
- Ce^{4+} / Ce^{3+} redox *activity often associated with presence of* Ce^{3+}

$$2Ce^{4+} + O^{2-} + CO \rightarrow 2Ce^{3+} + V_o + CO_2$$

Oxygen storage capacity

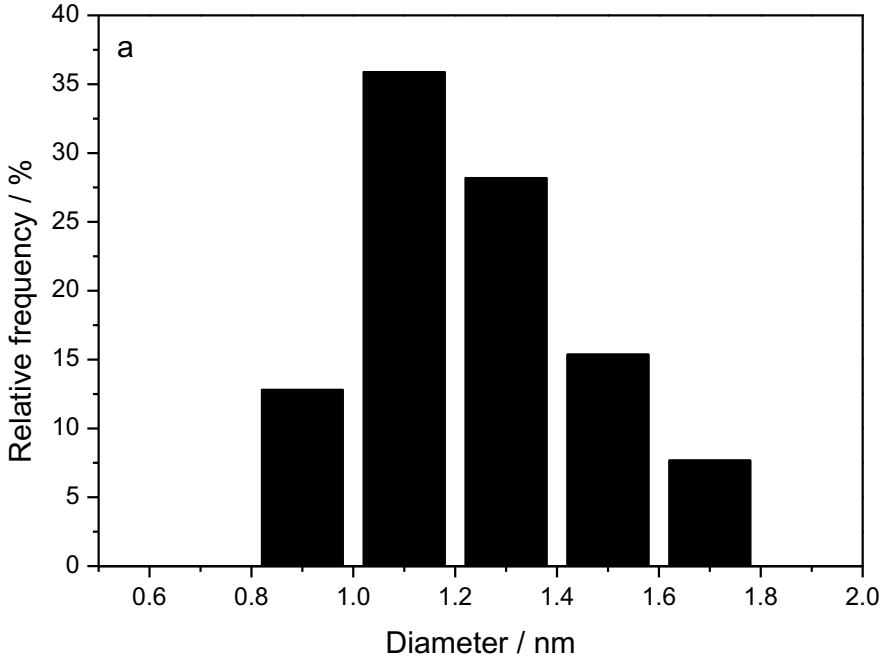
- Amount of oxygen that can be released at specific temperature
- High capacity often associated with high catalytic activity (?)

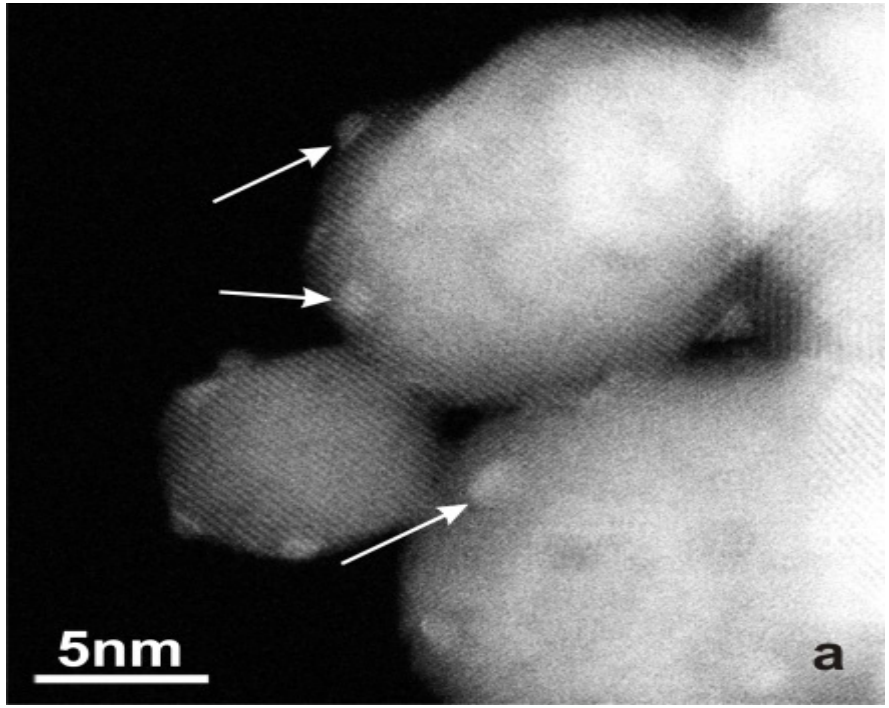
Questions addressed here:

Ce^{3+}

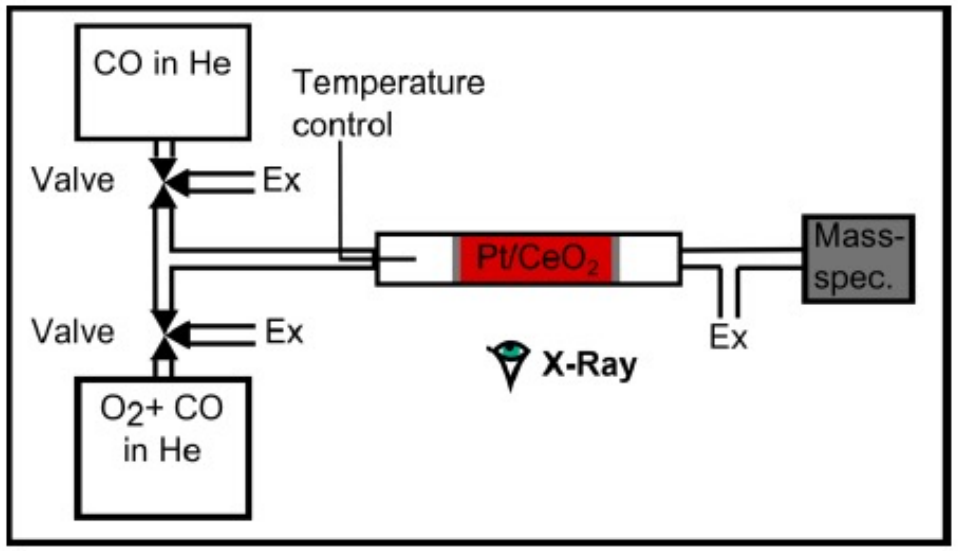
- ***what is its role in catalysis?***
- ***How does it look like?***
- ***Where is it?***

one nm Pt on polyhedral ceria particles

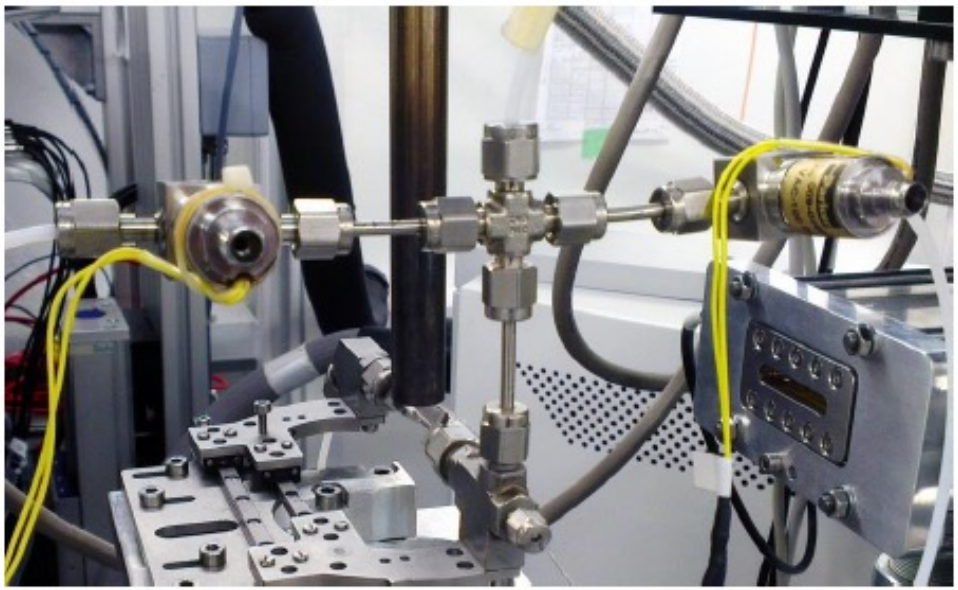




$CO + ½O_2 \rightarrow CO_2$



- **Solenoid valves**
- **Plug flow reactor**
- **Thermo couple**
- **Hot air blower**



Fast gas switches:

0.5% CO vs. 0.5% CO + 4.5% O_2

Excess O_2

Balanced with He

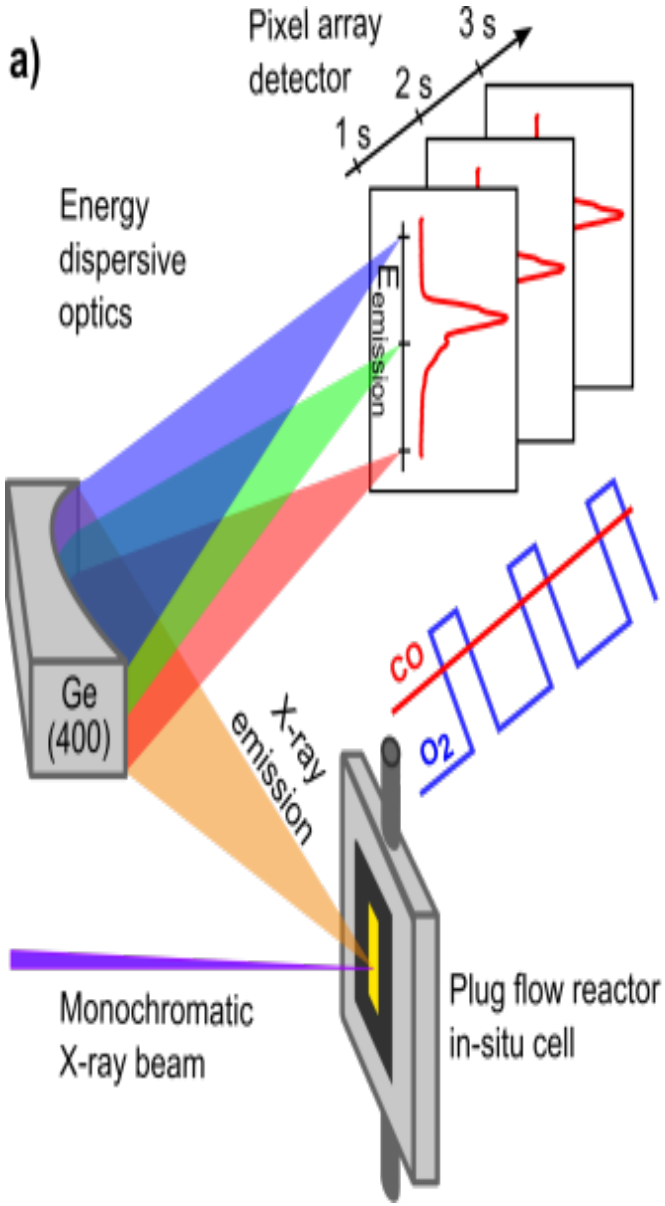
total flow: 50 ml/min

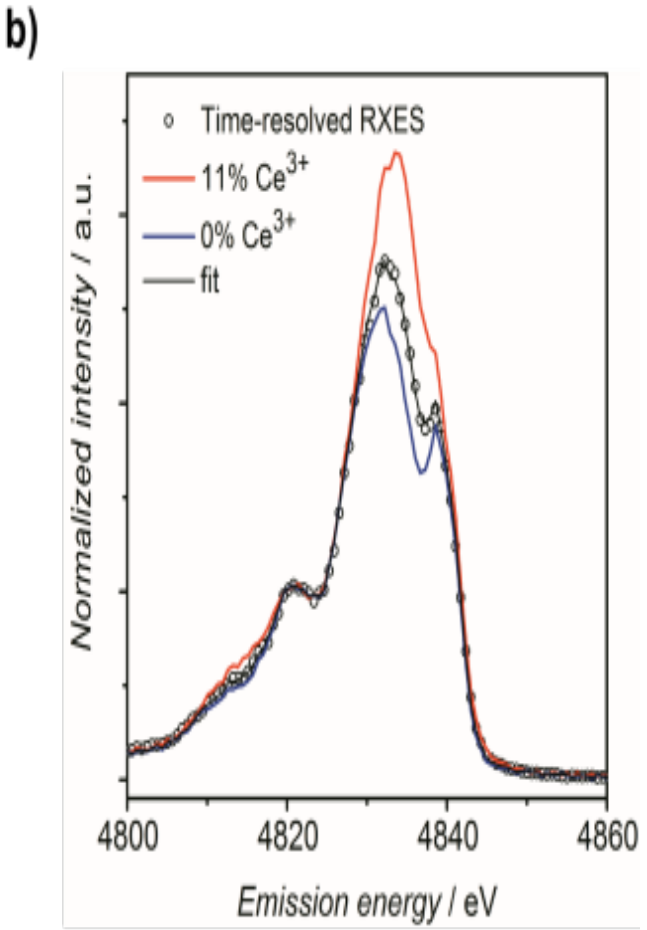
(low conversion)

