X-ray absorption spectroscopy

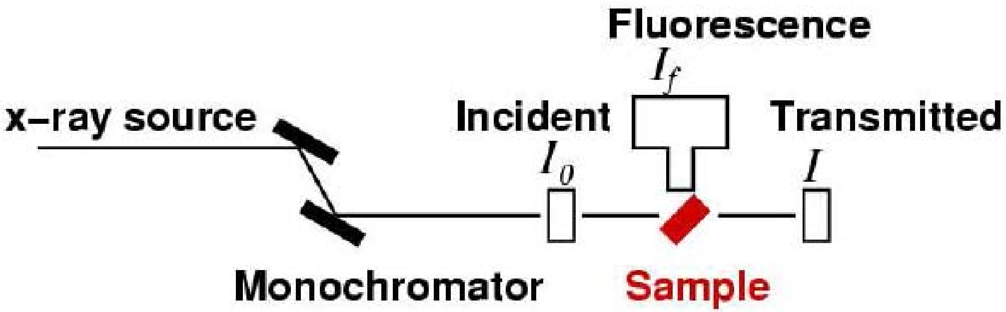
Literature recommendations

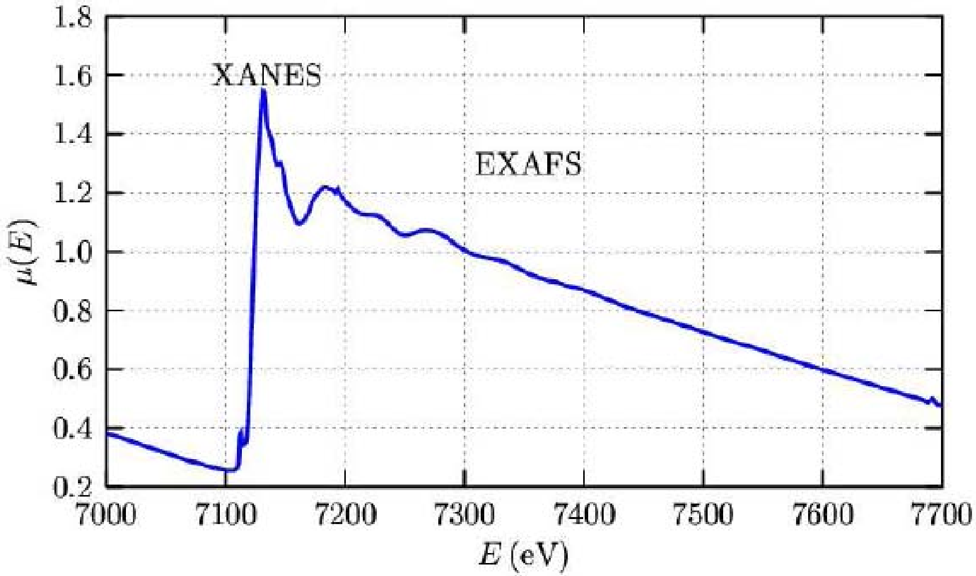
- J.C. Vickerman (editor), “Surface Analysis – The Principal Techniques”, Wiley, 1997
- J. W. Niemantsverdriet, “Spectroscopy in Catalysis – An Introduction”, VCH, 1993
- B. K. Teo, “EXAFS Spectroscopy: Principles and Applications”, Plenum Pub Corp, 1981

Jagdeep Singh

Jeroen A. van Bokhoven

What is XAS?

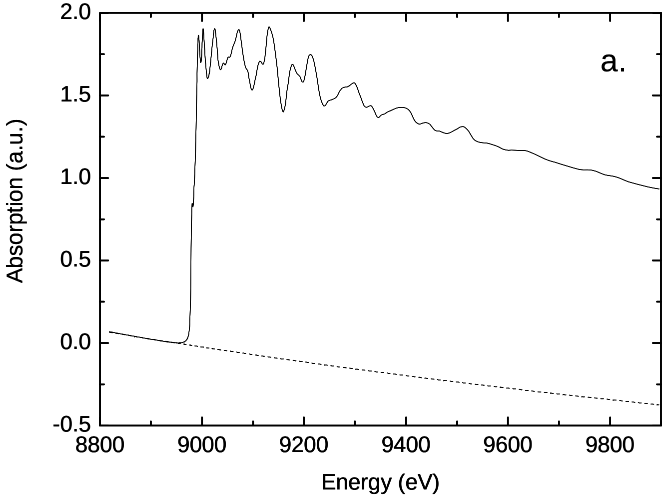




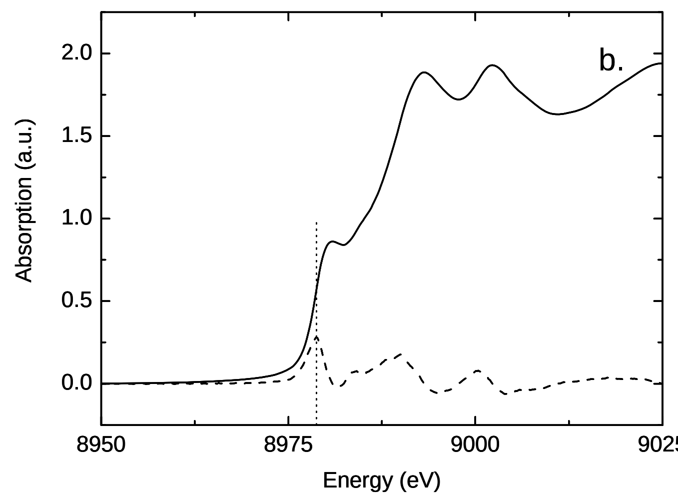
Absorption as function of energy of the x-ray

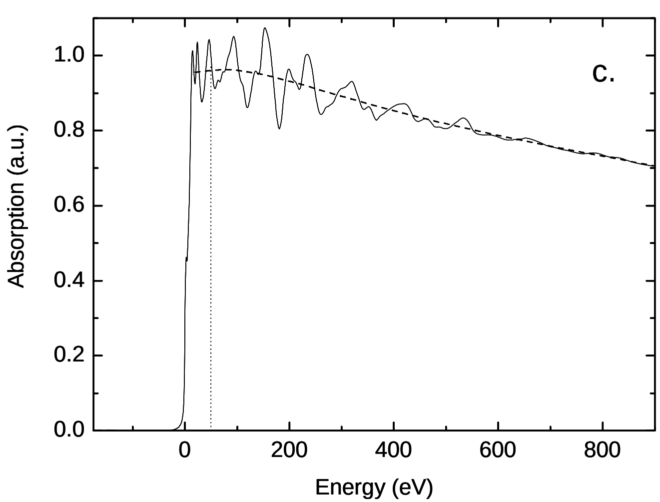
Data-analysis

Pre-edge subtraction

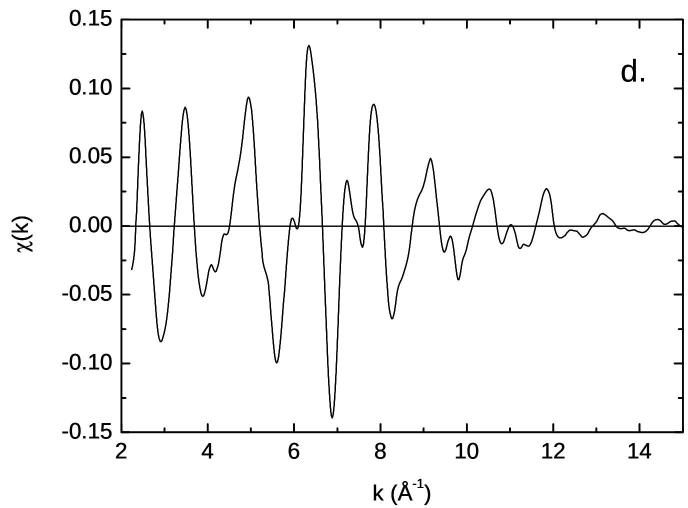


Edge energy determination





Background and Normalization

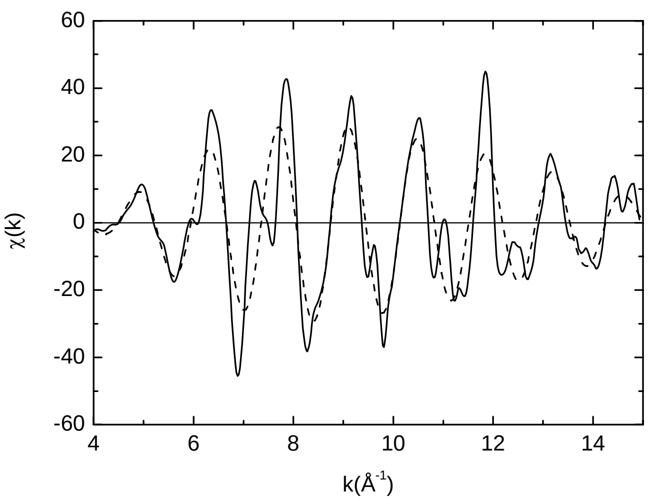


EXAFS Function

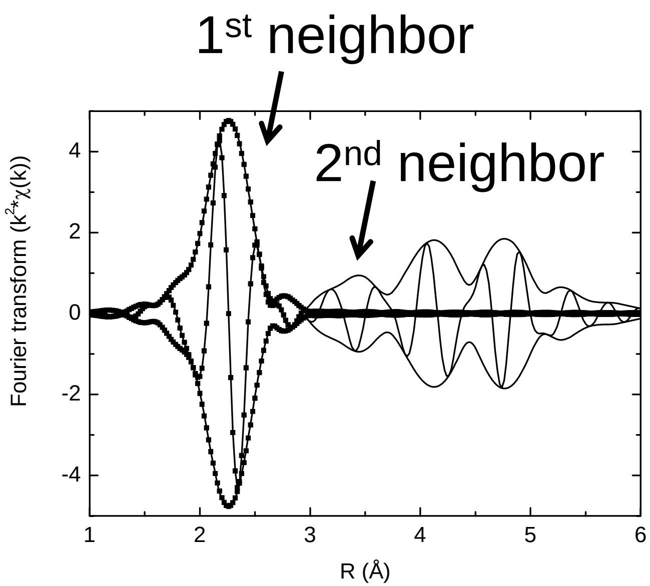
EXAFS formula

$$\chi(k) = \sum_i N_i F_i(k) \frac{S_0^2}{kR_i^2} \exp\left(\frac{-2R_i}{\lambda}\right) \exp\left(-2\sigma_i^2 k^2\right) \sin\left(2kR_i + \varphi_j(k)\right)$$

Scatter power — Damping — Disorder



Fourier transformation →



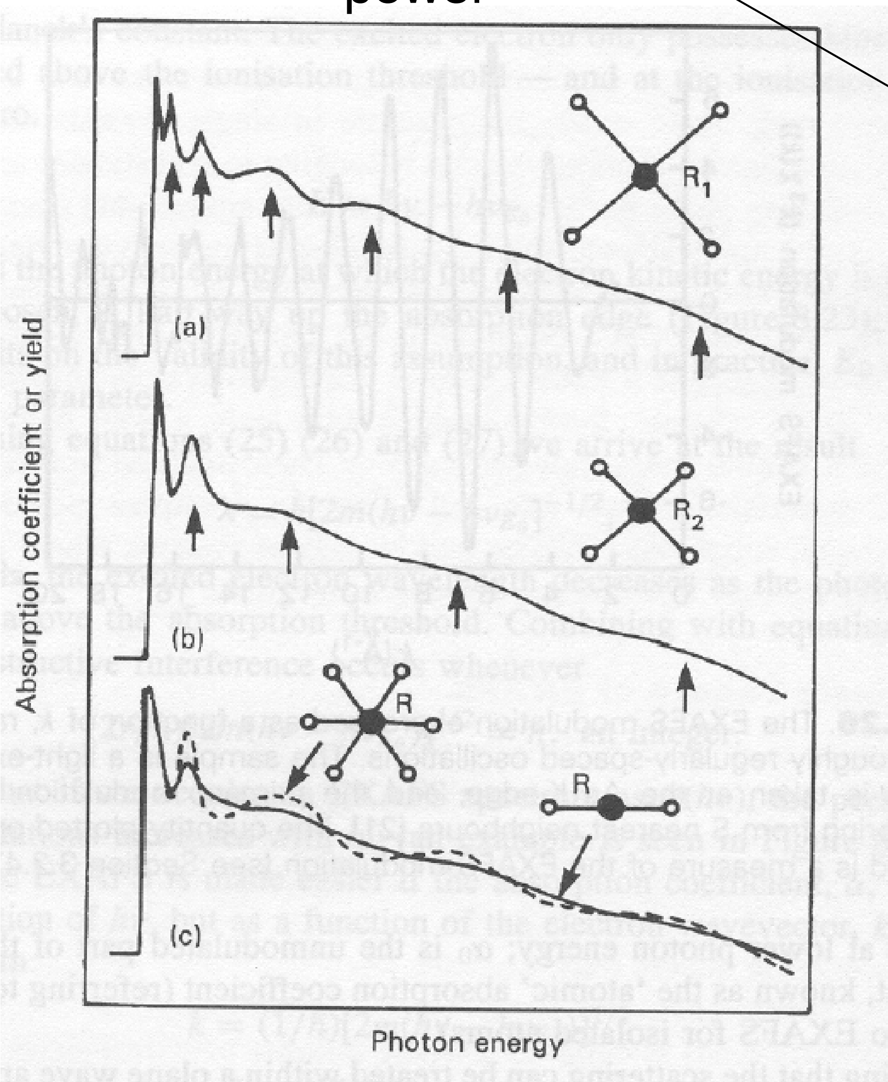
radial distribution function

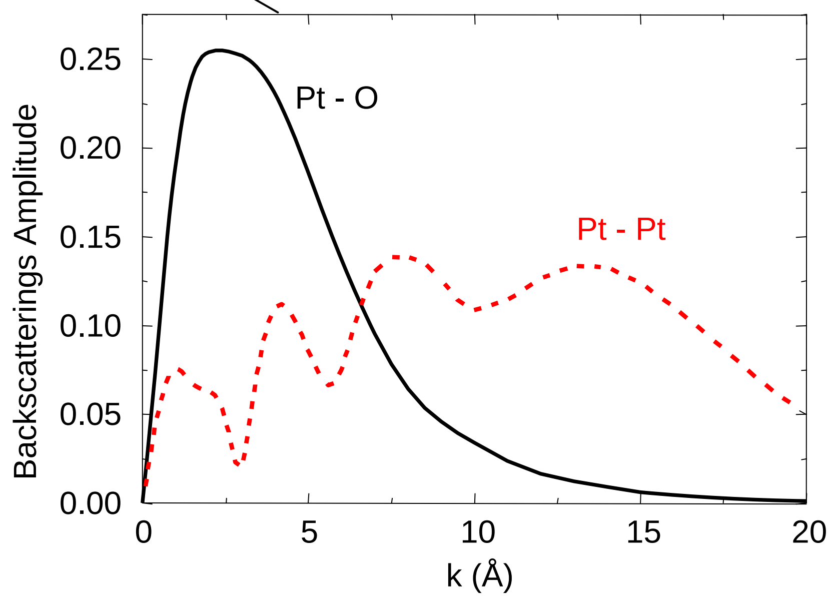
$$\chi(k)=\sum_i N_i F_i(k)\,\frac{S_0^2}{kR_i^2}\,\exp\left(\frac{-2R_i}{\lambda}\right)\exp\left(-2\sigma_i^2k^2\right)\sin\left(2kR_i+\varphi_j(k)\right)$$

Scatter power

Damping

Disorder





Temperature effect on EXAFS / XANES

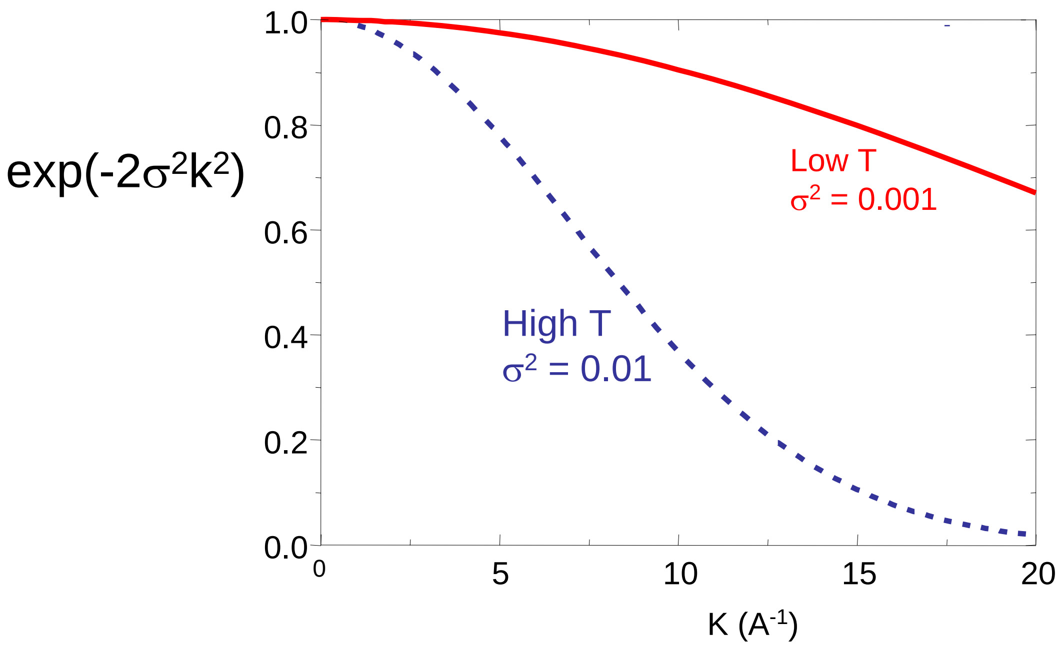
$$\chi(k) = \sum_i N_i F_i(k) \cdot \frac{S_0^2}{kR_i^2} \cdot \exp\left(\frac{-2R_i}{\lambda}\right) \cdot \exp\left(-2\sigma_i^2 k^2\right) \cdot \sin\left(2kR_i + \varphi_j(k)\right)$$

Scatter power

Damping

Disorder

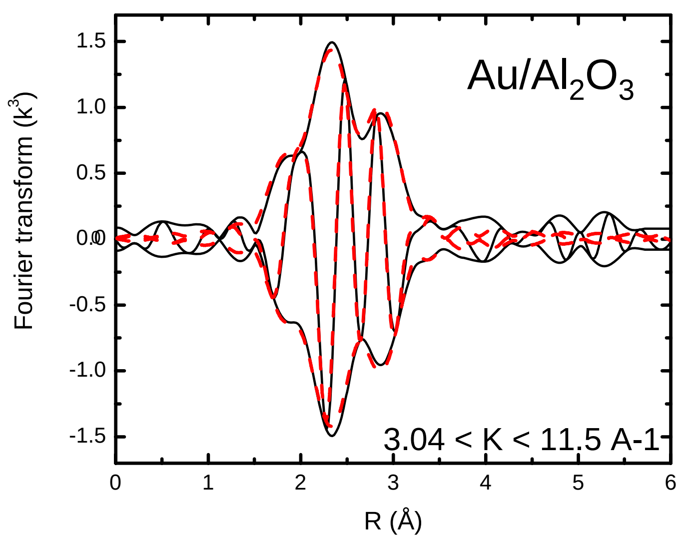
Temperature effect



Getting structural information from EXAFS

$$\chi(k) = \sum_i N_i F_i(k) \cdot \frac{S_0^2}{kR_i^2} \cdot \exp\left(\frac{-2R_i}{\lambda}\right) \cdot \exp\left(-2\sigma_i^2 k^2\right) \cdot \sin\left(2kR_i + \varphi_j(k)\right)$$

F_j, φ_j, and S_o^2 from reference compound or theory



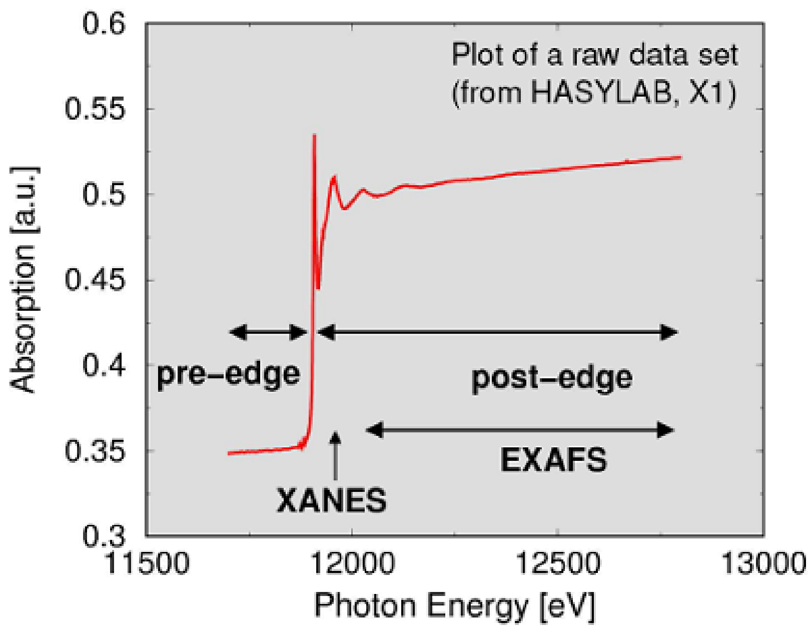
Coordination number	**6.8**
Au-Au distance	**2.76 Å**
ΔDWF	**0.0058**
C3	9 E-6
C4	3E-6

Added parameter: ΔE_0

Abstract

- EXAFS gives local structure
- XANES gives geometry and oxidation state (empty density of states)

Information contained in an XAS Spectrum



Fine Structure is given by

- single scattering → EXAFS
- multiple scattering → EXAFS, XANES
- electronic transitions → XANES