Time-resolved X-ray emission

Sub-second time resolution *(Spectra recorded in a single shot)*

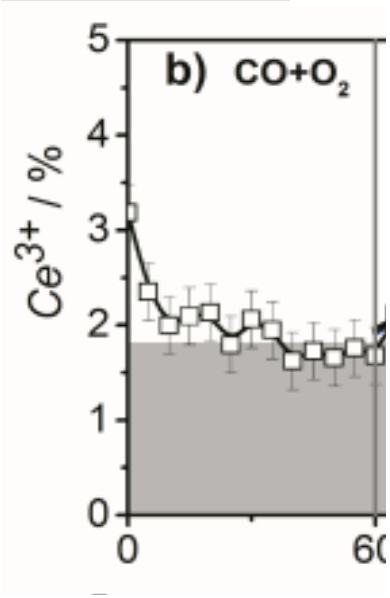
in situ



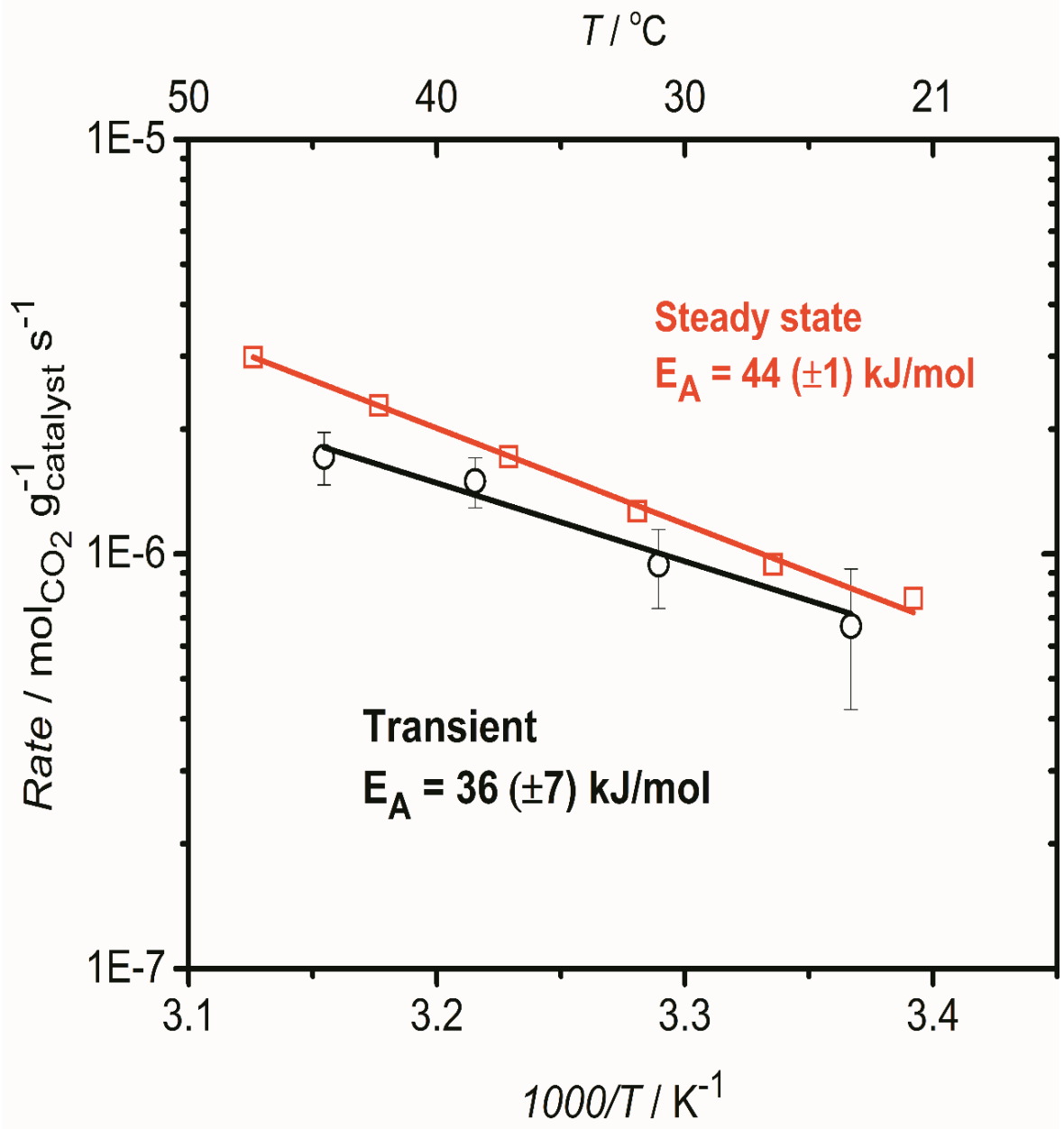


Ratio Ce^{III} / Ce^{IV}

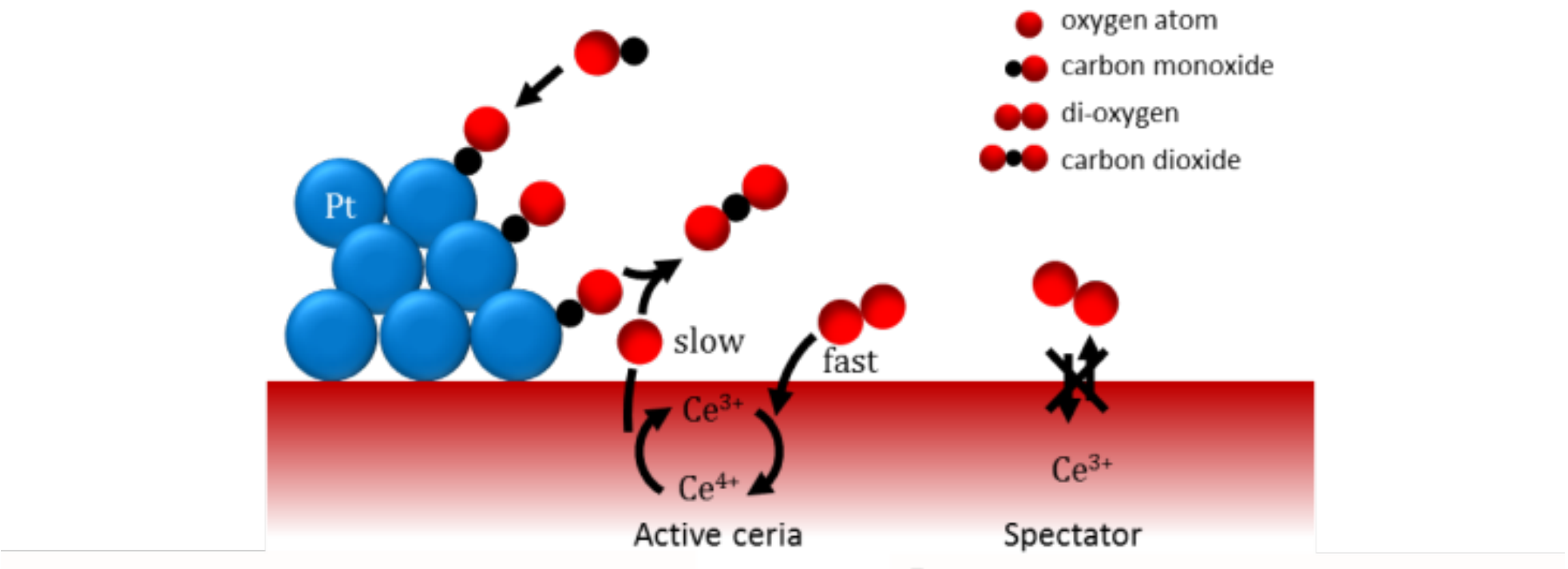
Ce^{III} after switch from $CO + O_2$ to CO



8% conversion at 35 °C



Steady state and transient rates are really very similar….



$$2Ce^{4+} + O^{2-} + CO \rightarrow 2Ce^{3+} + V_o + CO_2$$

Angew. Chem. Int. Ed. **54** (2015) 8728-8731

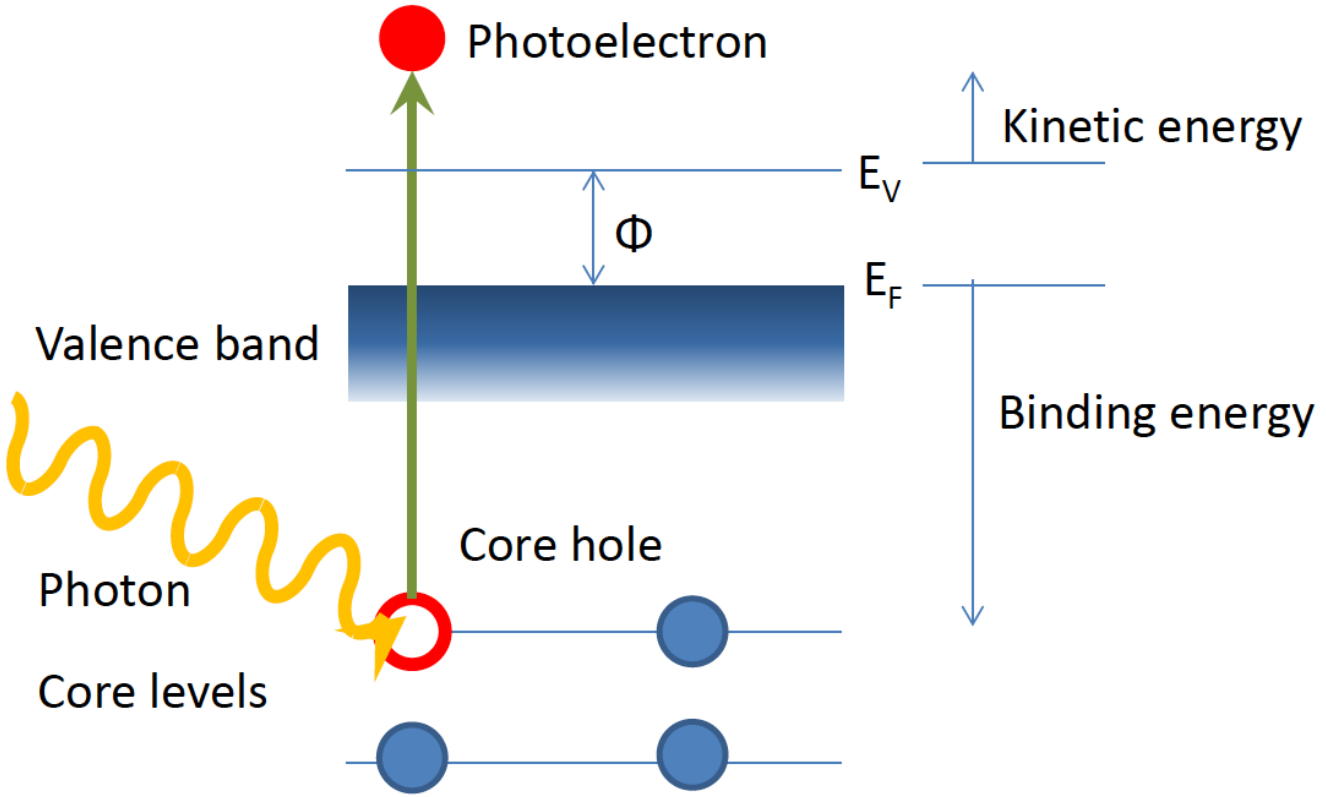
Oxygen storage capacity

- It is the rate of oxygen release that matters
- Not the total storage capacity

Structural depth profiling

In situ XPS at the synchrotron

The photoemission process

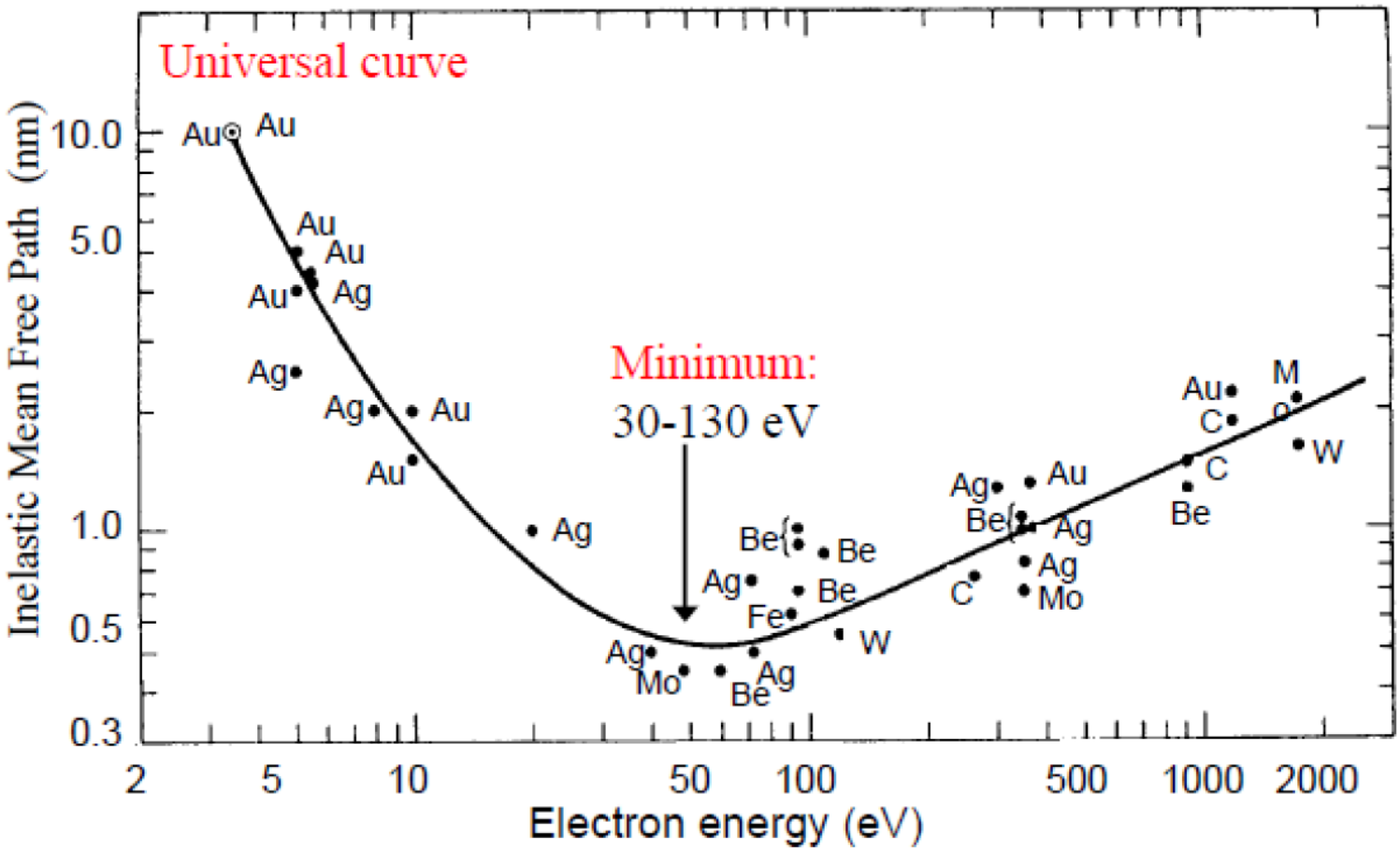


KE = hν – BE – Φ for a solid

KE = hν – IP for a gas

Φ : photoelectric workfunction (4-6 eV)

Electron inelastic mean free path



Rule of thumb:

$h\nu$=1000 eV

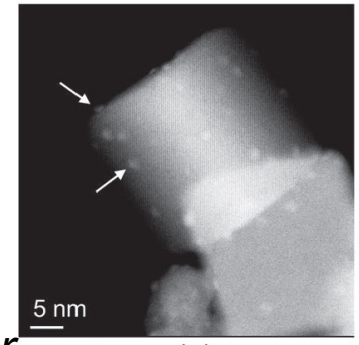
λ_{mfp}:

5-10 Å metals
15-40 Å oxides
15-30 Å polymers

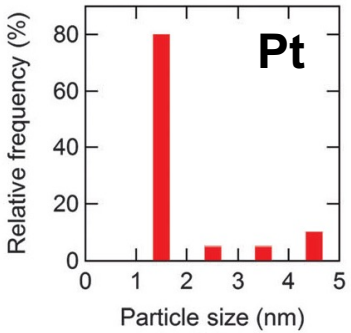
At close to normal detection angles 95% of the signal comes from atoms within 3λ of the surface

Structural depth profiling

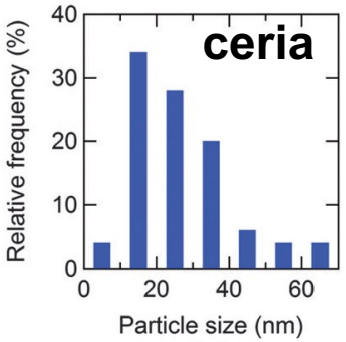
In situ XPS at the synchrotron



(a)

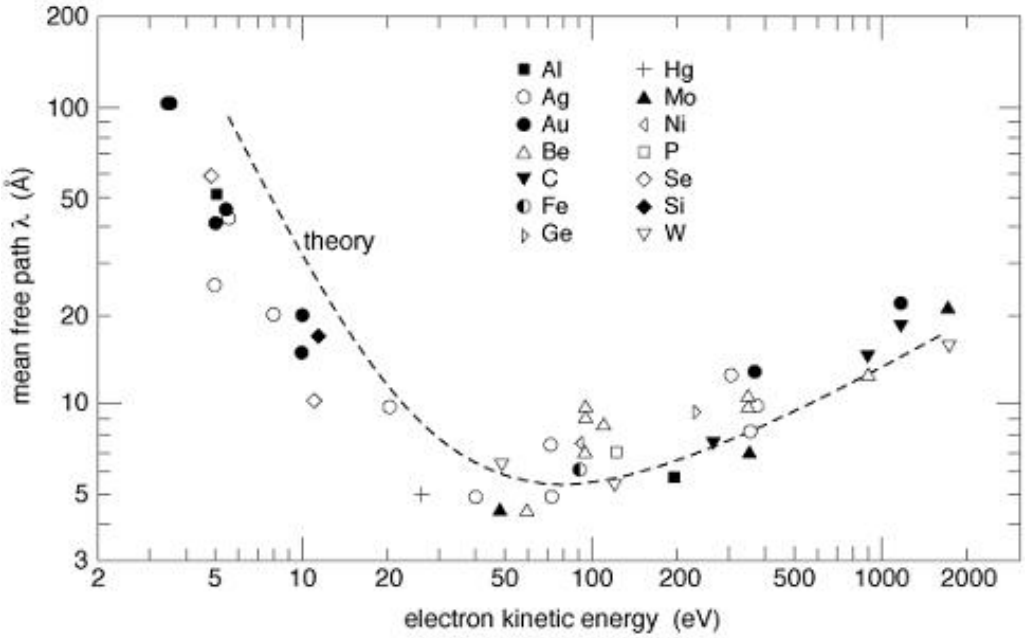


(b)



(c)

High energy electrons travel further



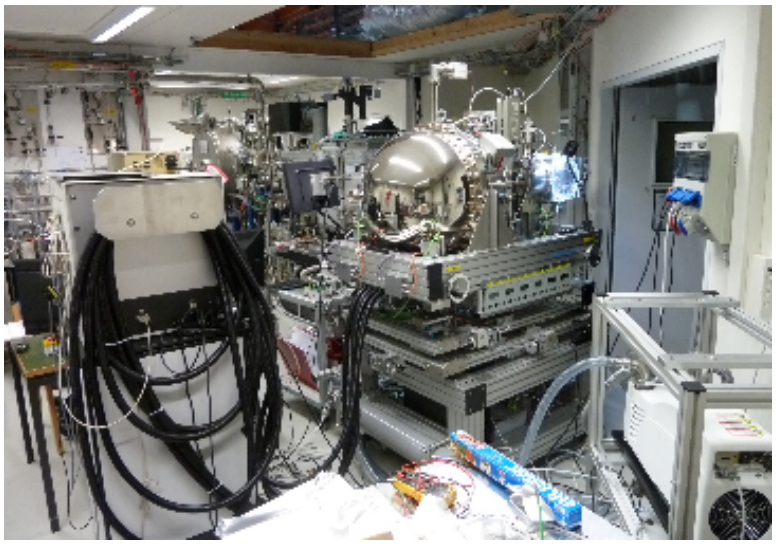
Measure concentration and depth profile of Ce^{III} under oxygen respectively hydrogen

$$E_{kin} = h\nu - E_{bin}$$

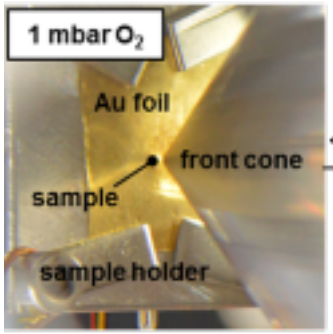
Determines the probing depth

Set by the synchrotron

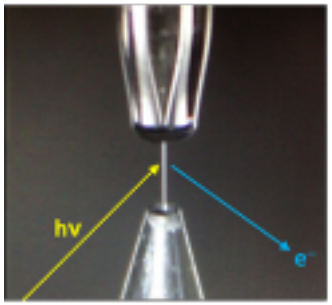
NEAR AMBIENT PRESSURE XPS ENDSTATION AT SLS

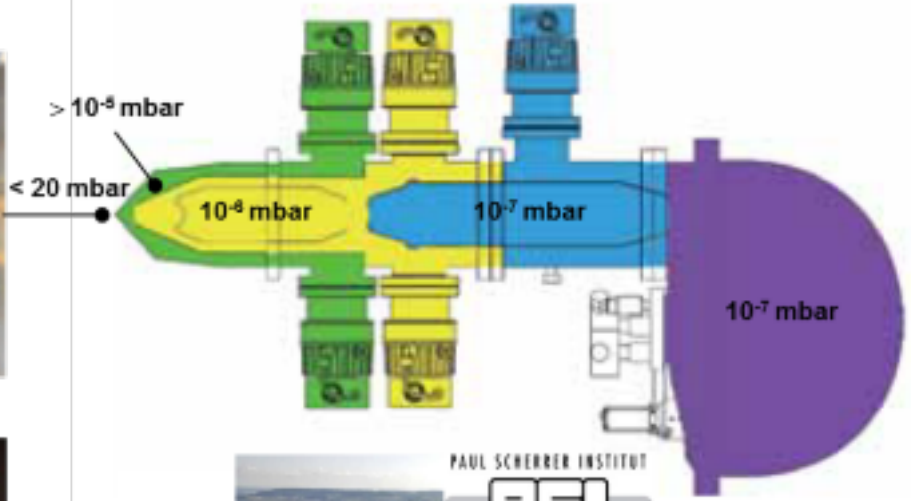


- **Near ambient pressure photoelectron spectroscopy endstation**
- **Operation from UV to tender X-ray (7 keV)**
- **Use of novel pre-lens (VG SCIENTA) for combined high pressure and high kinetic energy measurement**



(in analysis chamber)

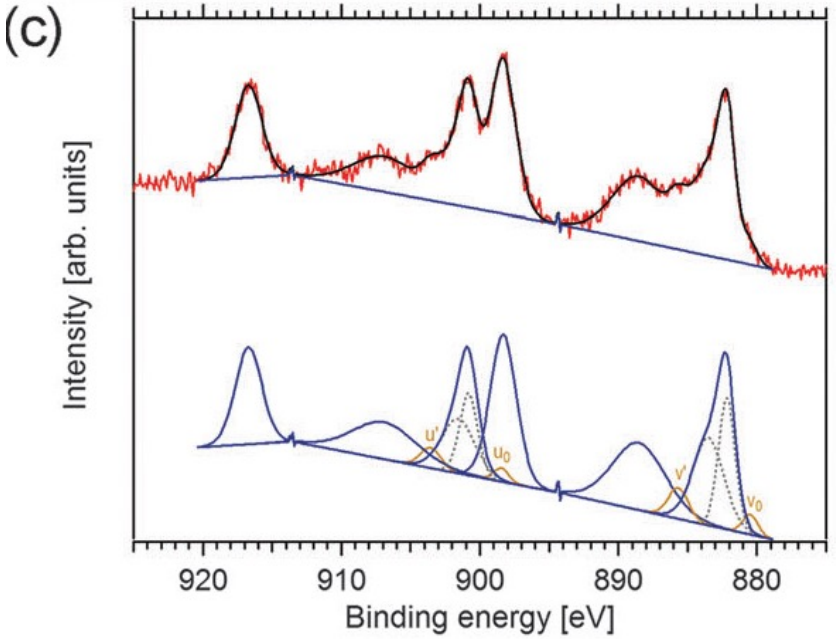




PHOENIX beam lines

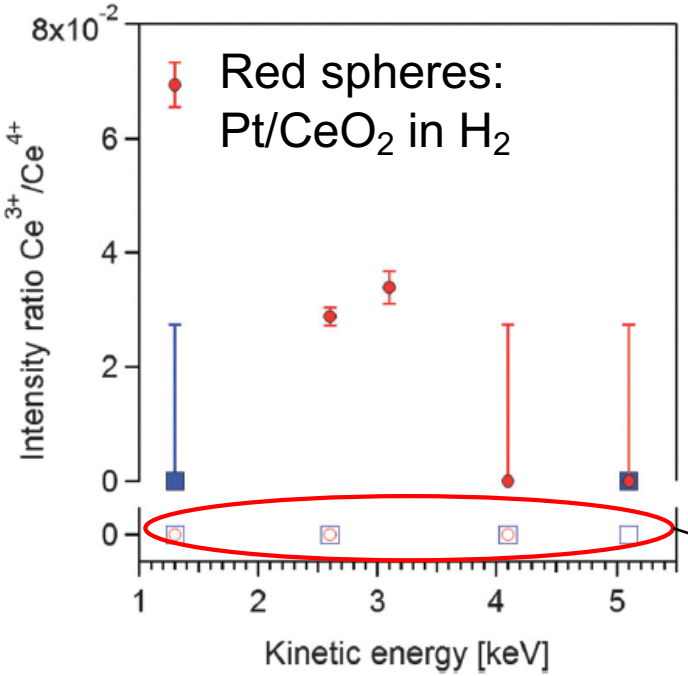
Thomas Huthwelker
Markus Ammann

Ce 3d XPS sensitive to cerium oxidation state



Pt/CeO_2 in 1 mbar H_2

Spectrum measured at low kinetic energy
surface sensitive

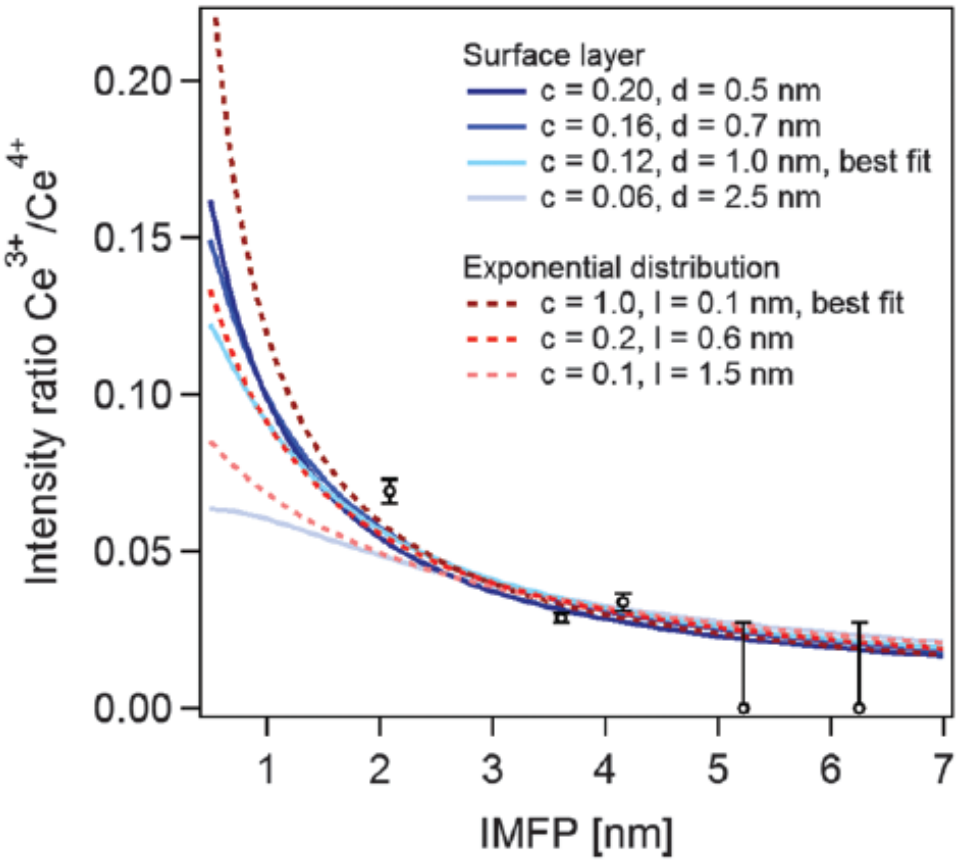


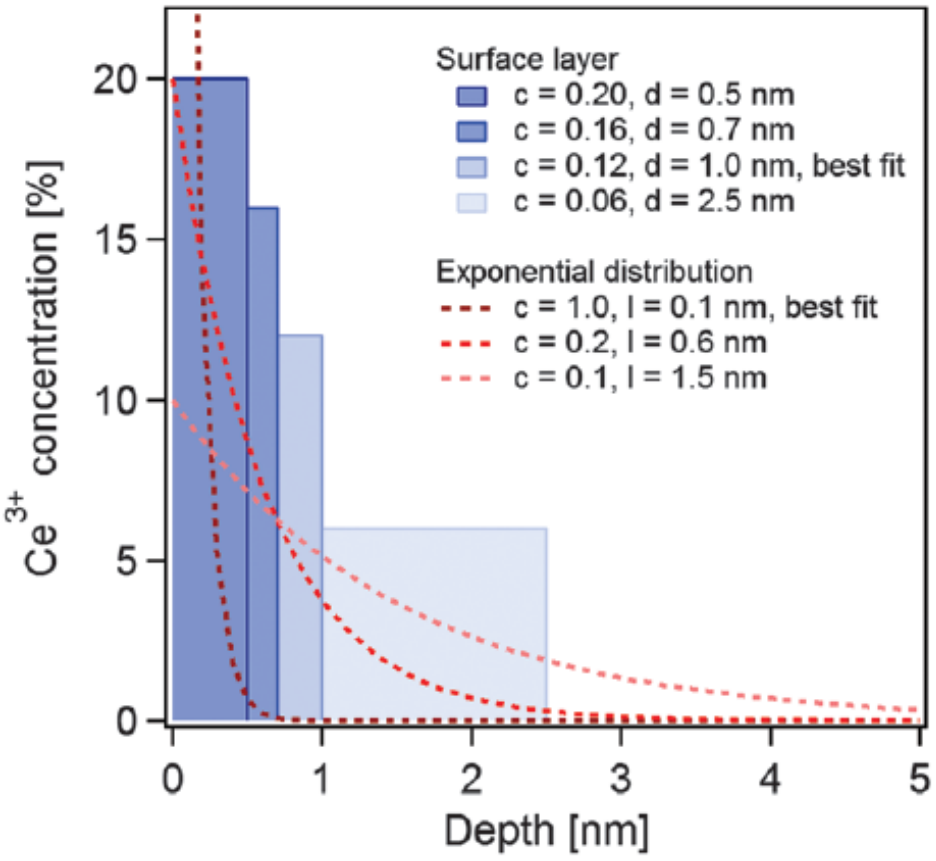
H_2 and Pt needed to reduce ceria
Ce^{III} more at the surface

Blue squares: Pt/CeO_2 in O_2

CeO_2 in 1 mbar H_2 respectively 1mbar O_2

Quantification needs a model



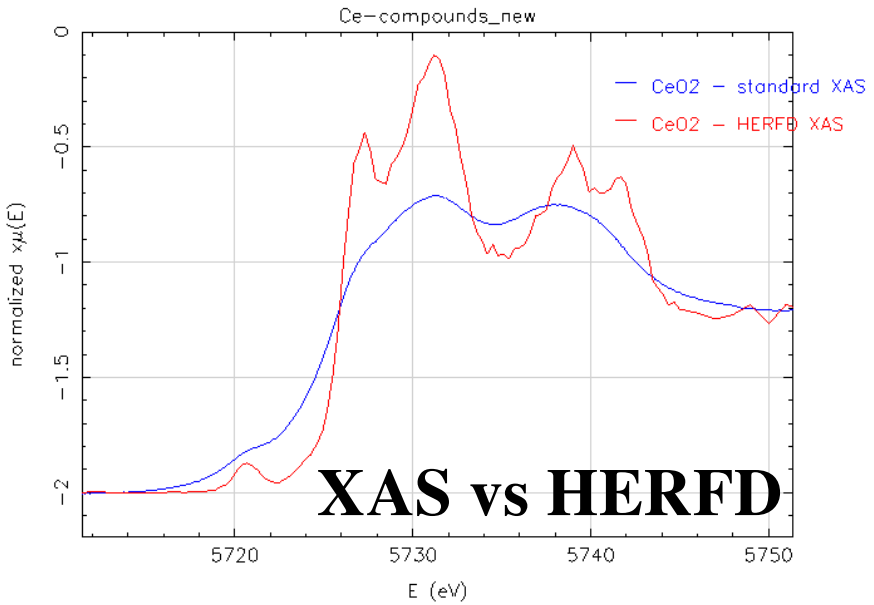


Best fit with data: only Ce^{III} within the outermost 5-10 Å

Shunsuke et al. PCCP 17 (2015) 5078-5083

Ce L_3 High energy resolution fluorescence detected XAS

NASA pictures before and after upgrade of HUBBLE



Structure of Ce^{3+}?

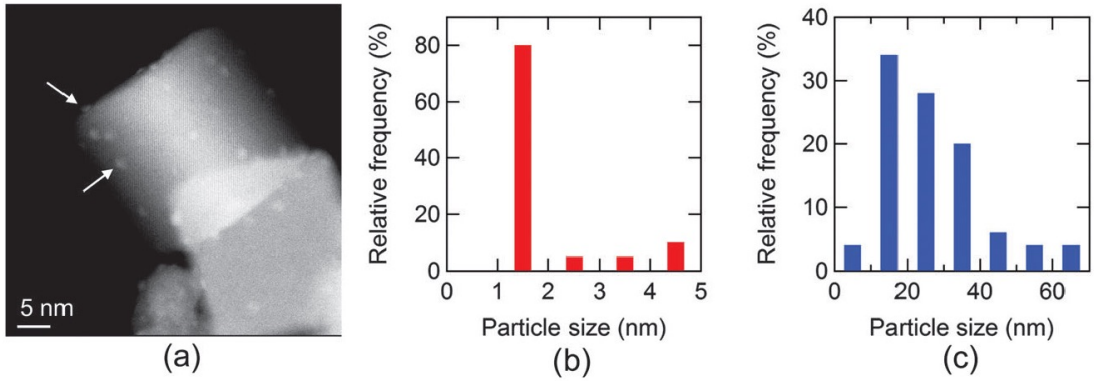
"HERFD"
Safonova, O. V., Tromp, M., van Bokhoven, J. A., de Groot, F. M. F., Evans, J., Glatzel, P.
J. Phys. Chem B. 110 (2006) 16162-16164

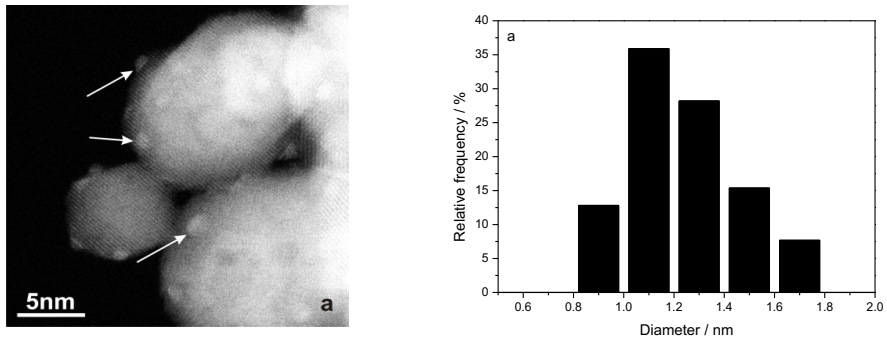
Polyhedral CeO_2 nanoparticles: Size-dependant geometrical and electronic structure
Paun, C., Safonova. O. V., Szlachetko, J., Abdala, P. M., Nachtegaal, M., Sa, J., Kleymenov, E., Cervellino, A., Krumeich, F., van Bokhoven, J. A.
J. Phys. Chem. C 116 (2012) 7312-7317

Electronic and geometric structure of Ce3+ forming under reducing conditions in shaped ceria nanoparticles promoted by platinum
Safonova, O. V., Guda, A., Paun, C., Smolentsev, N., Abdala, P., Smolentsev, G.,Nachtegaal, M., Szlachetko, J., Soldatov, M., Soldatov, A., van Bokhoven, J. A.
J. Phys. Chem. C. 118 (2014) 1974-1982

Shaped ceria particles

Pt/CeO_2



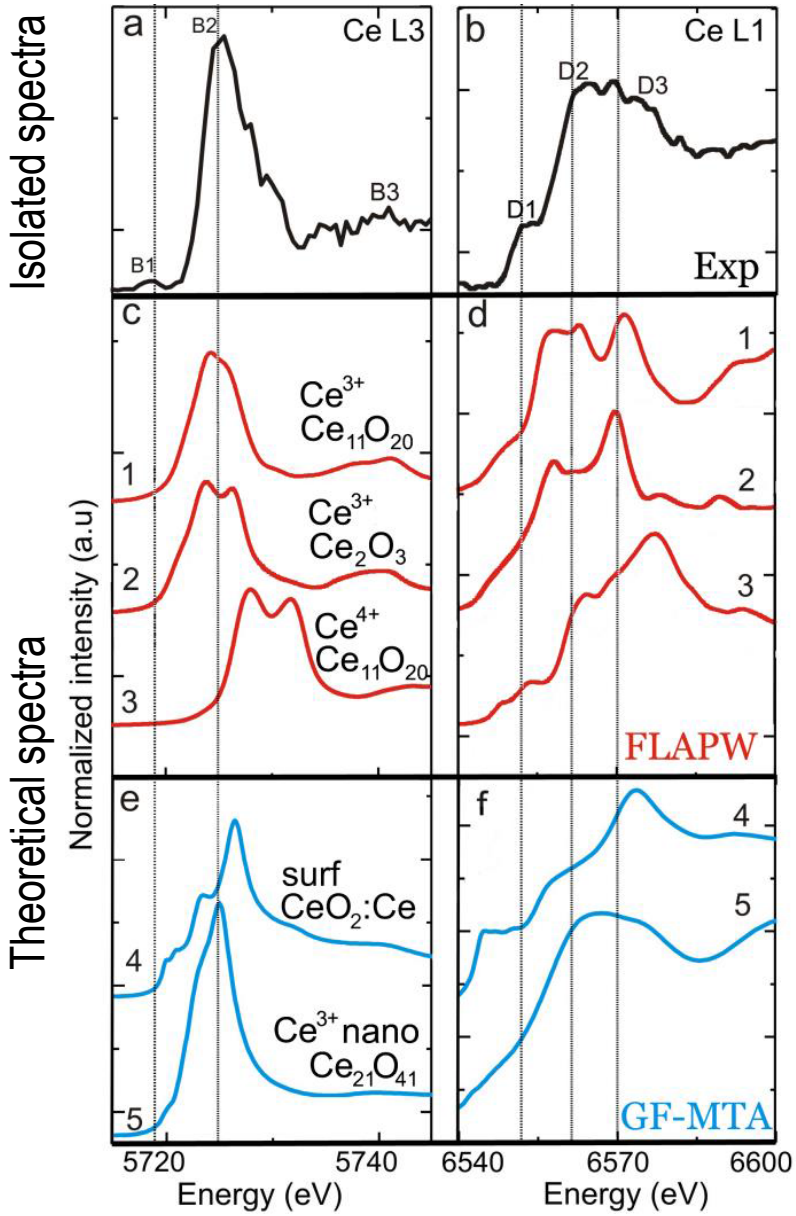


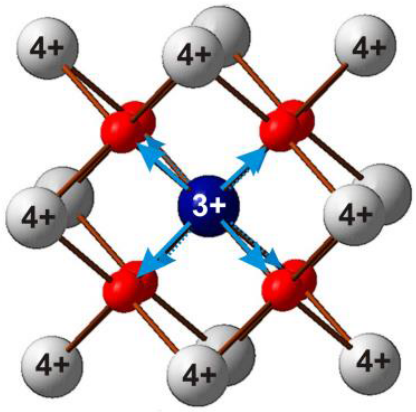
Polyhedral CeO_2 nanoparticles: Size-dependant geometrical and electronic structure
Paun et al. *J. Phys. Chem. C* 116 (2012) 7312-7317