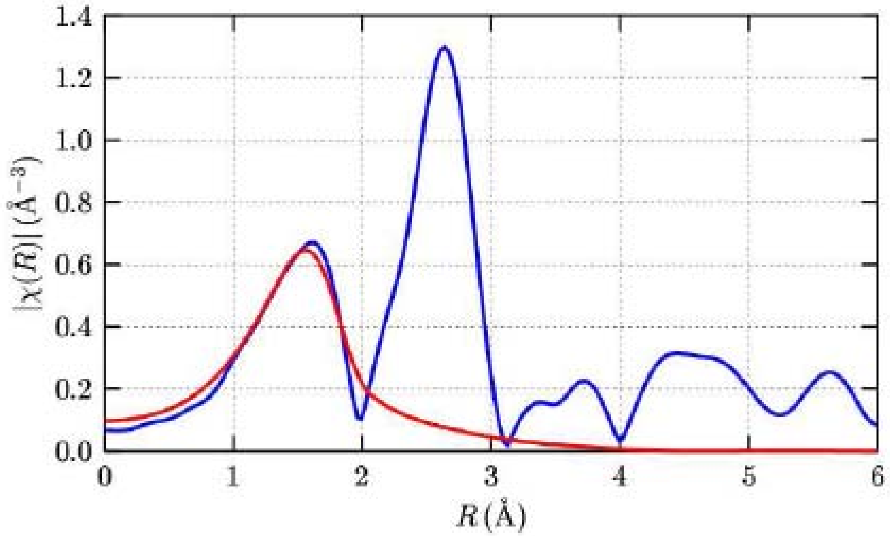
Electronic Information

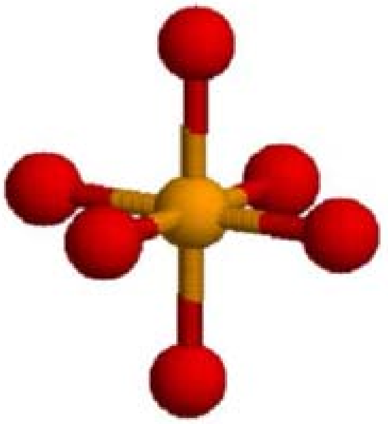
- Angular momentum projected DOS
- transition probabilities

Structural Information

- position of atoms
- degree of order
- phase composition
- *in-situ* conditions

Data Analysis: Fitting Process 1st coordination shell





Parameter	Value
N	5.8
R	2.1
ΔE_0	-3.1
σ^2	0.015

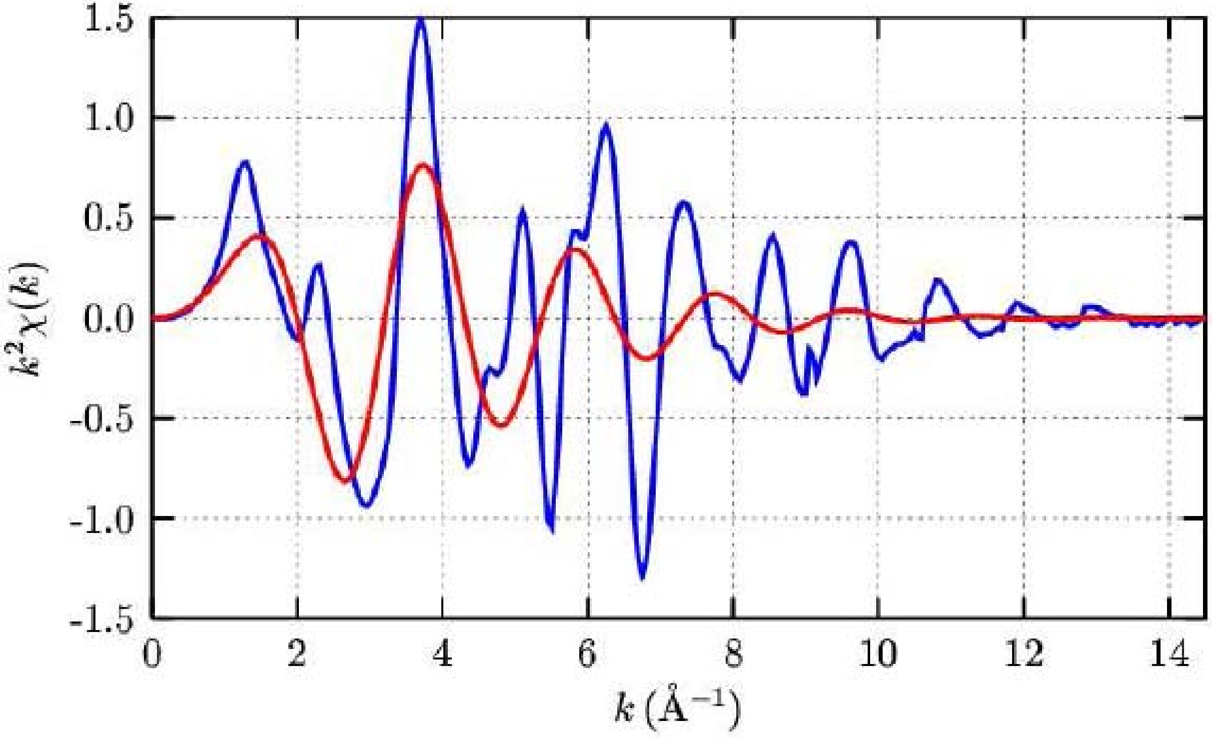
$$\chi(k) = \sum_i N_i F_i(k) \frac{S_0^2}{kR_i^2} \exp\left[\frac{-2R_i}{\lambda}\right] \exp\left(-2\sigma_i^2 k^2\right) \sin\left(2kR_i + \varphi_j(k)\right)$$

Scatter power

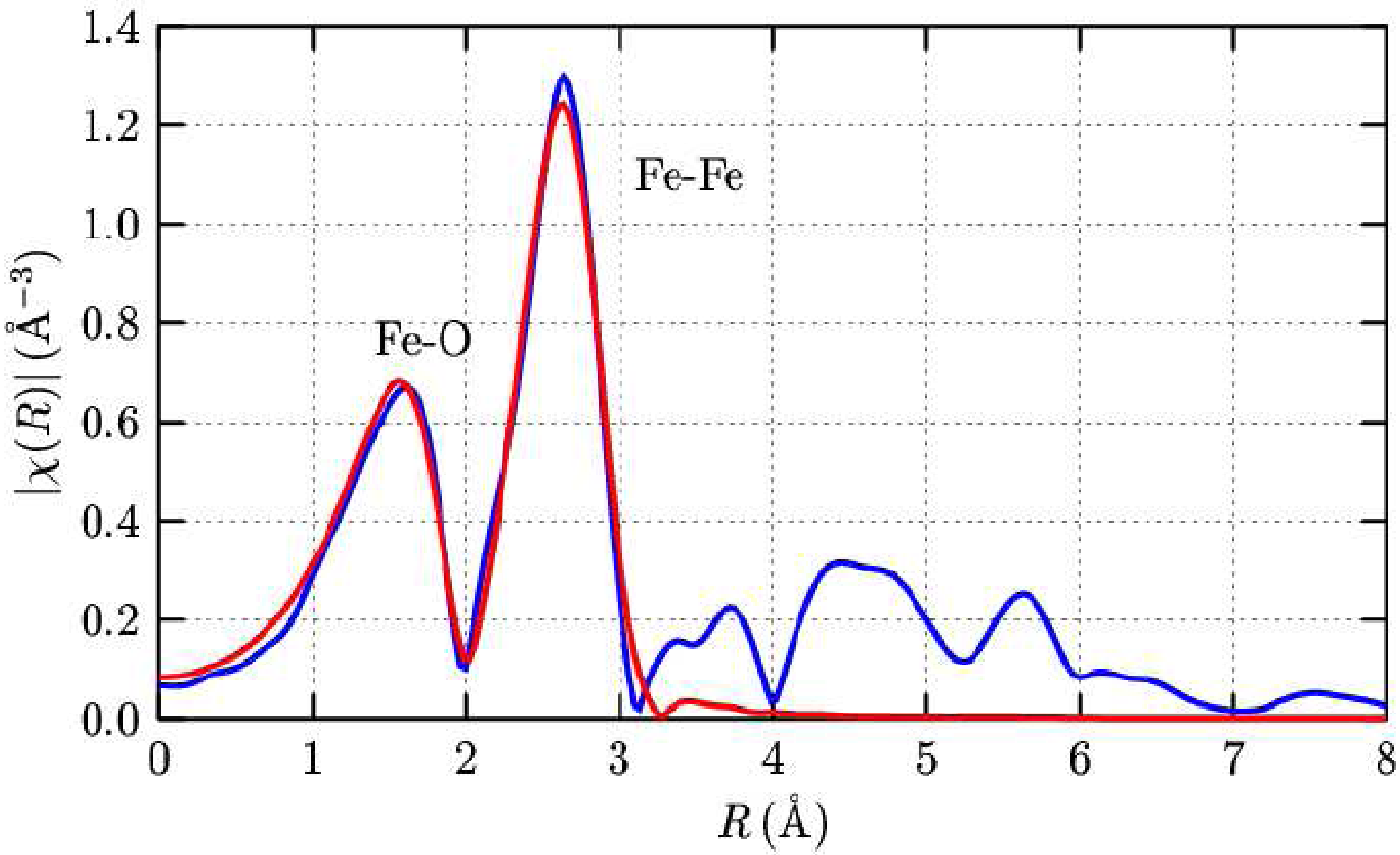
Damping

Disorder

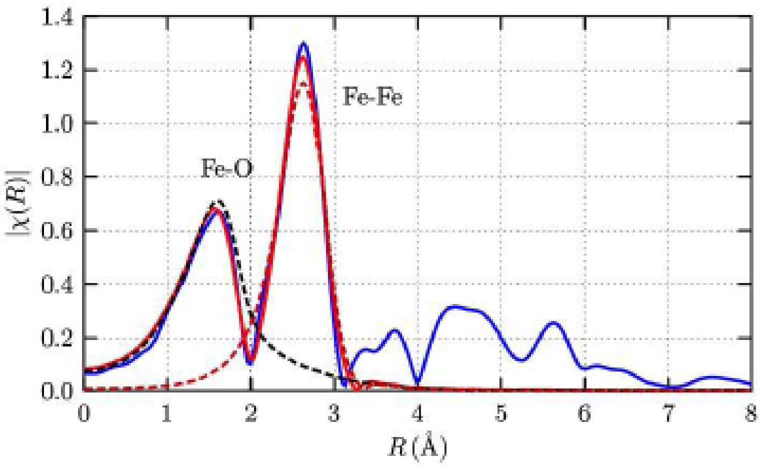
Data Analysis: 1st coordination shell in k-space