In situ hydrogen reduction at 150ºC

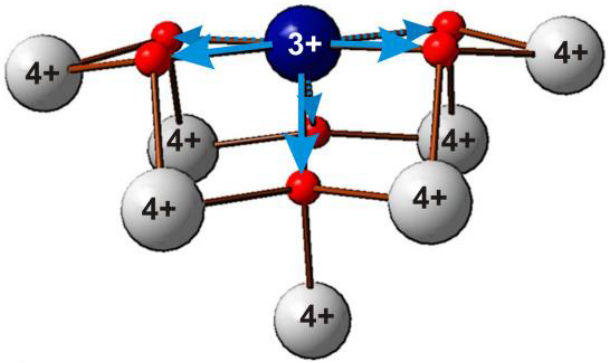
difference between spectrum CeO_2 and $CeO_{2-\delta}$

Isolation of Ce^{3+} spectrum: deduction of its structure





bulk Ce^{3+}



surface Ce^{3+}

Two types of Ce^{3+}

- Surface, six-coordinate
- Sub-surface, eight-coordinate

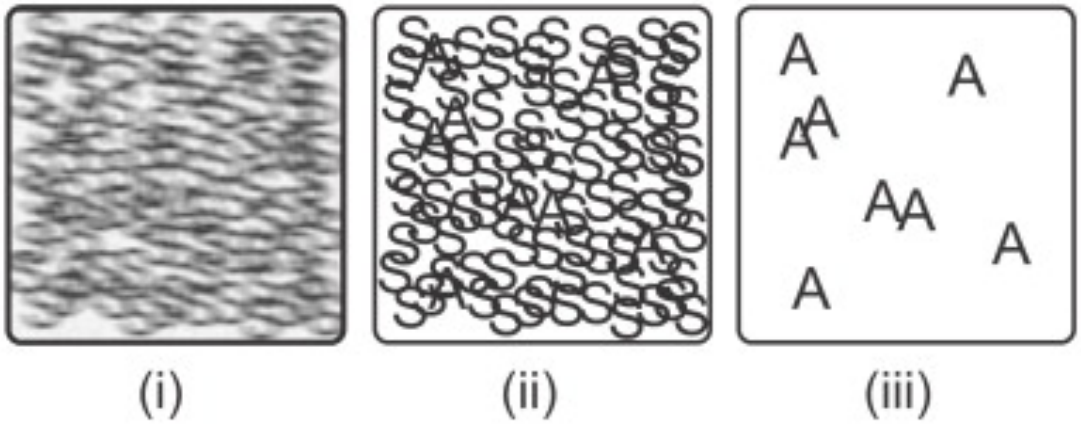
Take-home message I

Ce^{III} that is observed in an in situ / operando experiment is a spectator

for carbon monoxide oxidation

Ce^{III} that participates in the reaction is too short-lived to see

S = spectator
A = active site



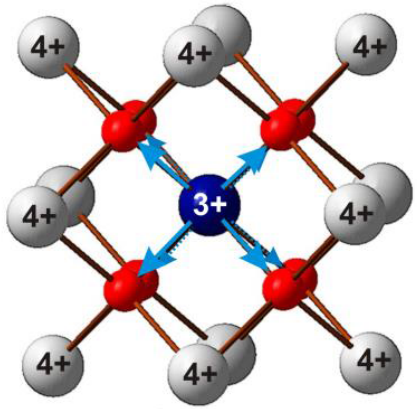
Take-home message II

Knowledge of rate-limiting step essential

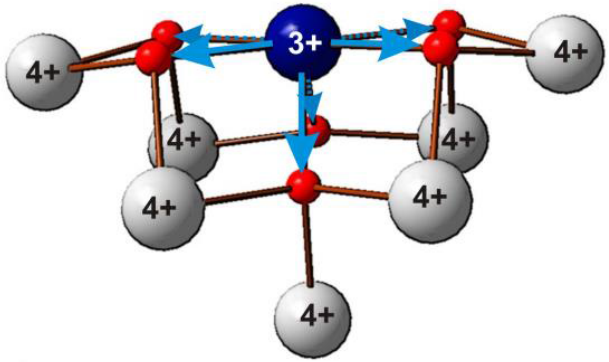
Measuring in the time domain brings significant advantages

Intermediate conclusions

- Ce^{III} actively participates in the catalytic cycle
- Transient methods enable distinguishing spectator species from active ones
- Ce^{III} remains at the surface



bulk Ce^{3+}



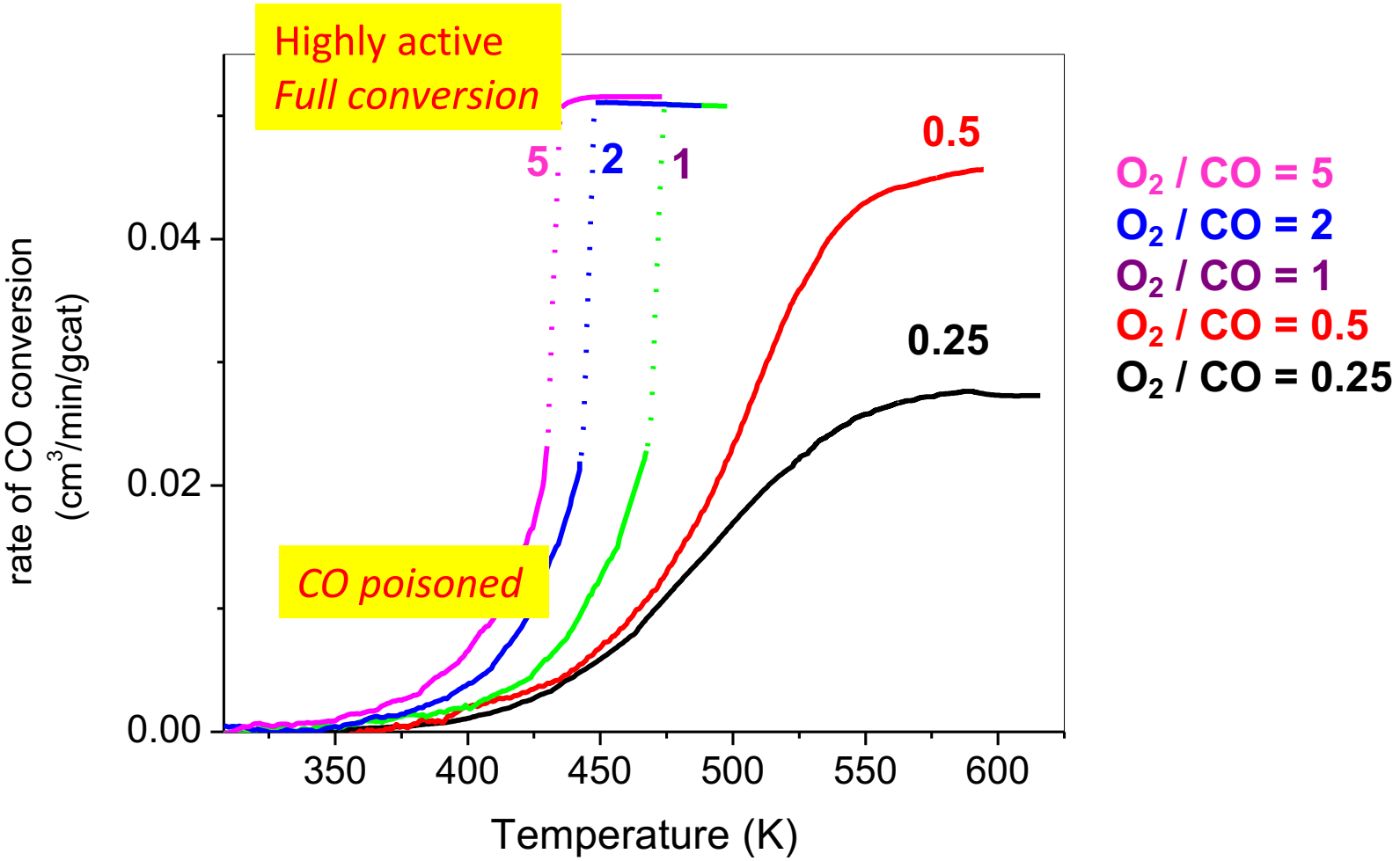
surface Ce^{3+}

Platinum on inert support

How does the platinum structure relate to activity in a plug-flow reactor?

conversion vs temperature

At constant CO space velocity, except for 0.25

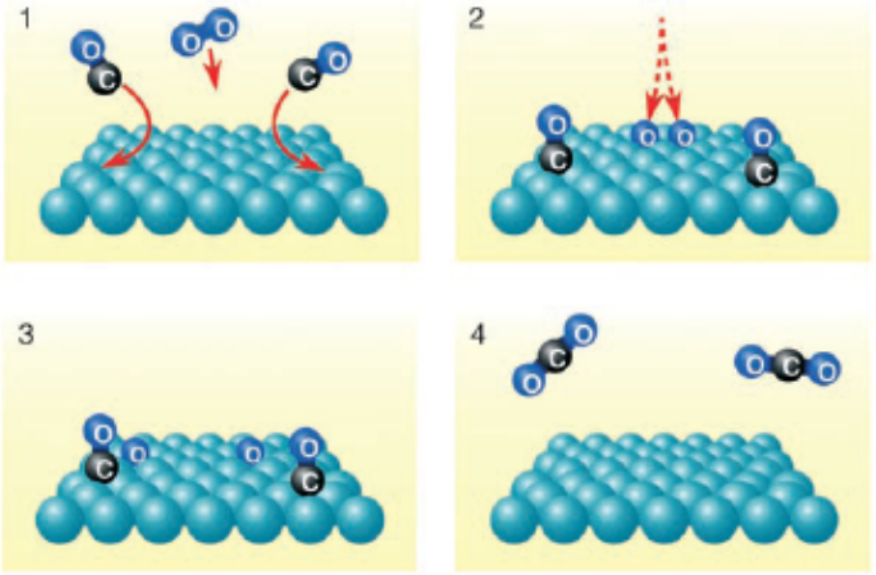


two reaction regimes

Active phases in carbon monoxide oxidation

Ultra-high vacuum → **High pressure**

well established



Langmuir-Hinshelwood

Two *(or more)* reaction regimes:

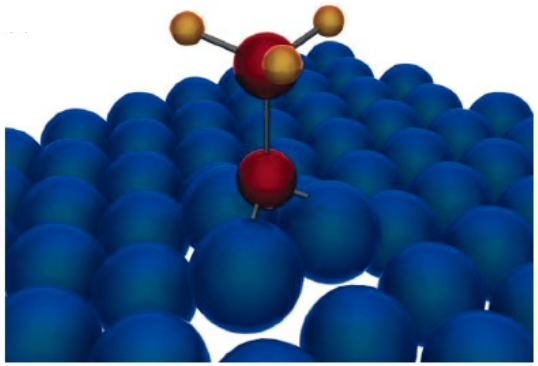
- **Low activity: CO poisoned**
- **High activity: *controversy***

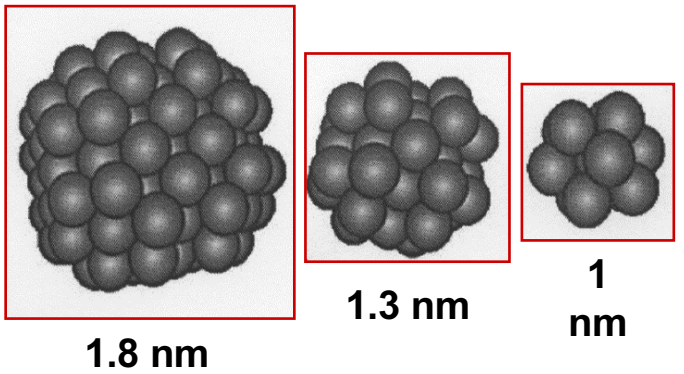
"chemisorbed oxygen-dominant phase is hyperactive state"
Goodman *Surf. Sci.* 601 (2007) 5326

"surface oxide is most active"
Frenken *Phys. Rev. Lett.* 89 (2002) 046101

"defect Pt surface sites are active sites"
Somorjai *J. Amer. Chem. Soc.* 119 (1997) 3994

"oxygen chemisorbed state is active state"
Delgass *J. Catal.* 204 (2001) 34



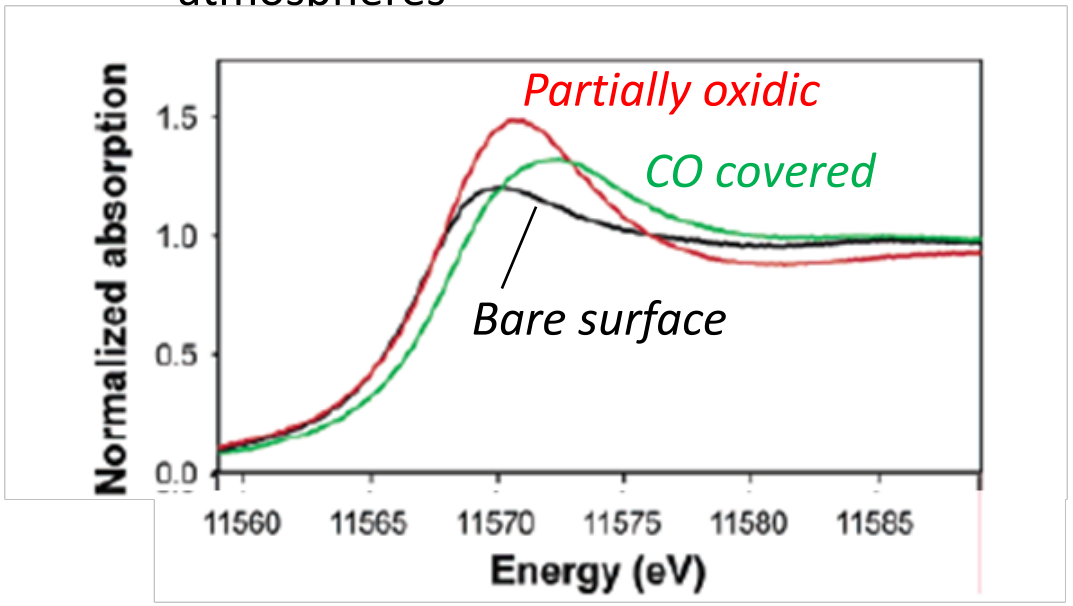


What about real catalytic particles in a real reactor?

Pt L_3-edge XANES

- Excitation from $2p_{3/2}$ to d-band
- Spectrum gives information on oxidation state and adsorbates

Pt L_3-edge XANES under different atmospheres

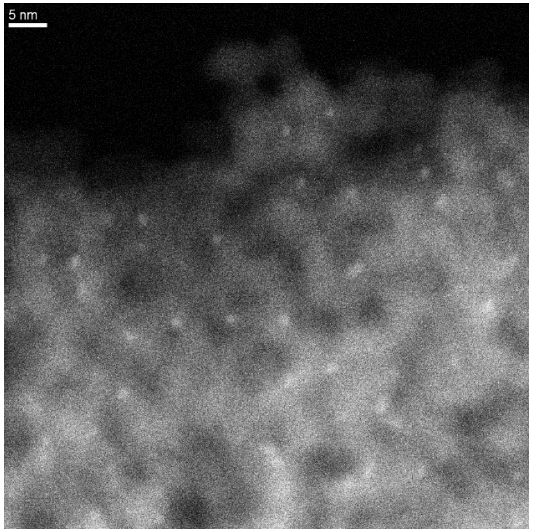


Safonova et al., *The Journal of Physical Chemistry B* **2006** *110* (33), 16162-16164

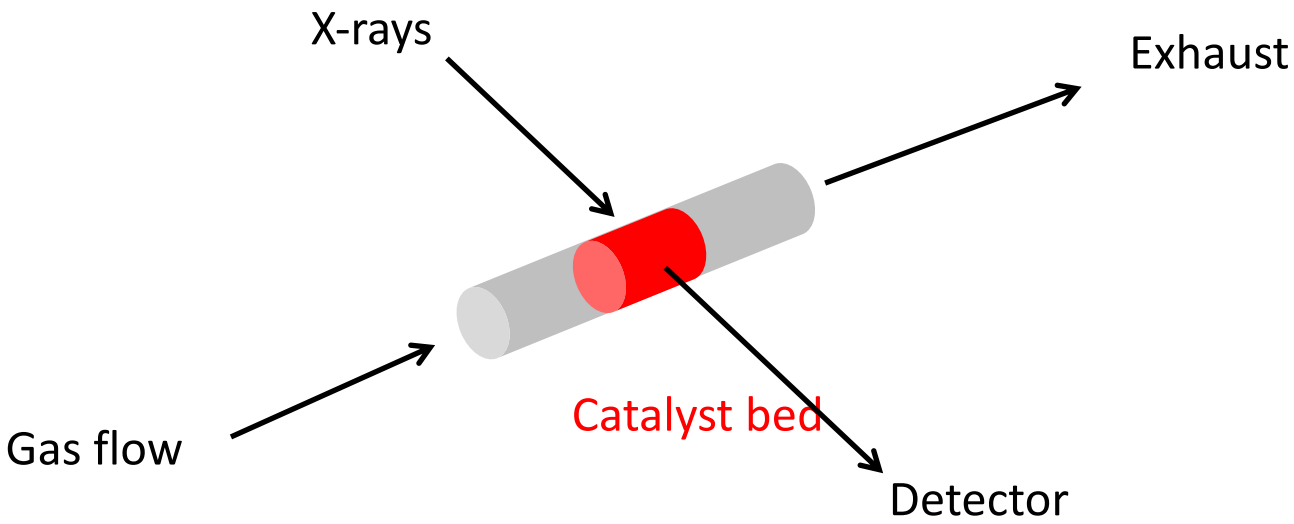
Measuring FAST XAS

- Quick EXAFS = QEXAFS

QEXAFS of platinum in transient conditions



- Catalyst: Pt/Al_2O_3
- System at high T (520 K)
- Switch from CO to CO + O_2 → from CO covered to catalytic conversion



Questions

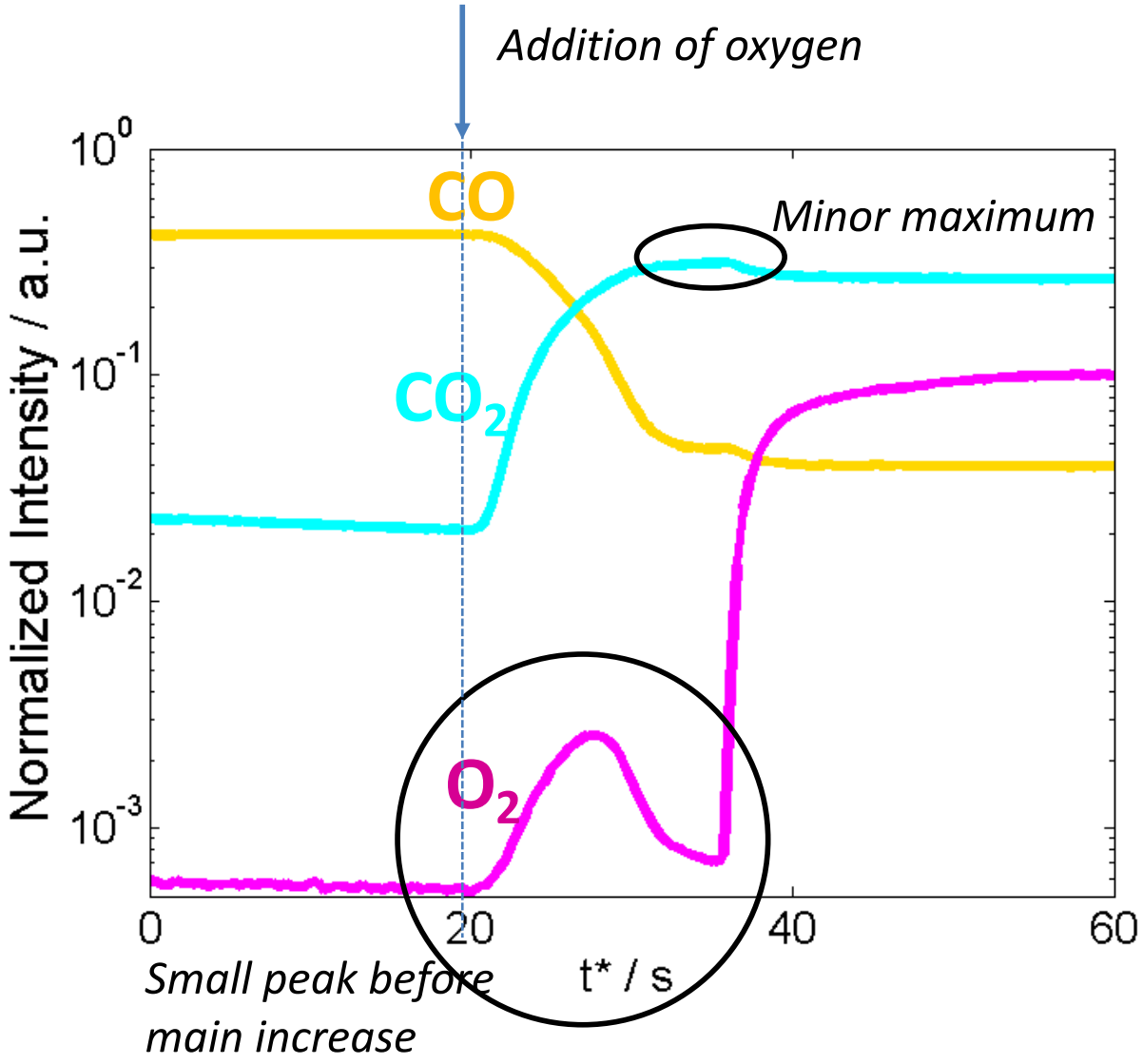
Catalyst response to the switch

From CO-covered to performing CO oxidation

from CO poisoned to highly active

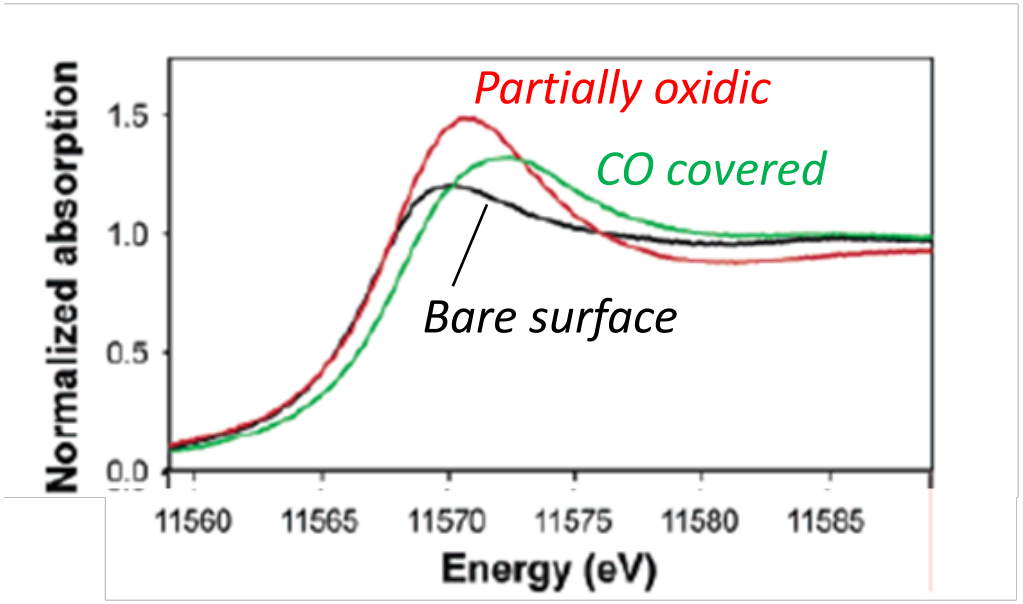
Catalyst structure is not necessarily the same everywhere in a reactor!!

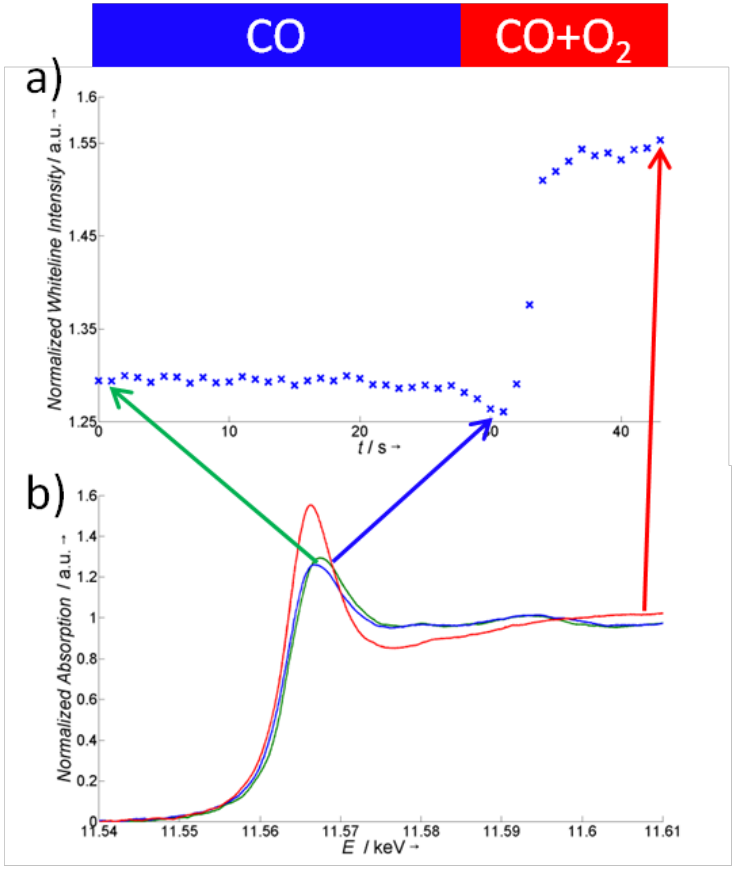
Mass spectrometry results



Normalized whiteline intensity

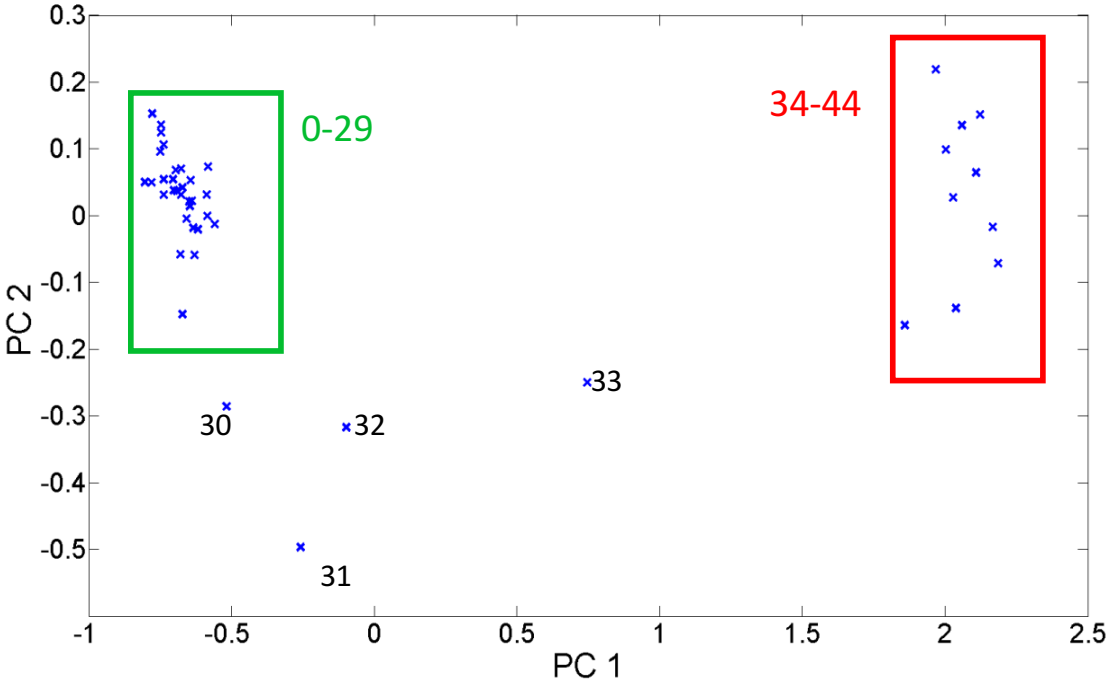
- Whiteline intensity changes during switch
- Small decrease, followed by large and rapid increase





Safonova et al., *The Journal of Physical Chemistry B* **2006** *110* (33), 16162-16164

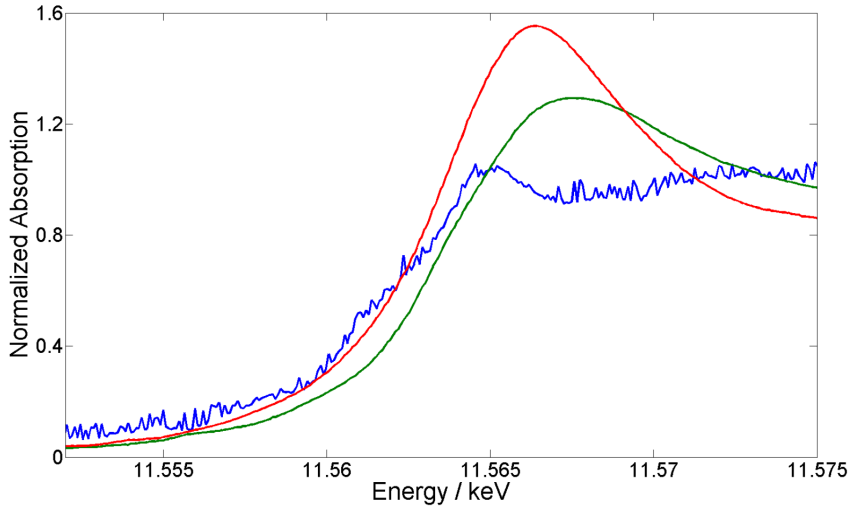
Principal component analysis



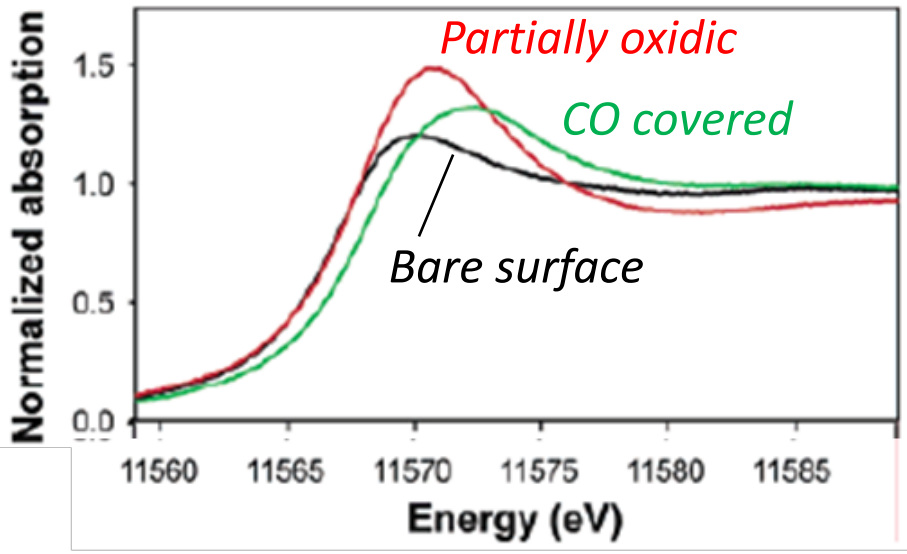
- First PC: oxidized / reduced transition
- Second PC: presence / absence of intermediate

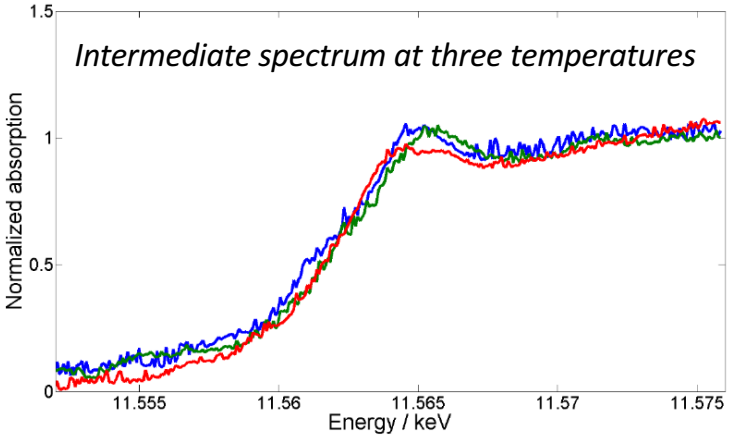
There is a transient state….