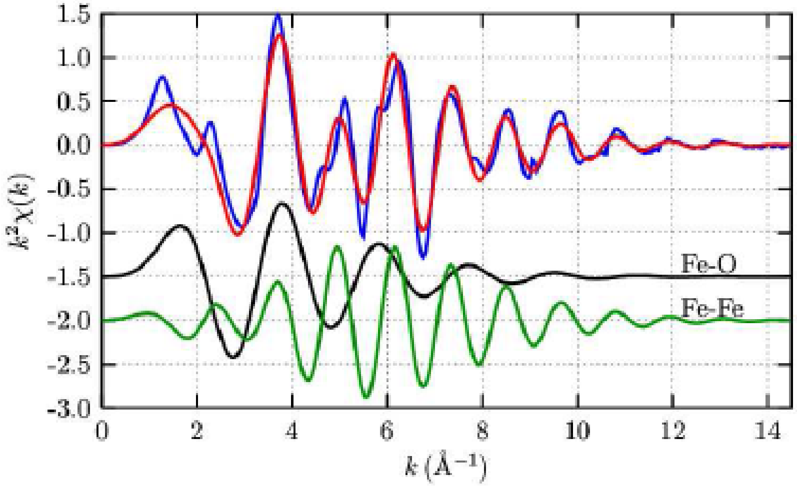


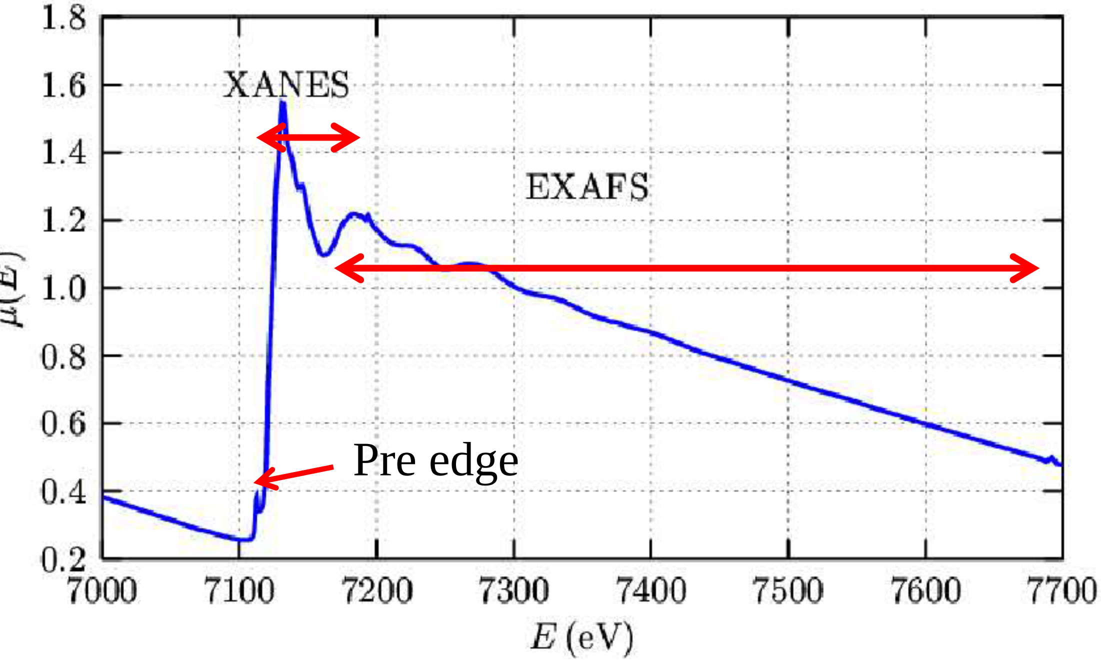
Data Analysis: Adding the 2nd coordination shell

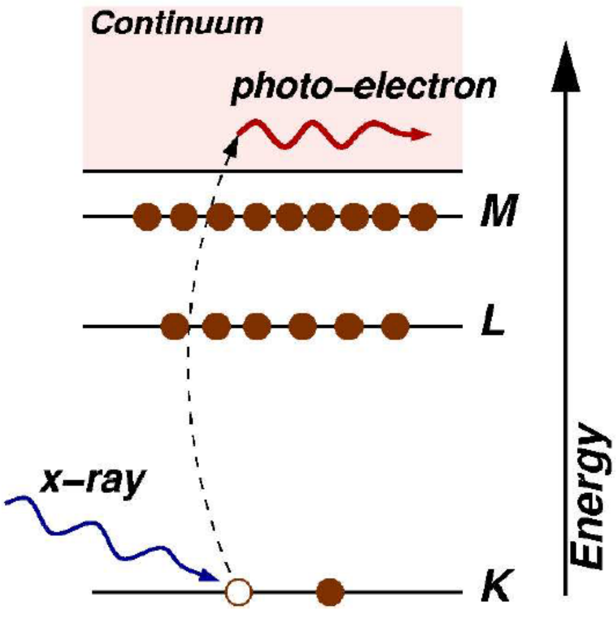


Data Analysis: Other ways of looking at the fit







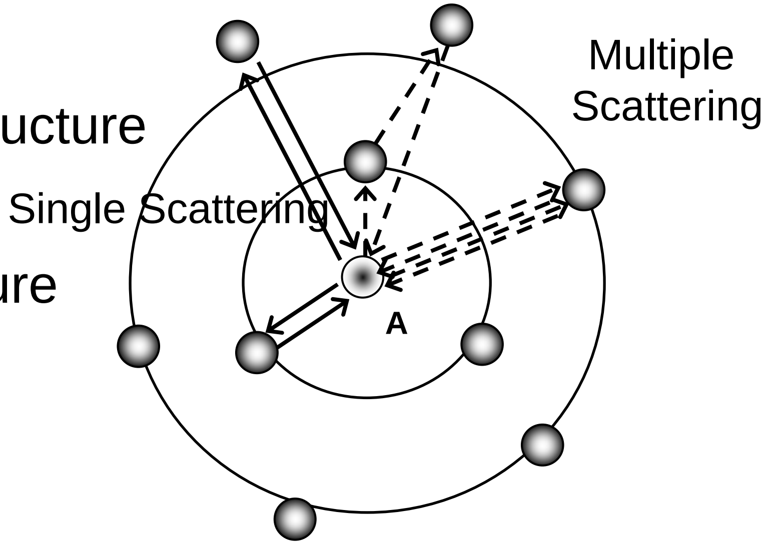


EXAFS (χ) Extended X-ray Absorption Fine-Structure

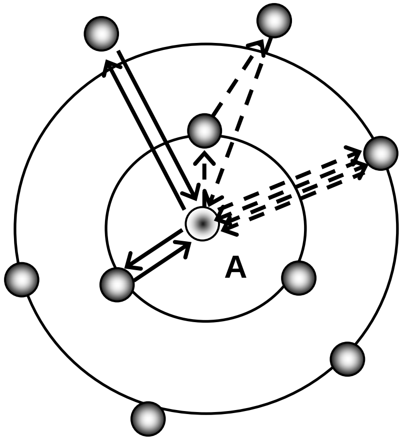
Single scattering

XANES X-ray Absorption Near-Edge Structure

Multiple scattering



XANES versus EXAFS



EXAFS

- Single scattering dominates

XANES

- Multiple scattering
- Electronic transitions
- Multiple electron transitions

Information

- Number & kind of neighbor
- Distance
- Disorder

- Geometry / subtle distortions
- Oxidation state
- Electronic information
- DOS in *final state*

Theoretical description of XANES

- Detailed electronic information
- Aids interpretation of spectra of unknown compounds
- Time-consuming
- Needs an expert

XAS in Catalysis

Goal

Local structure of catalysts under well-defined conditions

precursor state

during / after activation

during reaction

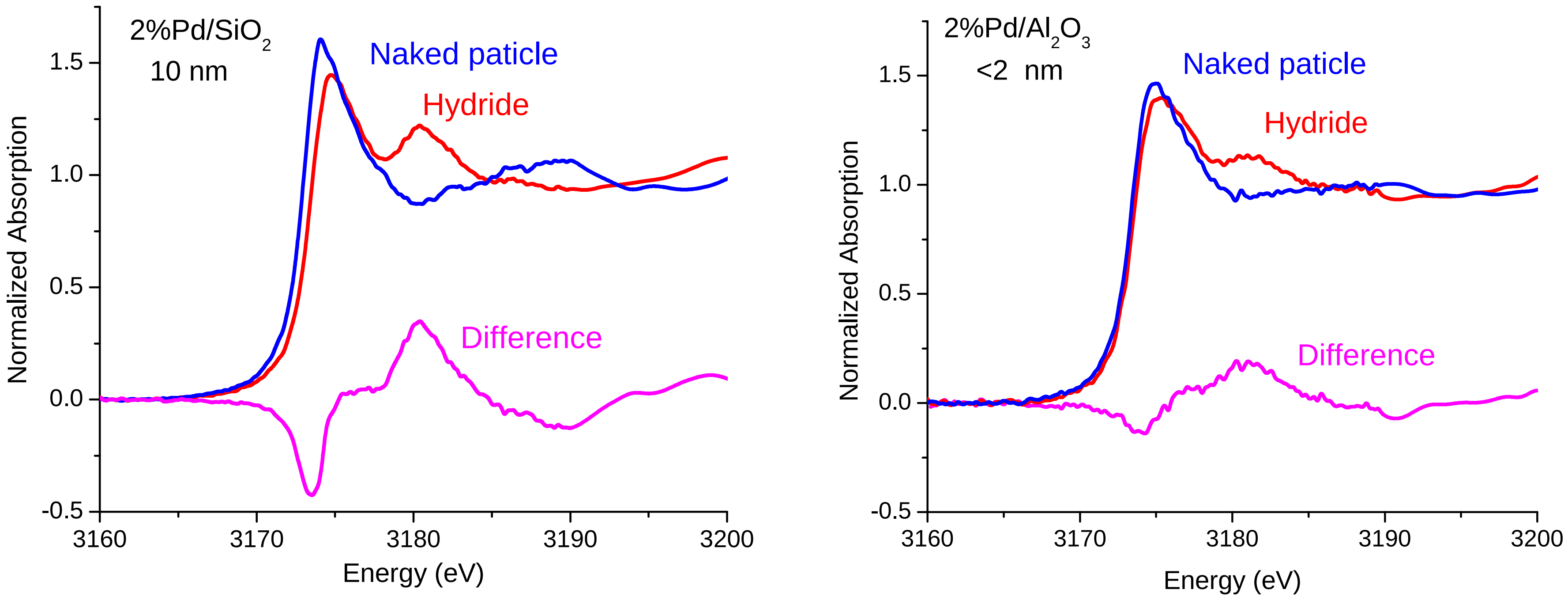
deactivation

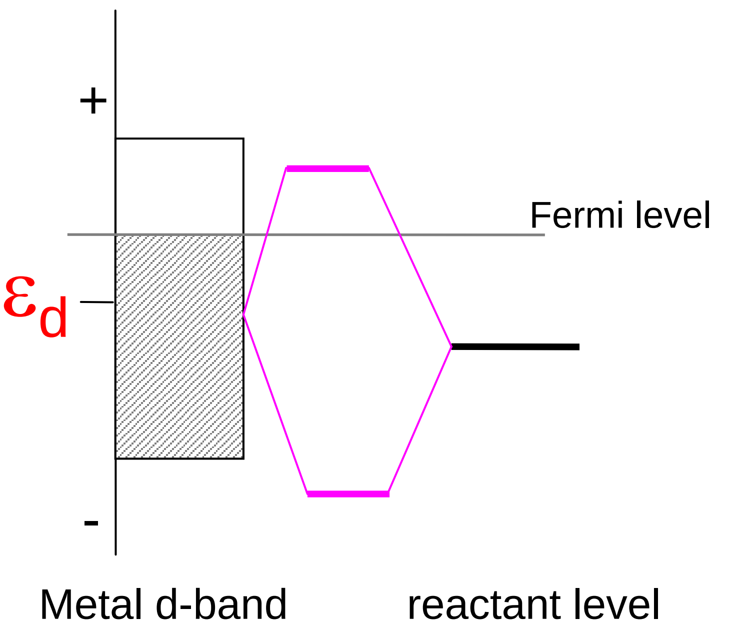
time-resolution (few msec)

space-resolution (few μm)

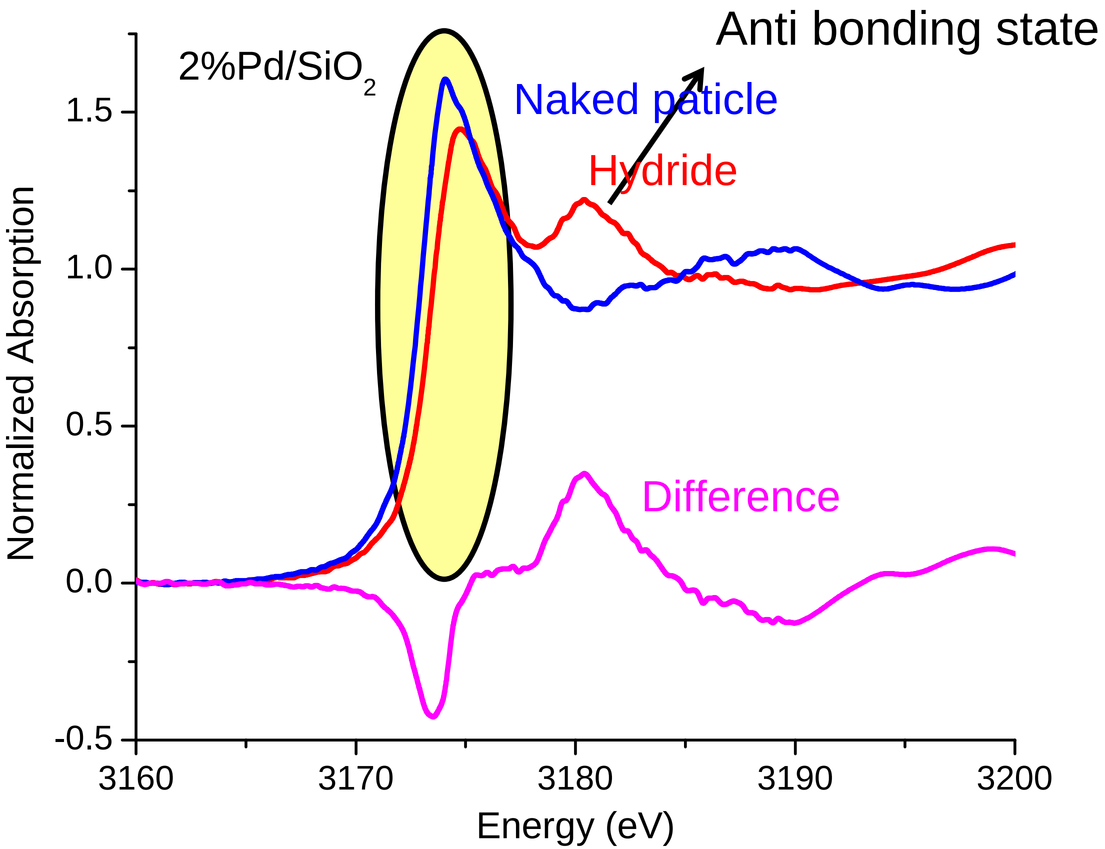
… … .

Palladium hydride formation

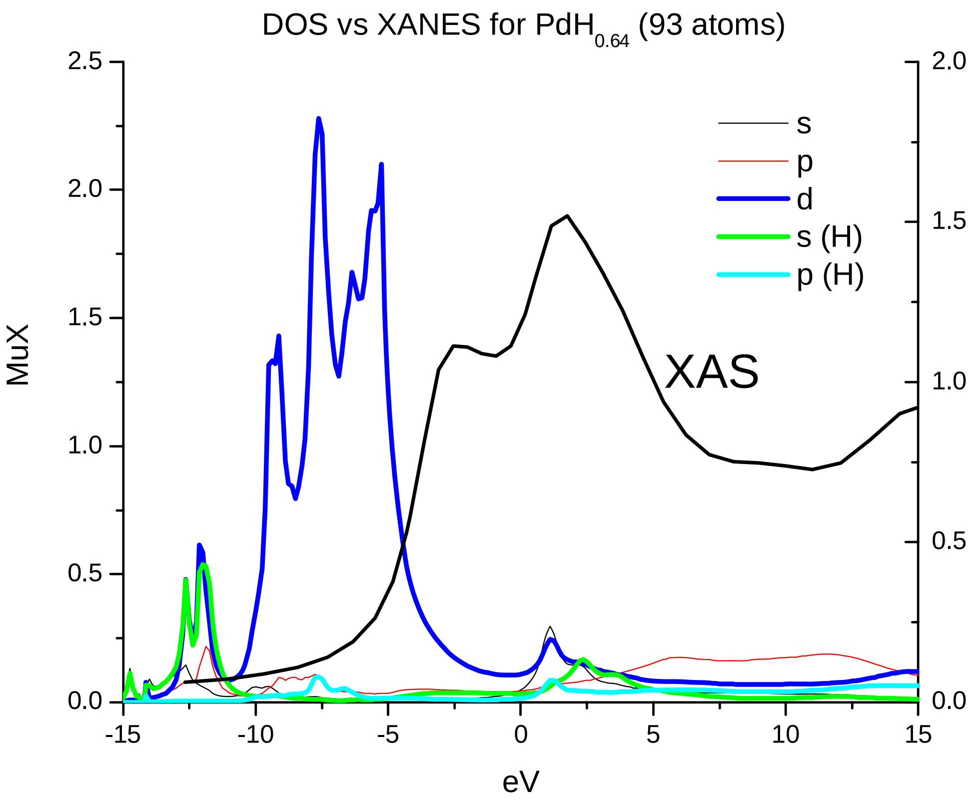


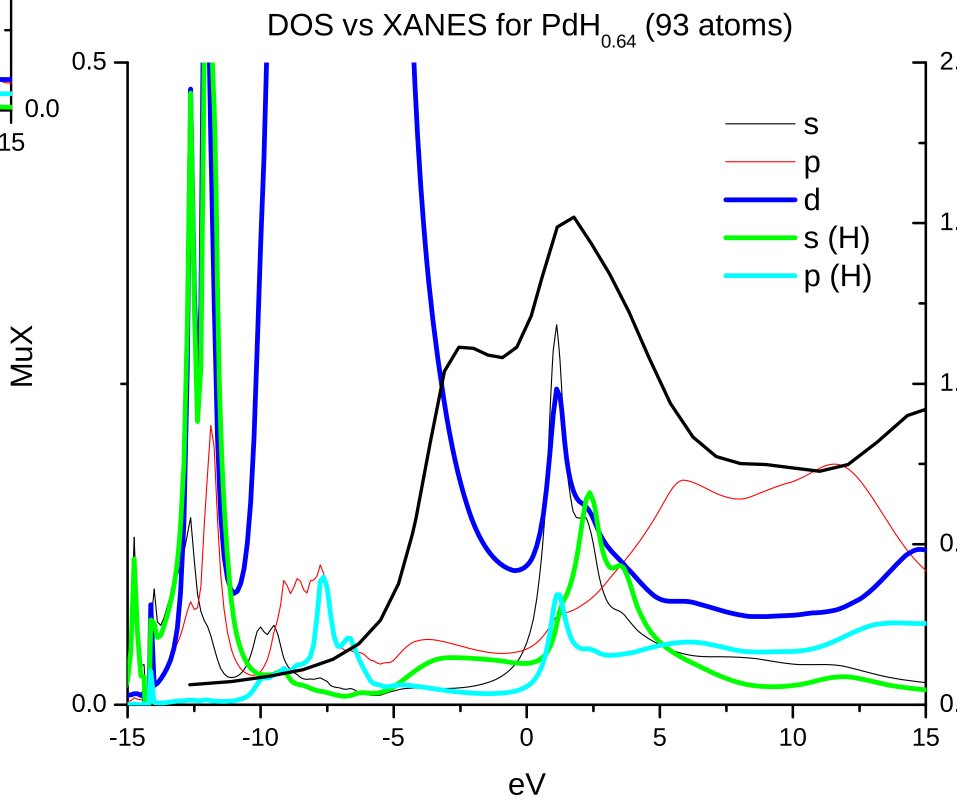


+
Fermi level
ε_d
-
Metal d-band
reactant level



Anti bonding state
2%Pd/SiO_2
Naked paticle
Hydride
Difference
Normalized Absorption
1.5
1.0
0.5
0.0
-0.5
3160
3170
3180
3190
3200
Energy (eV)


DOS vs XANES for $PdH_{0.64}$ (93 atoms)
MuX
eV
XAS
s
p
d
s (H)
p (H)
2.5
2.0
1.5
1.0
0.5
0.0
-15
-10
-5
0
5
10
15


DOS vs XANES for $PdH_{0.64}$ (93 atoms)
MuX
eV
s
p
d
s (H)
p (H)
0.5
0.0
2.0
1.5
1.0
-15
-10
-5
0
5
10
15

Catalysis by Gold

Partial / complete oxidation of hydrocarbons
methane, alkenes, methanol

Hydrogenation / dehydrogenation reactions
alkenes, alkynes, alkadienes, (un)saturated ketones

Methanol synthesis
$CO + 2H_2 \rightarrow CH_3OH$
$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O$

WGS
$H_2O + CO \rightarrow CO_2 + H_2$

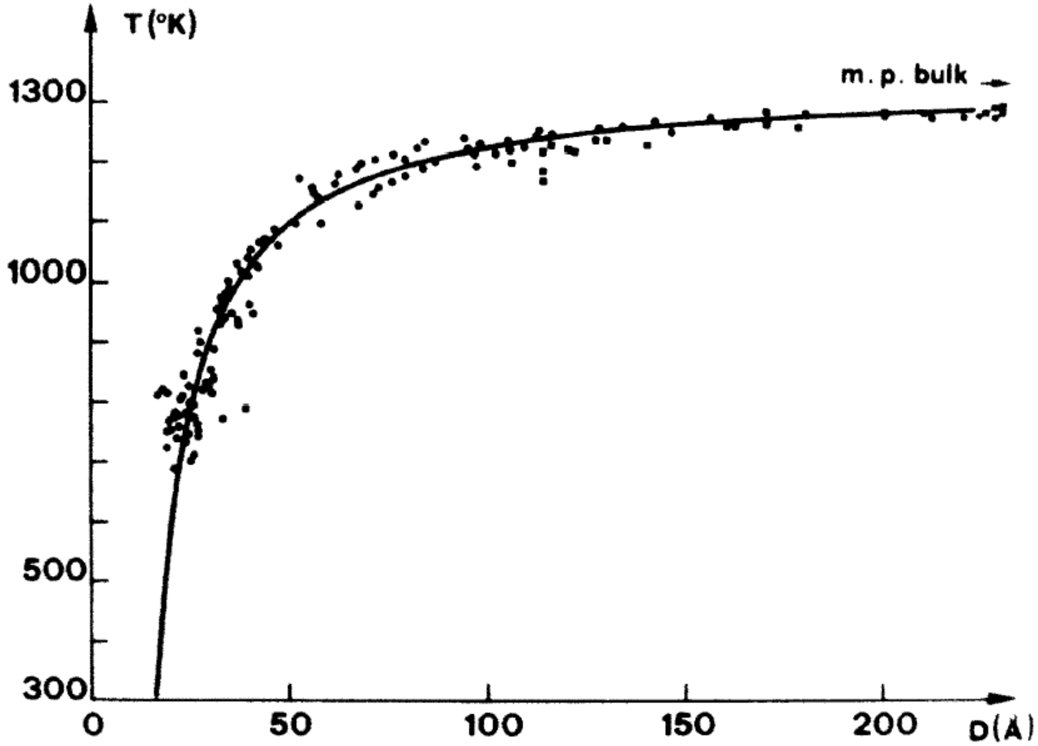
Nitric Oxide reduction (with CO, olefins, or H_2)

CO oxidation
1925: Active in CO oxidation
highly active in presence of H_2: Haruta Catal. Today 36 (1997) 153
Selective CO removal, air purification, high-purity N_2 and O_2

Catalysis by Gold

Physical properties

- bulk metallic gold is thermodynamically stable
- melting point and metallicity of the particle is function of particle size