Isolation of the intermediate structure



Reference spectra



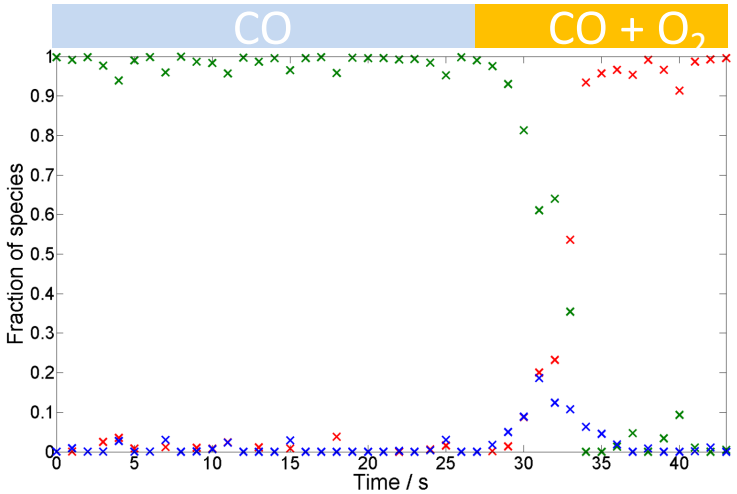


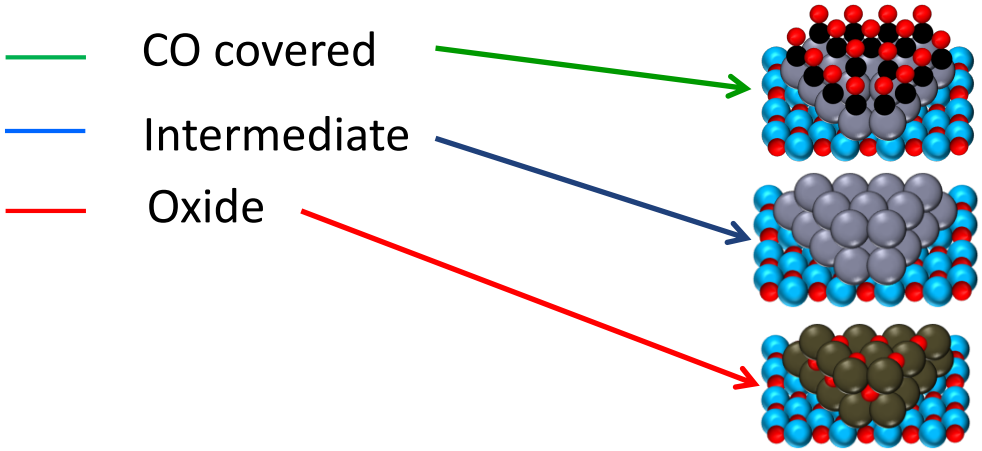
There is a transient state….

… and it is an empty surface

Can we kinetically describe these data?

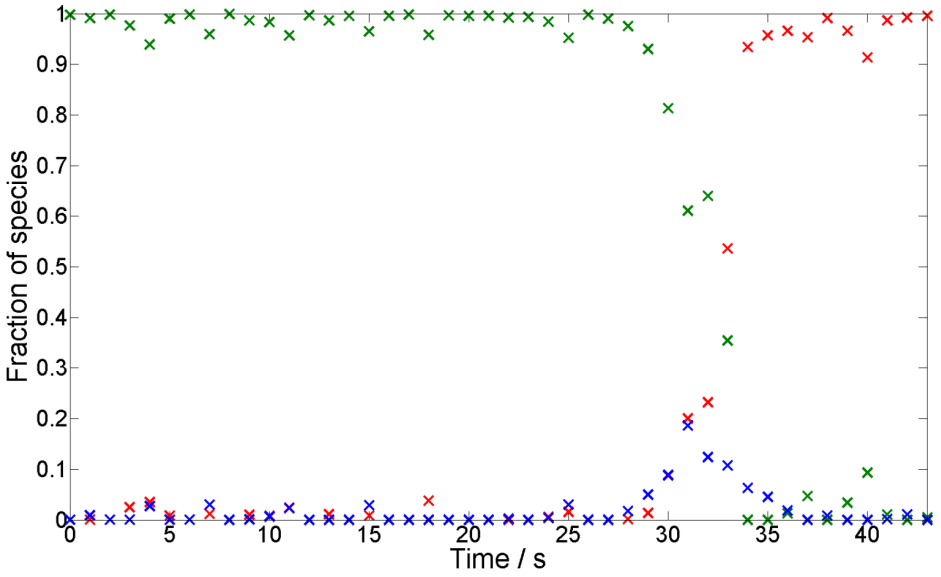
- Concentrations obtained from linear combination fit
- General behavior as expected





Can we kinetically describe these data?

Model 1: A→ B→ C

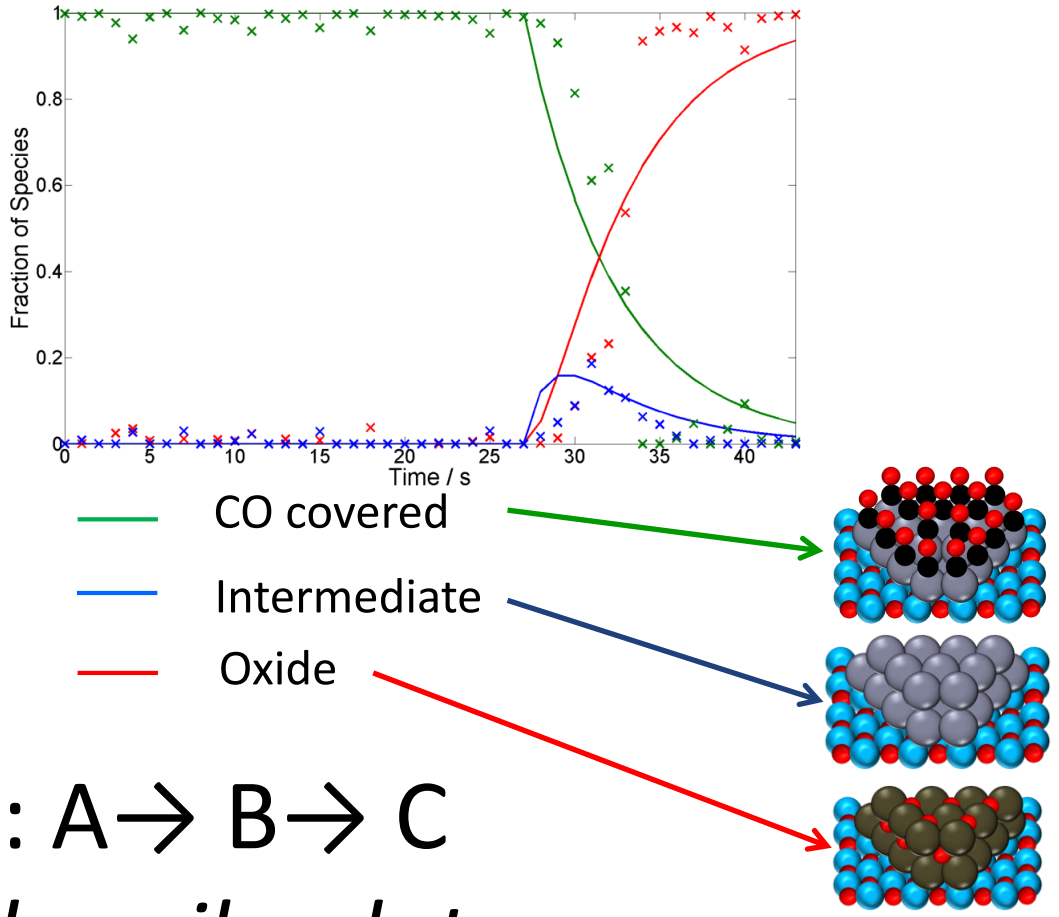


Model 2:

- Desorption of CO: CO_{ads} → CO + *
- Adsorption of O_2: O_2 → 2 O_{ads}
- Surface reaction: O_{ads} + CO_{ads} → CO_2 + 2*

Can we kinetically describe these data?

- Basic model clearly insufficient
- Observed kinetics: initially slow, then accelerated



Model 1: A→ B→ C

does not describe data

Kinetic model

- Desorption of CO: $CO_{ads} \rightarrow CO + *$
- Adsorption of O_2: $2 * + O_2 \rightarrow 2\ O_{ads} \rightarrow$ oxide
- Surface reaction: $O_{ads} + CO_{ads} \rightarrow CO_2 + 2*$

- Assumptions:
  - Fast desorption of CO_2
  - No readsorption of CO

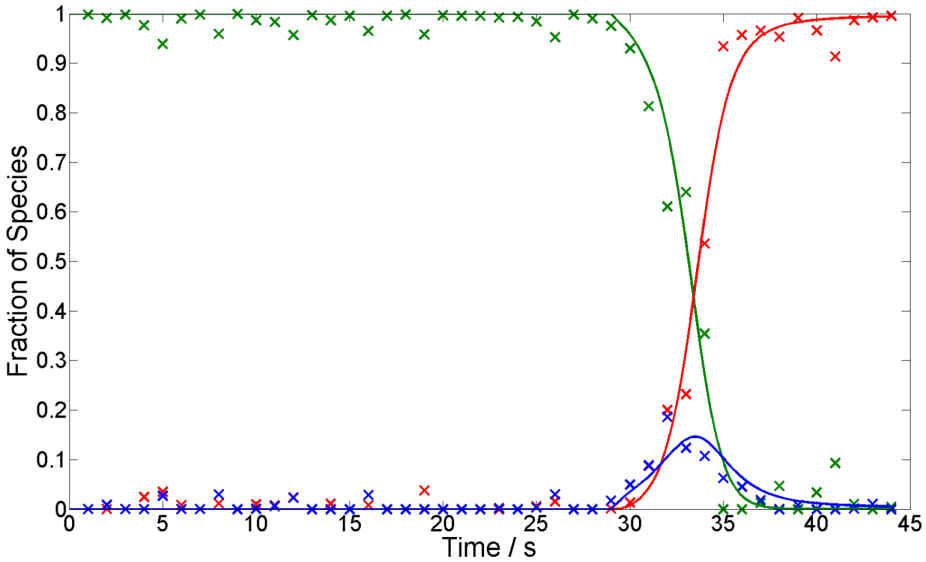
$$\frac{d\theta_{CO}}{dt} = -k_1 * \theta_{CO} - k_3 * \theta_{CO} * \theta_O$$

$$\frac{d\theta_O}{dt} = 2 * k_2 * c_{O_2} \theta_{free}{}^2 - k_3 * \theta_{CO} * \theta_O$$

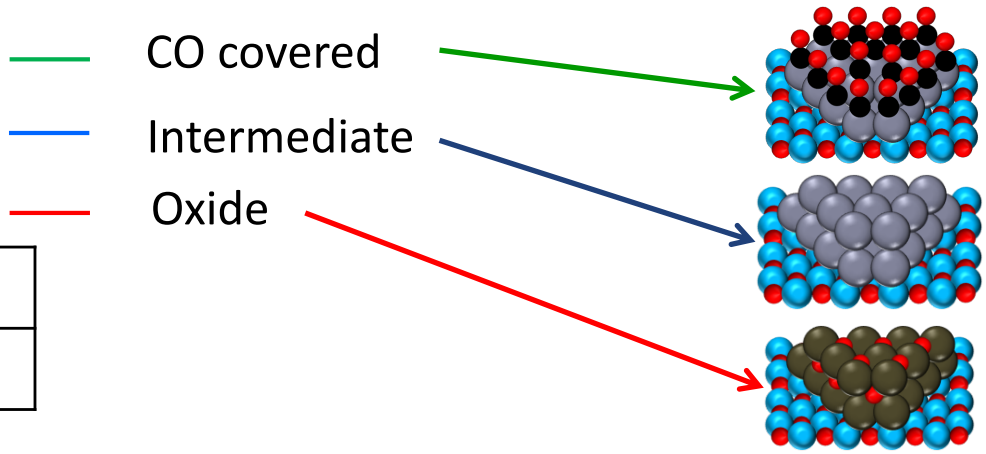
$$\frac{d\theta_{free}}{dt} = k_1 * \theta_{CO} + 2 * k_3 * \theta_{CO} * \theta_O - 2 * k_2 * c_{O_2} \theta_{free}{}^2$$

(Near) quantitative description of data

- Clear improvement on previous fit
- Captures the characteristics of the observed behavior



CO desorbs
Free site enables reacting with oxygen
More free sites form, until surface oxidizes



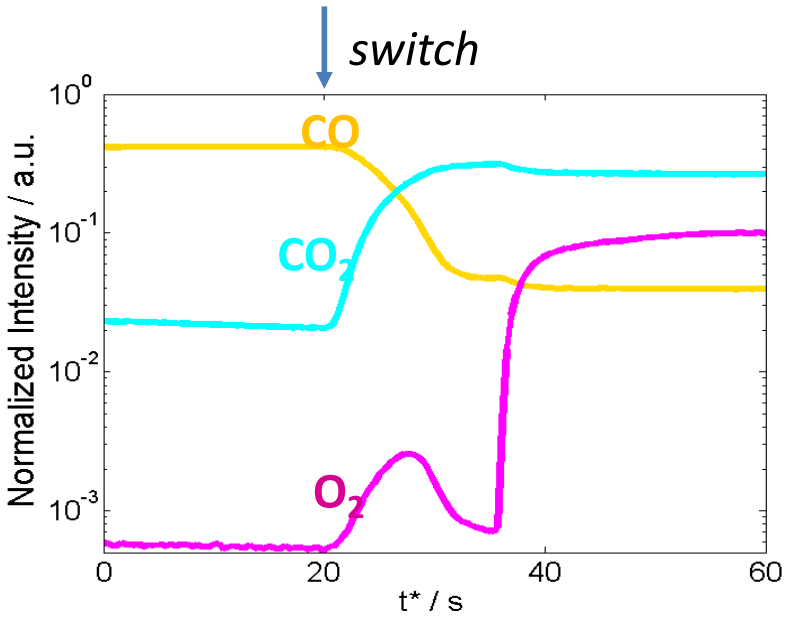
$k_{des,\ CO}$	$k_{ads,oxygen}$	$k_{surface}$
0.04 s^{-1}	12.5 s^{-1}	1.4 s^{-1}

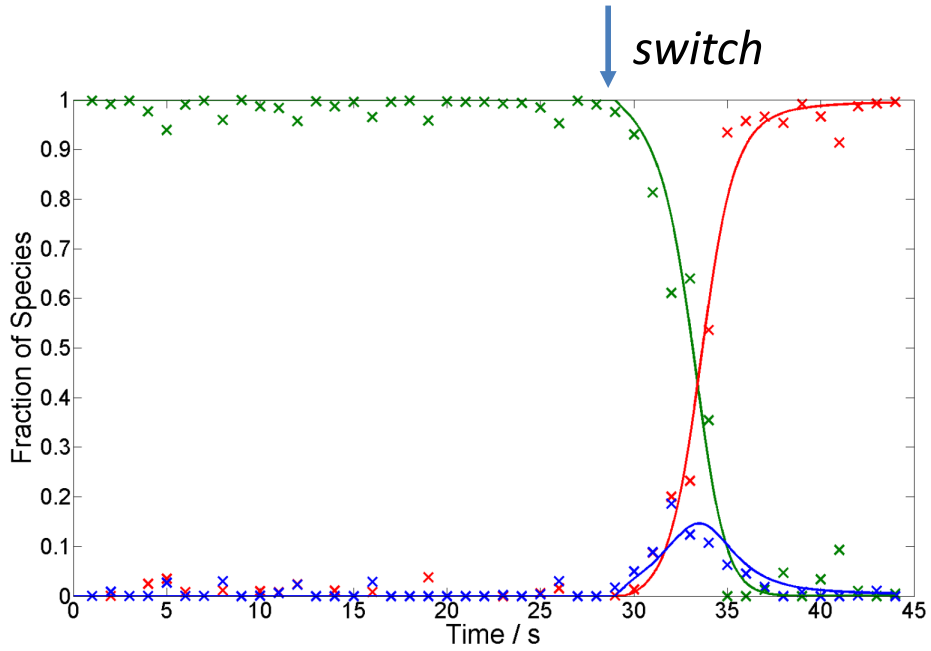
Chemisorbed oxygen reacts to surface CO or to Pt
Surface oxide rapidly forms

Extension to the reactor level

- XANES data so far reflects single point in the reactor
- Mass spectrometry gives integral view

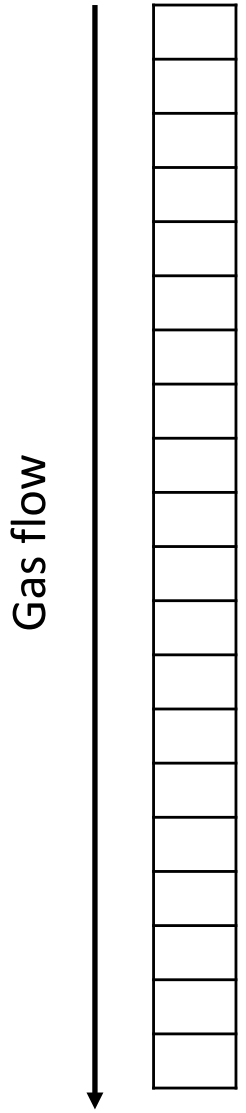
→ Make a model that explains both





Reactor model

- 1D reactor
- Consider only catalyst bed
- Simulation time 20 s
- We consider:
  - Adsorption and desorption
  - Reaction
  - Forced flow
- We neglect:
  - Diffusion
  - Radial distribution
  - Temperature effects



20 points through reactor
→ 4 points per mm

Time resolution:
500 Hz

Reaction steps

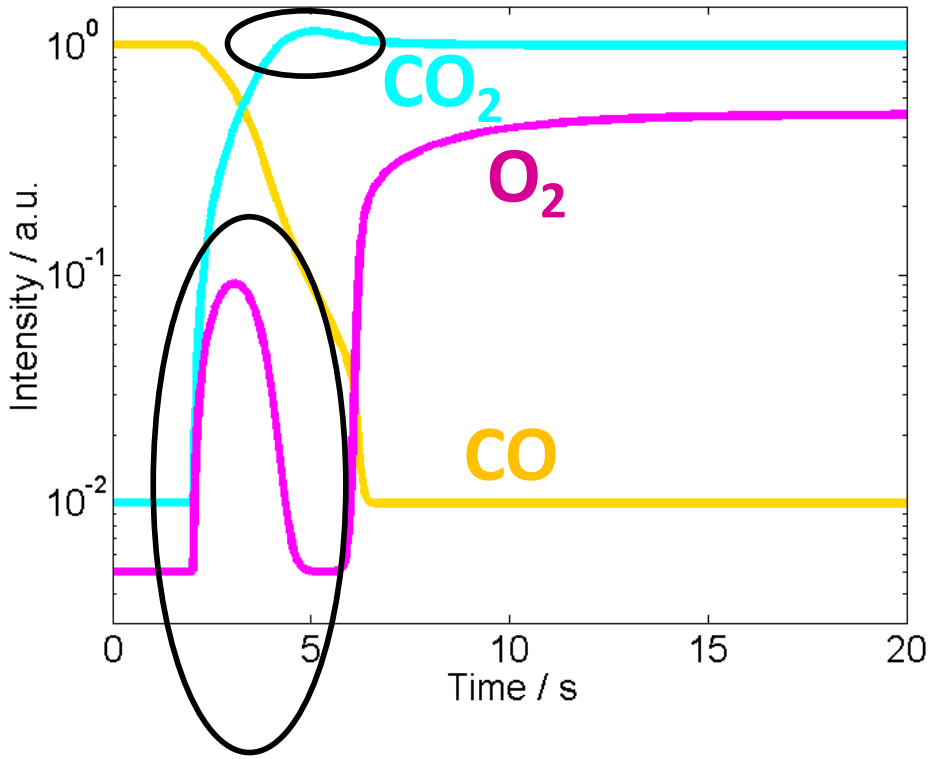
- Adsorption of CO: $CO + * \rightarrow CO_{ads}$
- Desorption of CO: $CO_{ads} \rightarrow CO + *$
- Adsorption of O_2: $O_2 \rightarrow 2\ O_{ads}$
- Desorption of O_2: $2\ O_{ads} \rightarrow O_2$
- Surface reaction: $O_{ads} + CO_{ads} \rightarrow CO_2 + 2*$
- Chemisorbed to surface oxide: $O_{ads} \rightarrow PtO_x$
- Reaction on oxidized surface: $PtO_x + CO \rightarrow CO_2 + *$

In short:

- CO must desorb for O_2 to react
- Number of free sites increases as CO reacts to O*
- O* may react to form surface oxide
- CO may react with surface oxide

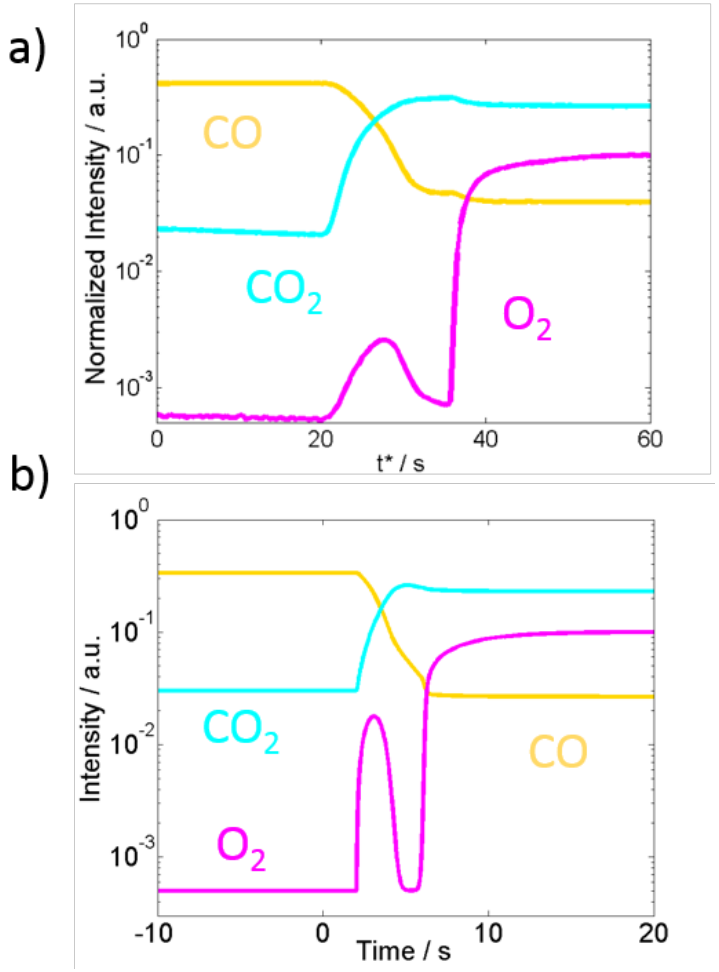
Simulation results – reactor exhaust

- Initial peak in O_2 reproduced
- Late decrease in CO_2 reproduced



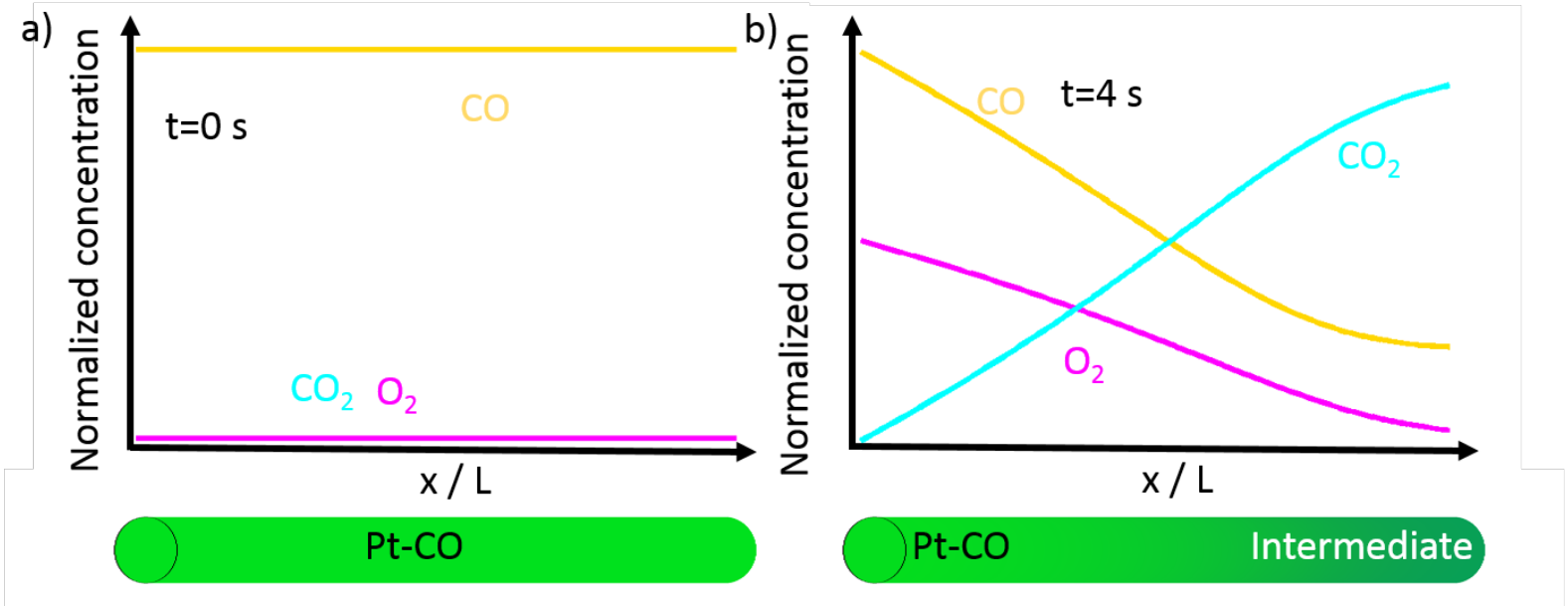
Reactor exhaust

- Initial peak in O_2 reproduced
- Maximum in CO_2 reproduced



Catalyst structure simulated as function of time *throughout* the reactor

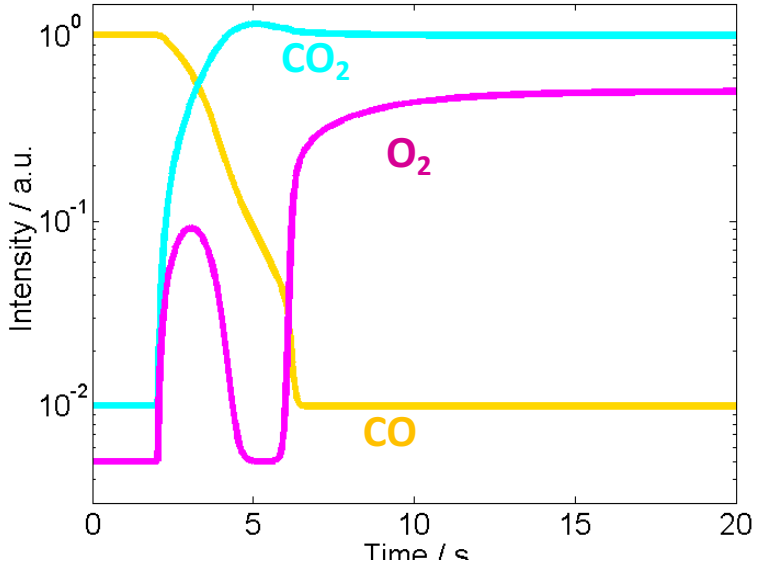
Surface and concentrations at t=0 s and t= 4 s



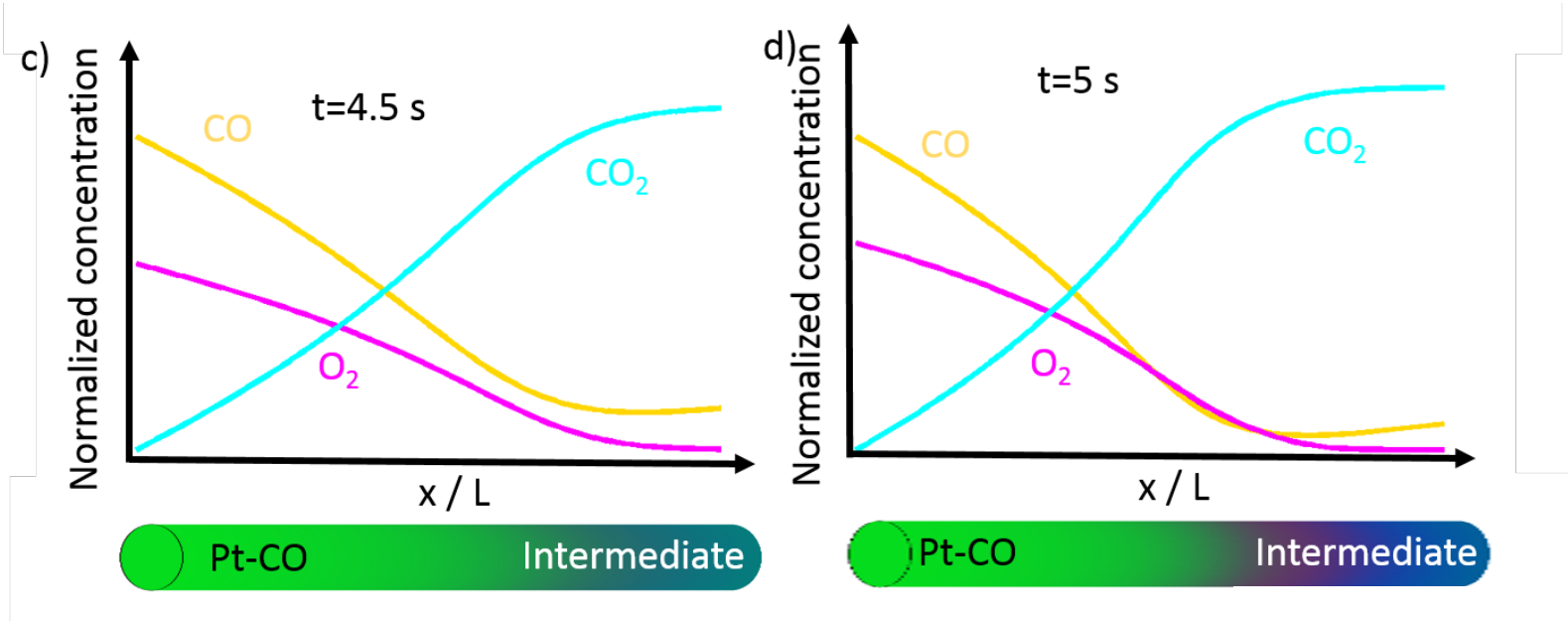
CO covered

Free surface

Oxide



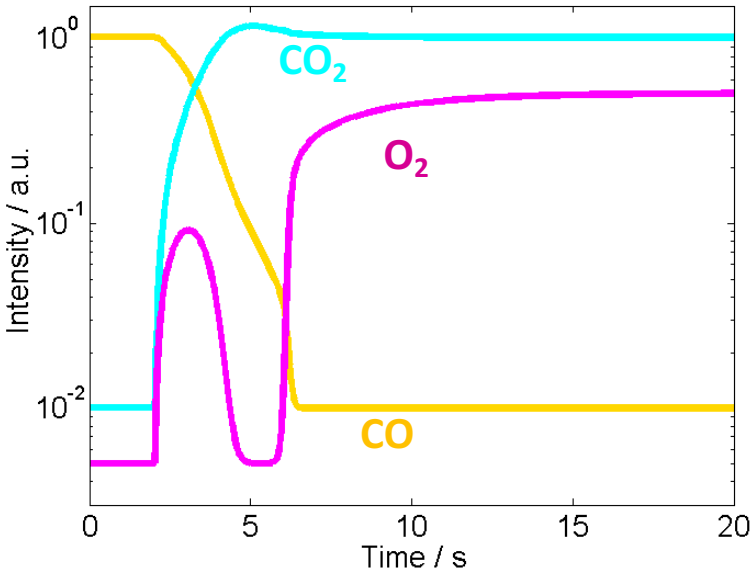
Surface and concentrations at t= 4.5 s and t= 5 s