Buffat Phys. Rev. A 13 (1976) 2287

Catalysis by Gold

Physical properties

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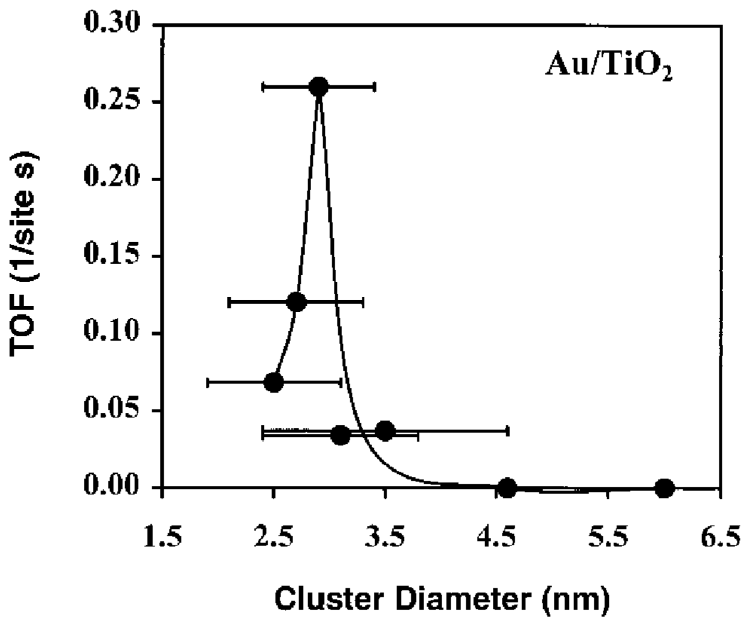
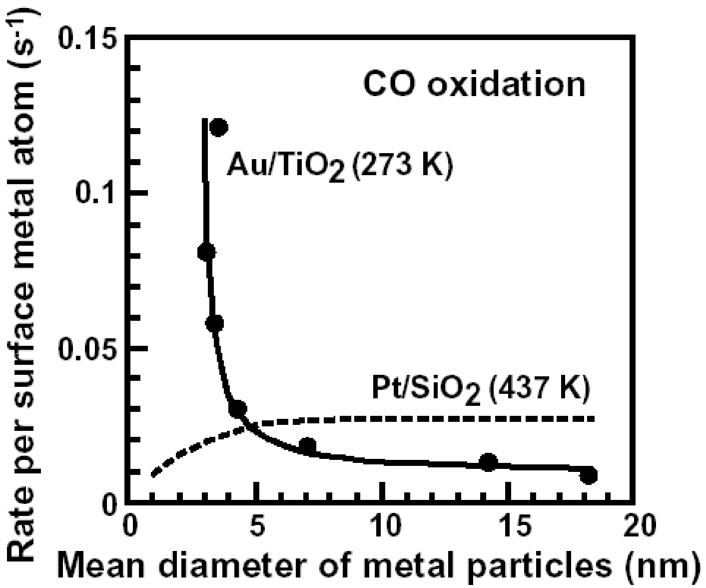
CO oxidation: particle-size effect





Goodman *Science* 281 (1998) 1648

Haruta *Cattech* 3 (2002) 102

Catalysis by Gold

Physical properties:

- bulk metallic gold is thermodynamically stable
- melting point and metallicity of the particle is function of particle size

CO oxidation: particle-size effect

Large support effects:

SiO_2: hardly active
Al_2O_3, MgO: moderately active
(TiO_2) Fe_2O_3, CeO_2, *other reducible supports:* very active & less dependent on particle sizes; No clear relation to reducibility of support

Active species in gold oxidation catalysis?

- Carbonate-mechanism excluded
- Small particles become active as soon as they are non-metallic (Goodman)
- Oxidic gold (I or III) is active species (Gates)
- Theory supports both gold-only and support-aided mechanism
- Support supplies oxygen *via molecularly (activated) adsorbed oxygen*
  via Mars van Krevelen

Geometry / coordination

Density of states

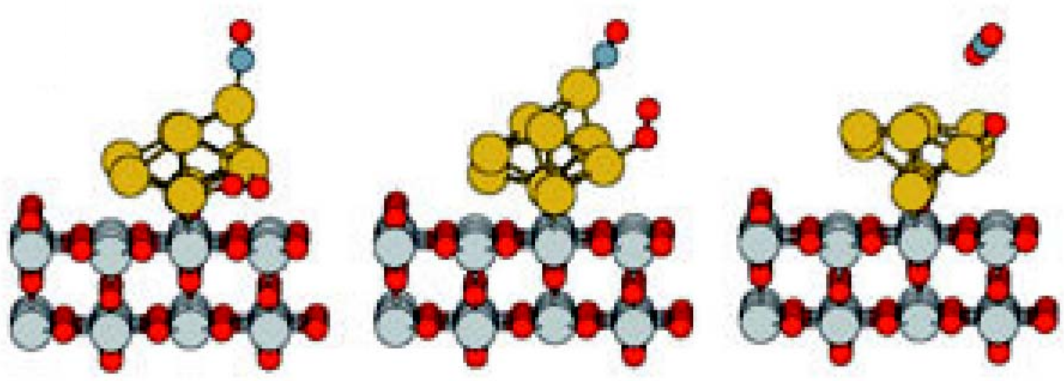
Oxidation state

Time resolved

In situ

How is oxygen activated on the catalyst?

How can the most inert metal be so active?



Nørskov *et al. Angew. Chem.* **44** (2005) 1824

Small gold particles adsorb oxygen (and react)

Structure of gold catalysts

Sample Preparation

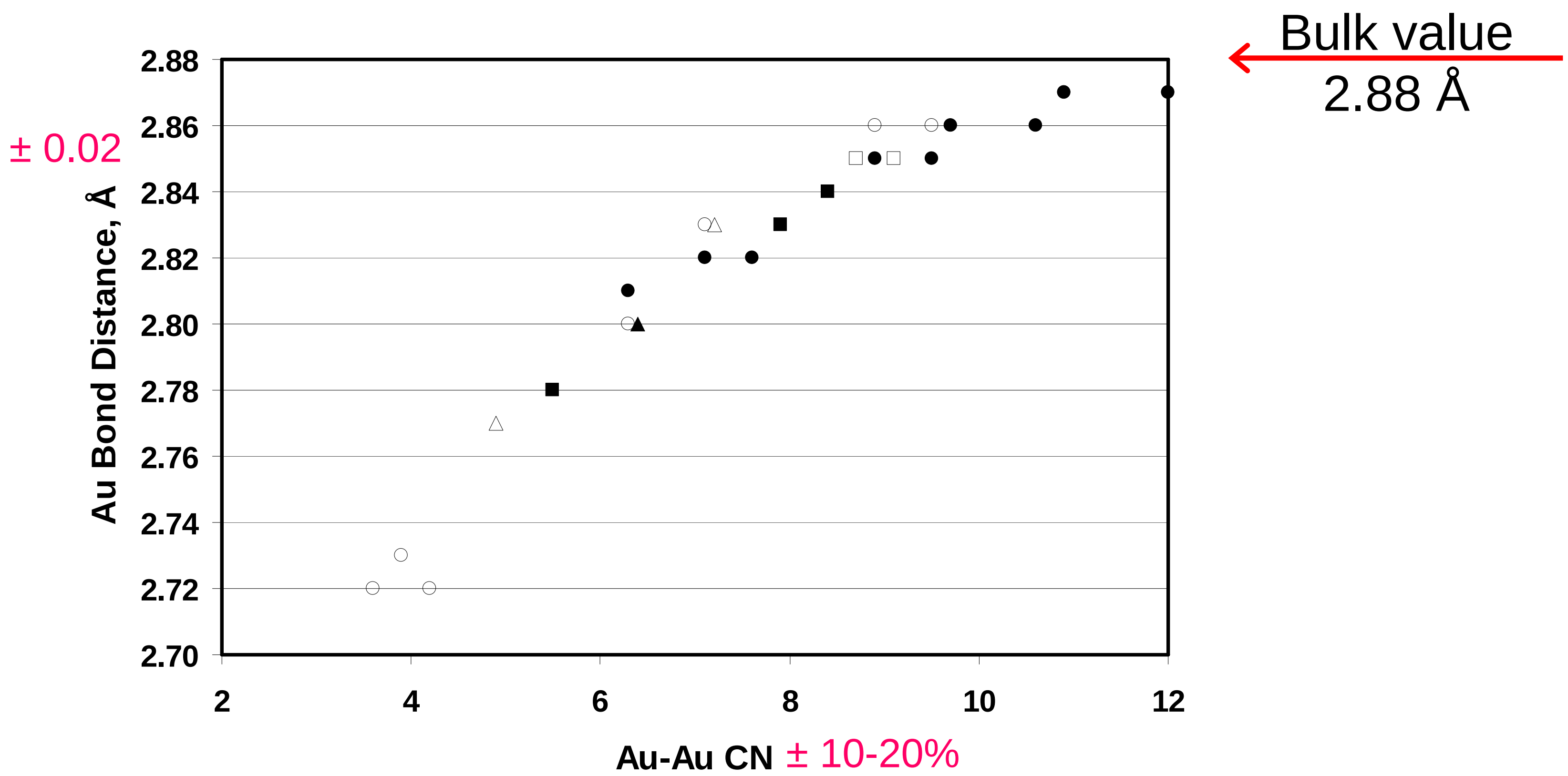
- Deposition precipitation $HAuCl_4$ adjusted pH
- Washing with a base to remove chlorine
- Reduction in hydrogen

Supports

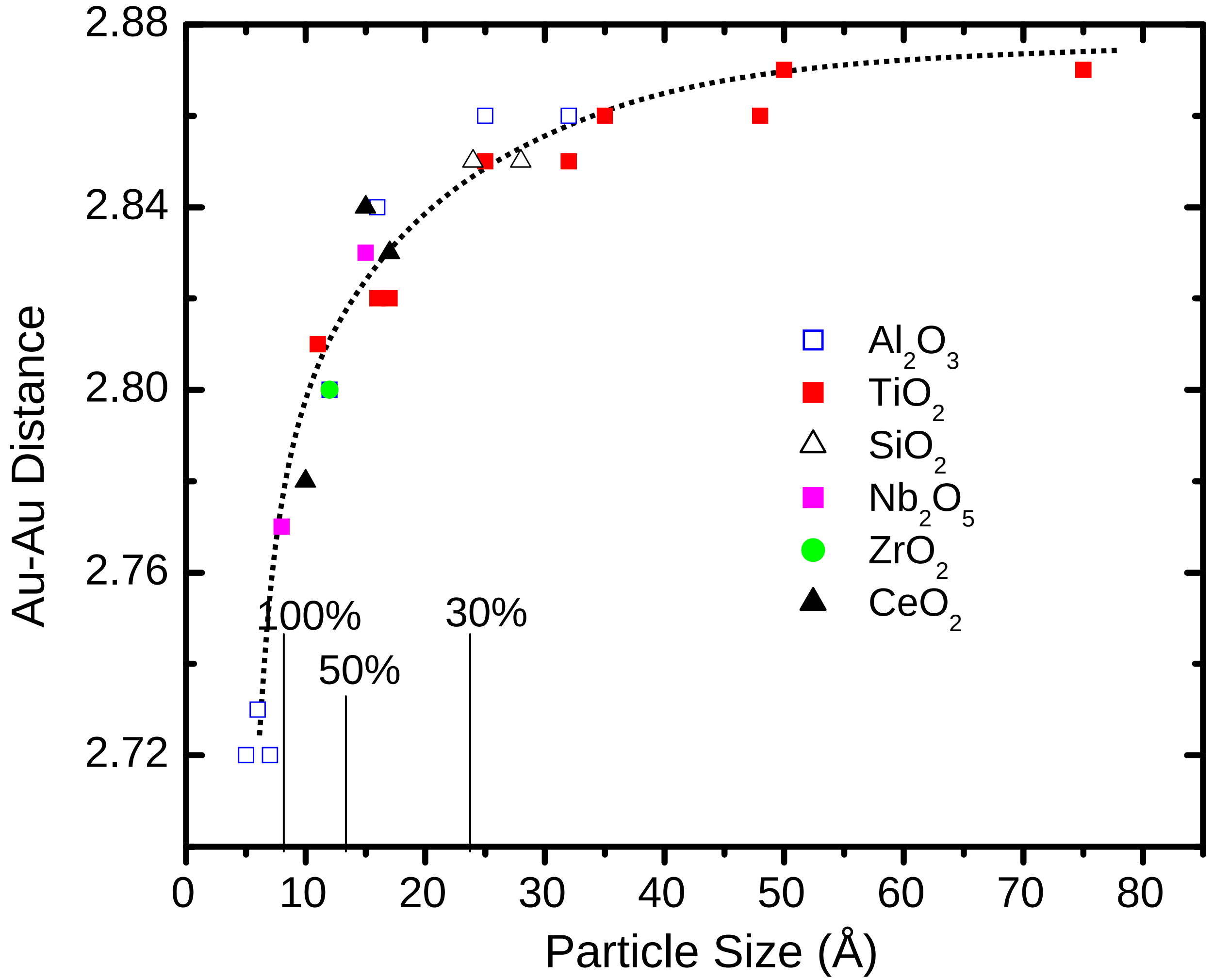
Al_2O_3, SiO_2, CeO_2, TiO_2, ZrO_2, Nb_2O_5