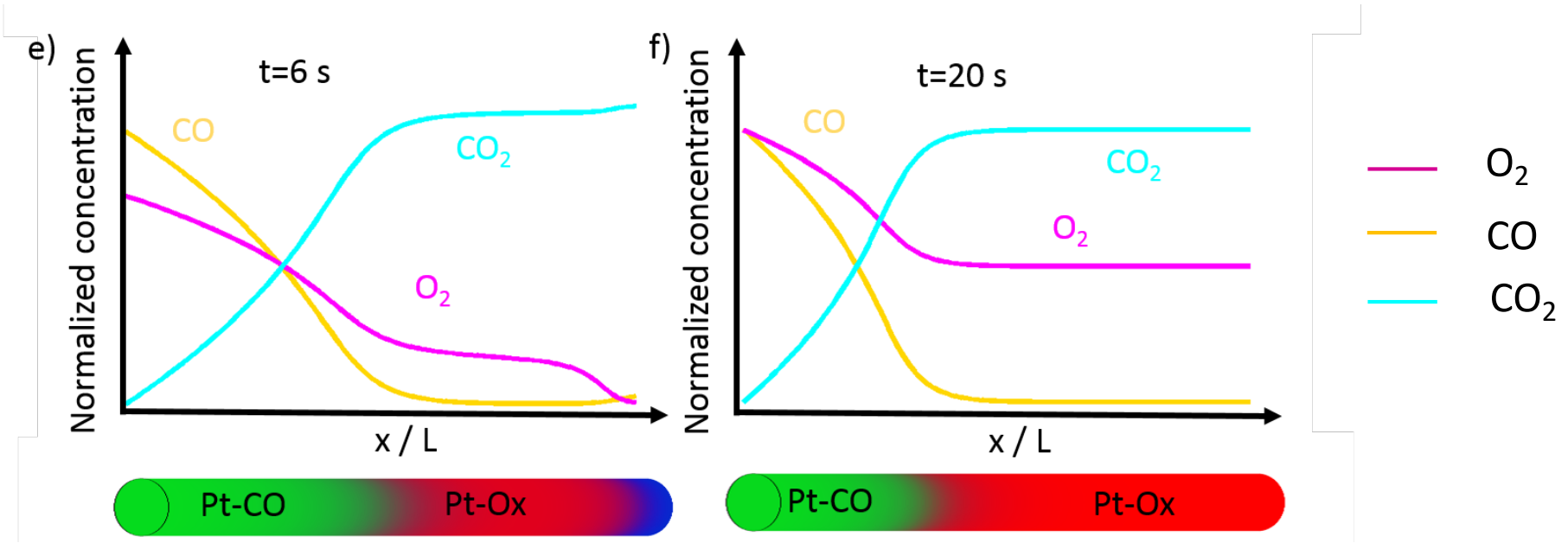
CO covered

Free surface

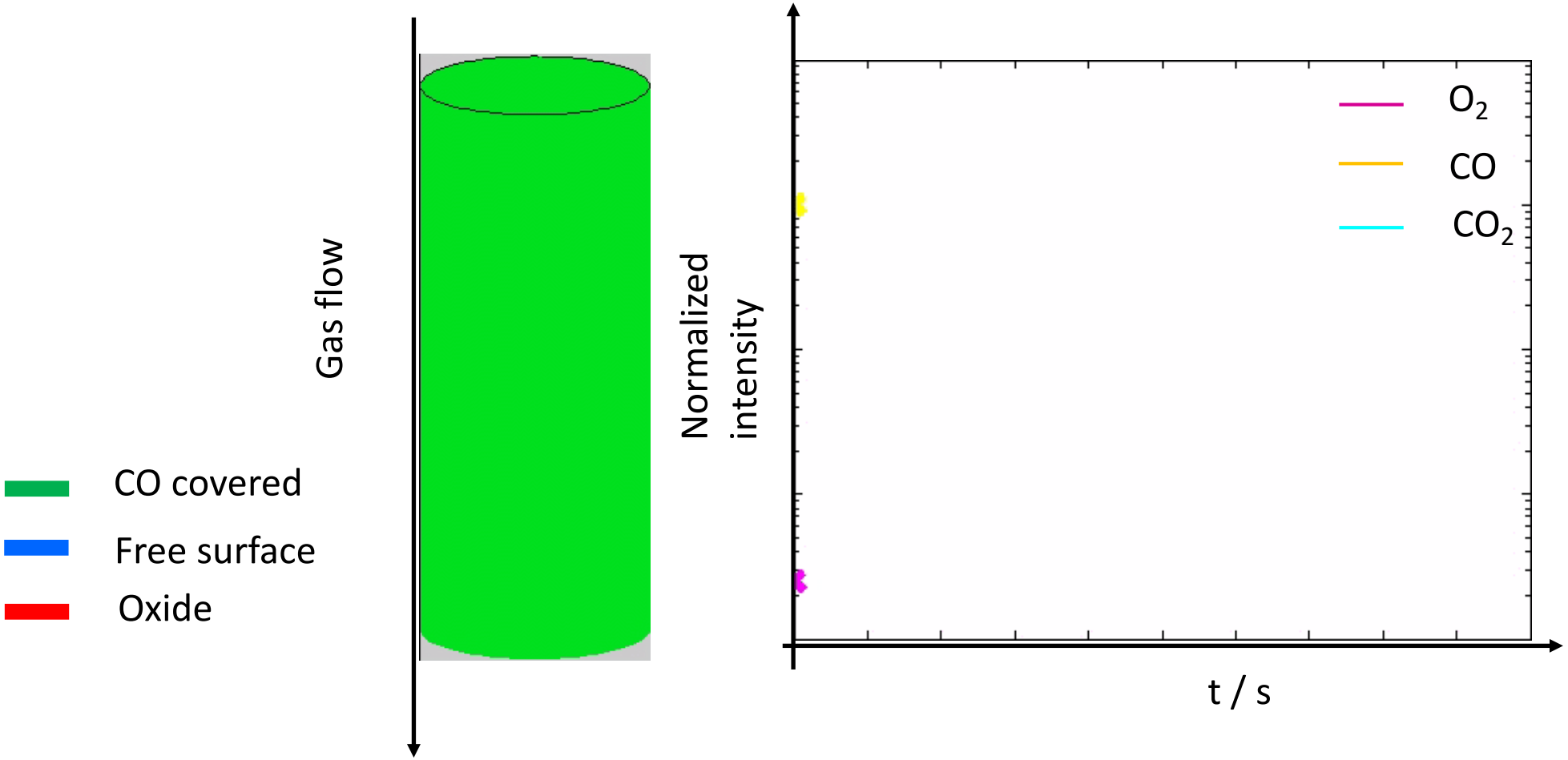
Oxide



Surface and concentrations at t=6 s and t= 20 s

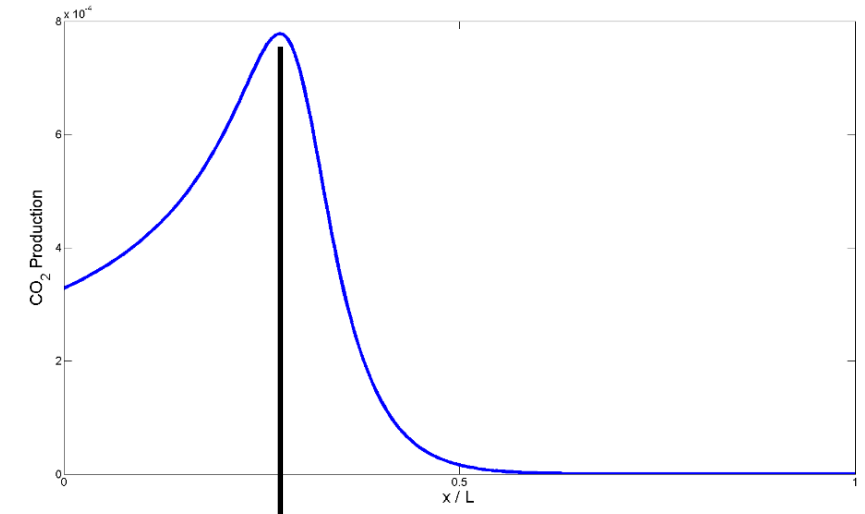


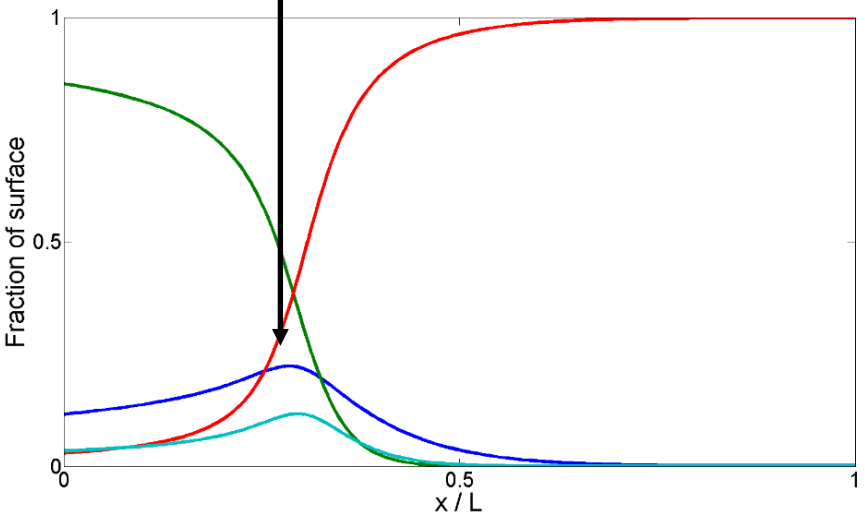
Reactor overview



CO_2 Production through the reactor

- Most CO_2 produced in region with all surface species present





CO covered

Free surface

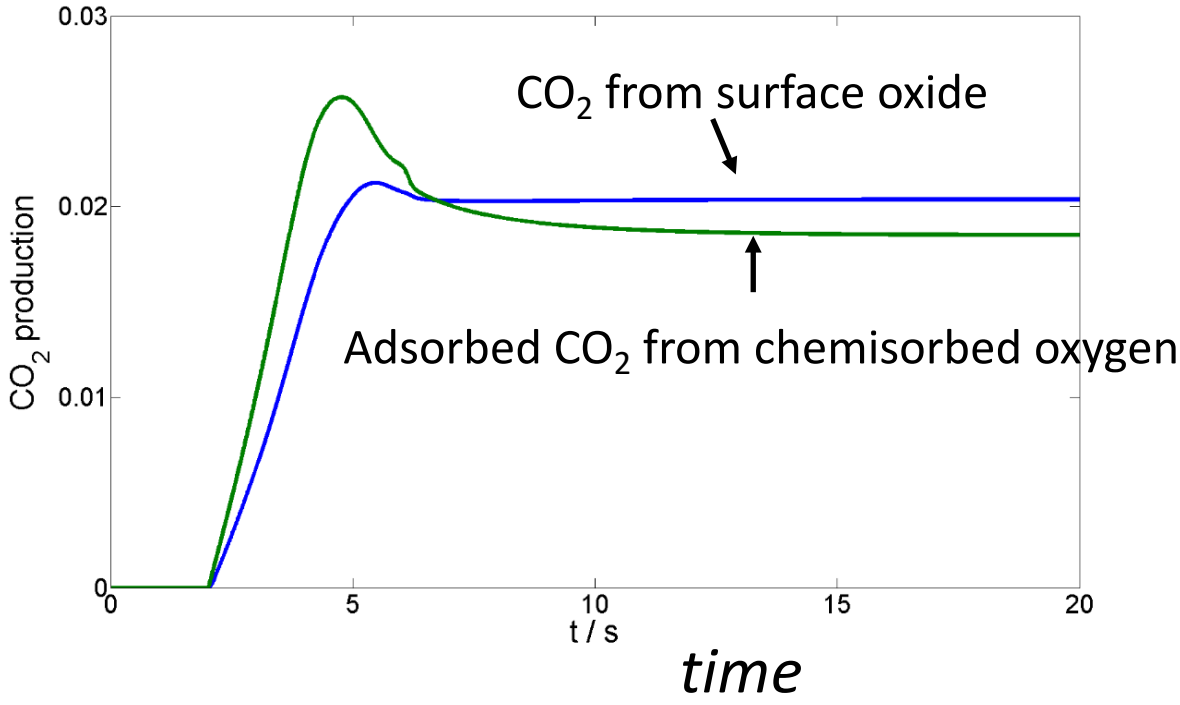
Oxide

Surface Oxygen x 20

Reactor length

CO_2 production by mechanism

- Both mechanisms contribute similarly
- Time course different



time

Conclusions reactor simulations

- XAS result fitted to reactor model
- Qualitative prediction of MS results
- Transition region key for reaction

Minority of the catalyst does the majority of the work...

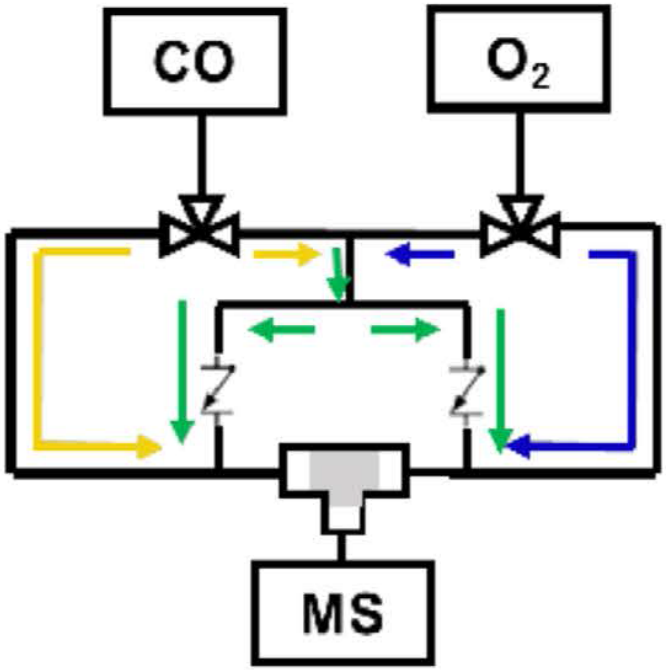
Minority of the catalyst does the majority of the work…

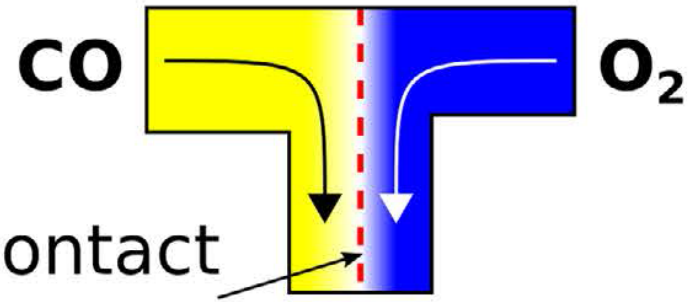
Most of the catalyst does not contribute to the work…

How to get more of the highly active phases … ??

The T-reactor

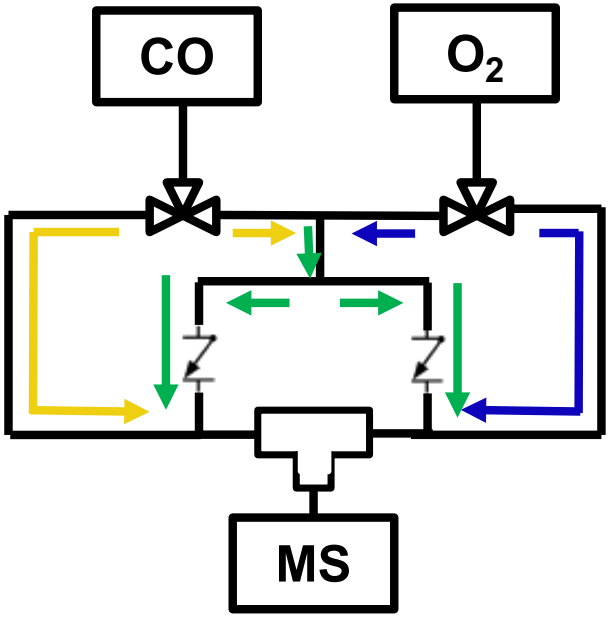
- T-shaped reactor to maximize mixing zone - Increase amount of the more active catalyst
- *Either* CO + O_2 from both sides
- *Or* CO from left
- O_2 from right

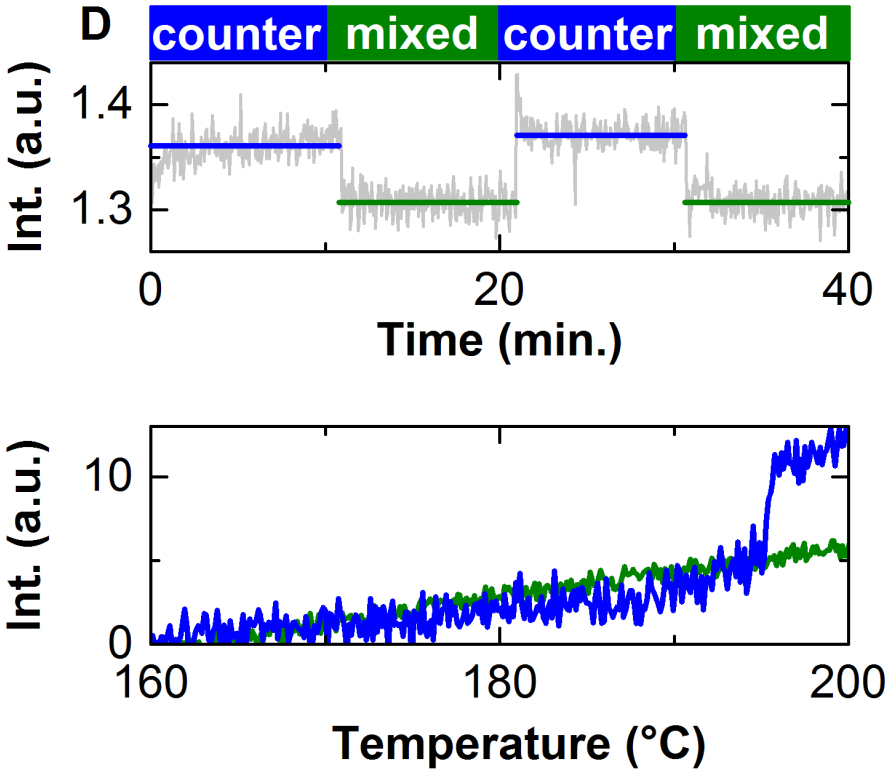




Maximized contact area of multiple phases

- Counter flow leads to dramatic increase in activity
- Light-off shifted to much lower temperatures



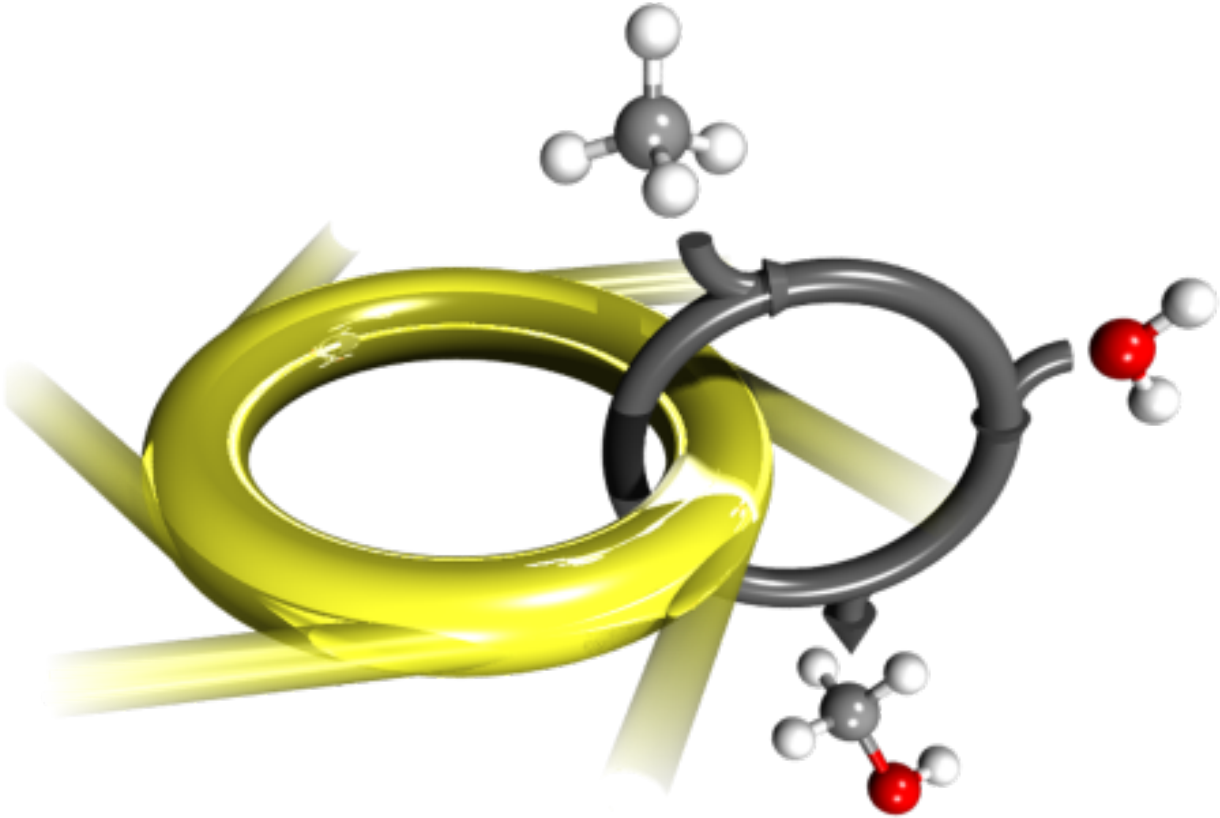


Higher conversion in counter flow
Ignition at lower temperature

Conclusion

- From spectators to active sites
- From structure to predicting reactor performance

- By reactor engineering, one can improve performance



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