Full EXAFS & XANES analyses

EXAFS Fitting Results of Reduced Catalysts



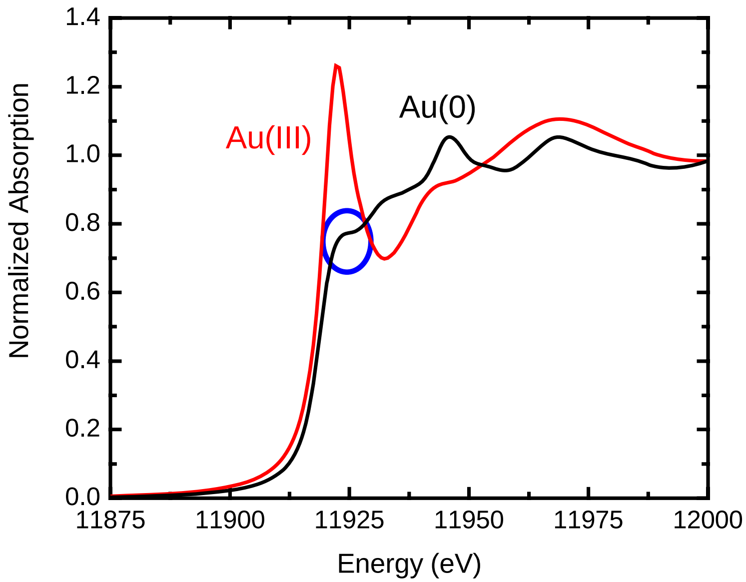
EXAFS Fitting Results of Reduced Catalysts



Strong reduction in Au-Au distance with particle size

No visible influence of support

Electronic structure from L_{III} XANES

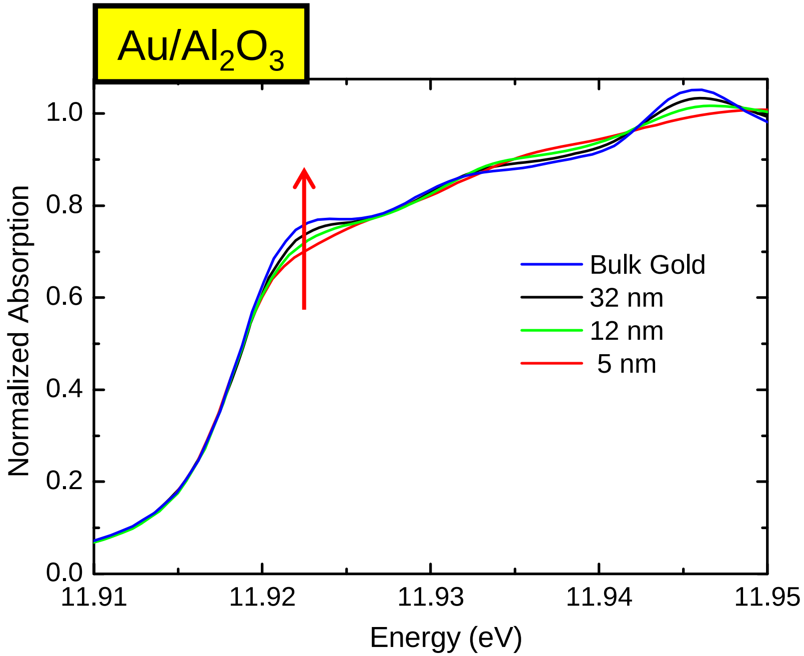


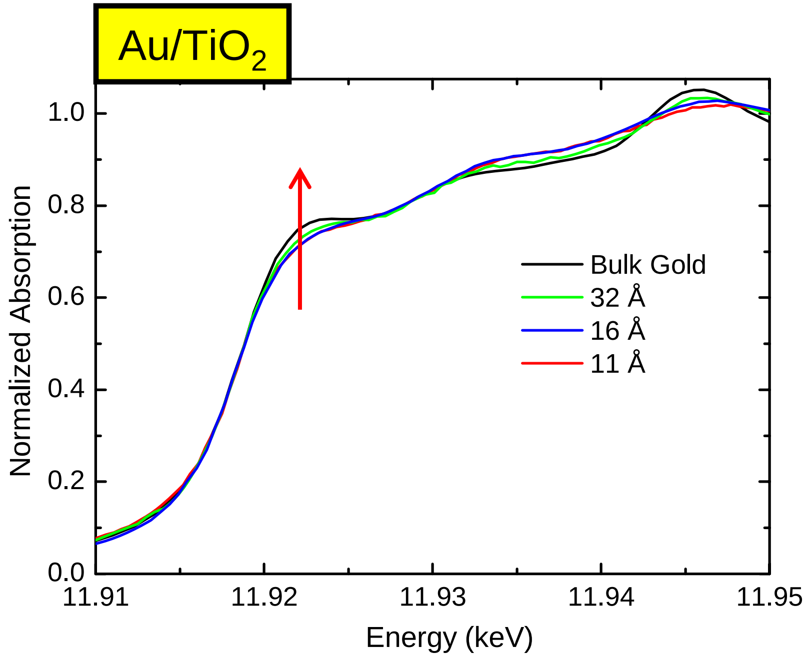
Whitelines reflect number of holes in the d-band

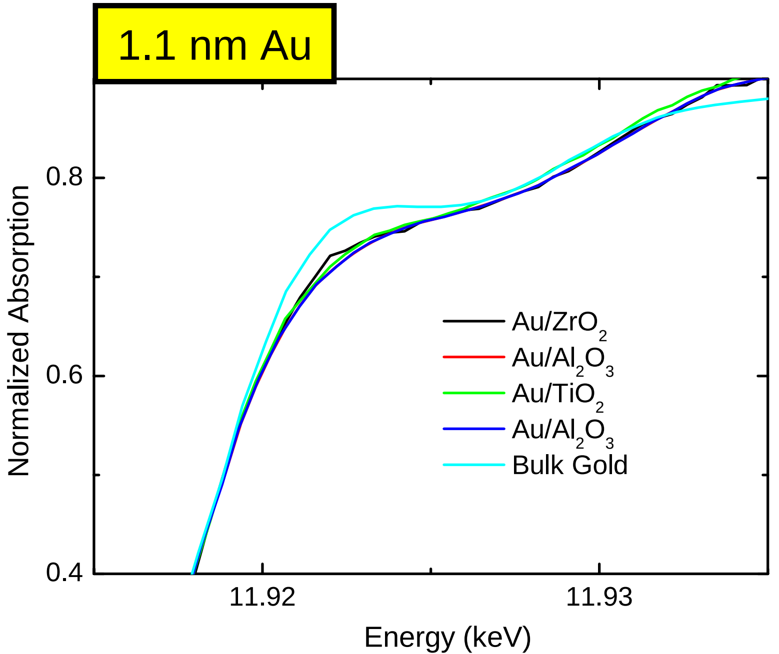
Gold whiteline: spd-rehybridization results in $5d^{10-x}6sp^{1+x}$

Mattheiss, L.F. *et al. Phys. Rev. B* **1980**, *22*, 1663

Whitelines reflect number of holes in the d-band



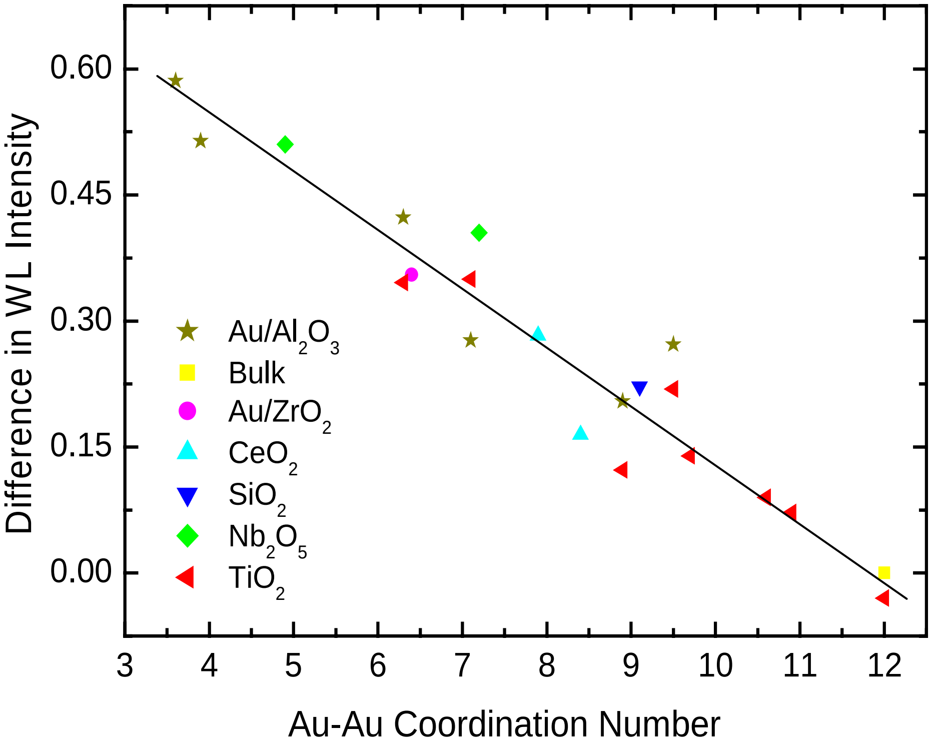


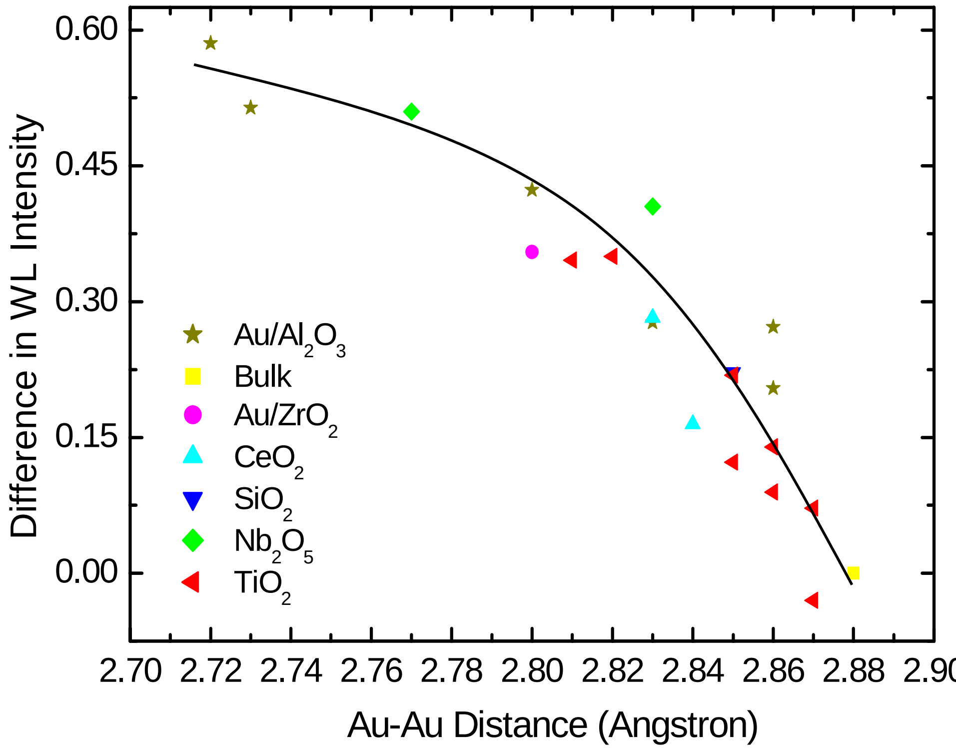


Whiteline is particle-size dependent

Whiteline intensity versus particle size

Difference intensity with bulk

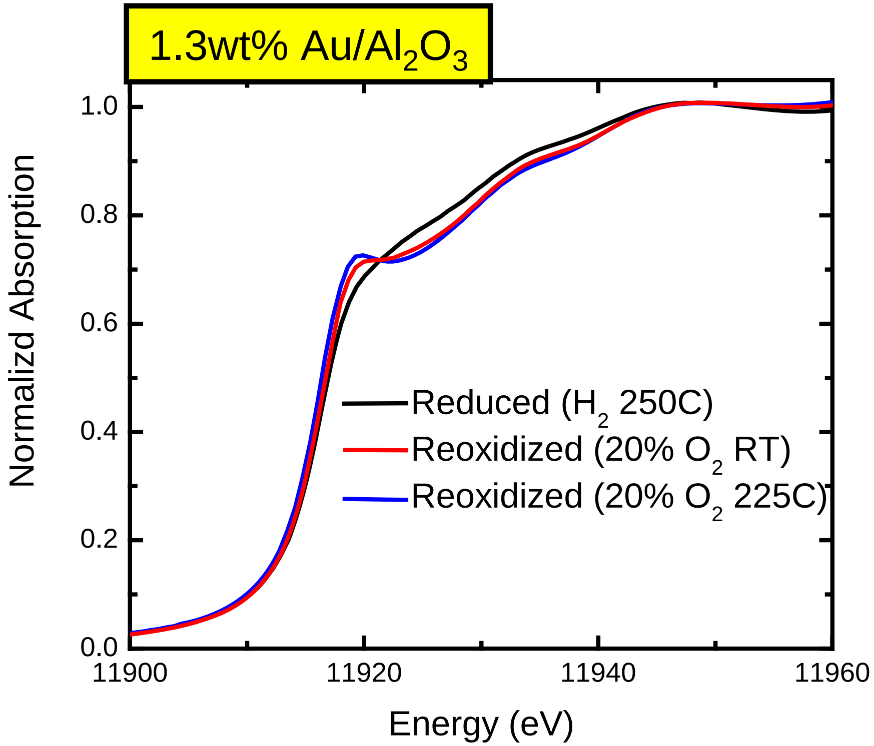


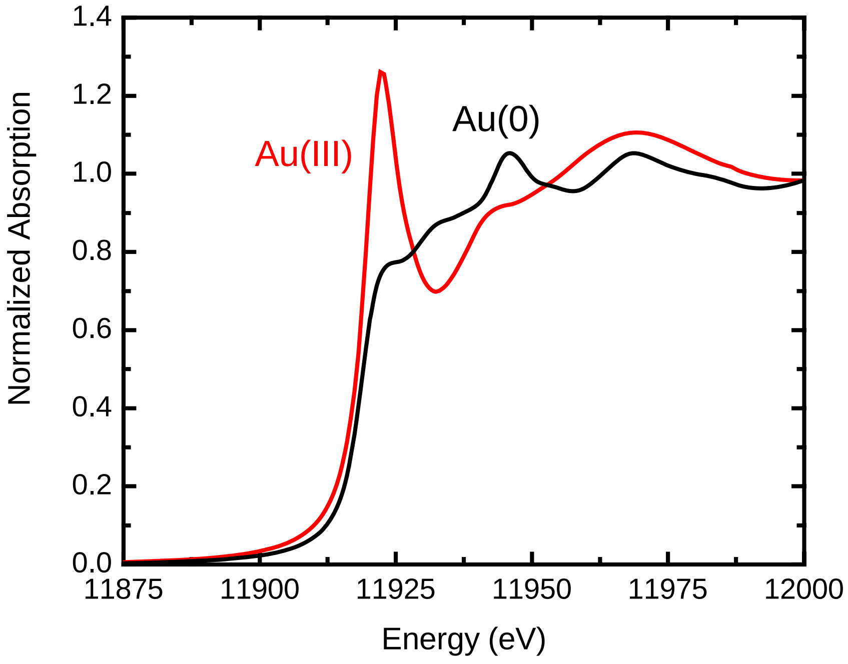


Six supports, one trend

Larger particles fewer d-electrons

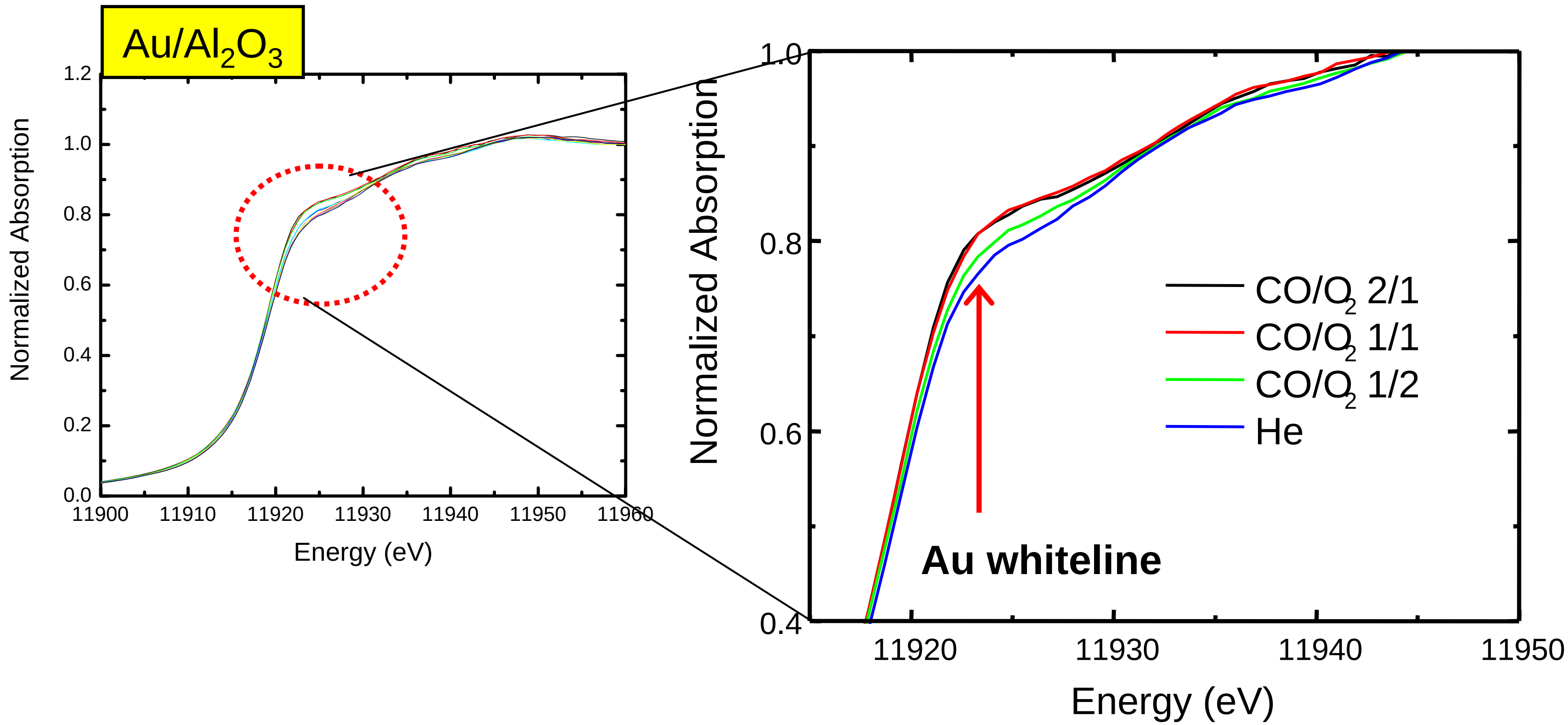
Exposure to 20% O_2





	CN	R(Å)	%Au(III)
Reduced	3.6	2.72	0
Reox. RT	3.6 / 0.3	2.72 / 2.04	10
Reox. 225C	2.7 / 0.5	2.71 / 2.04	15

XAS during CO Oxidation



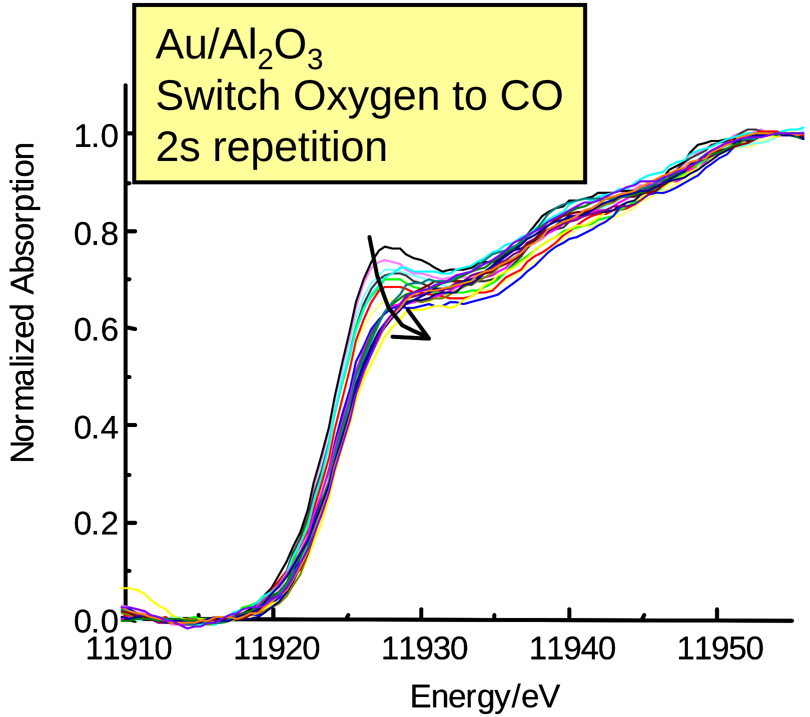
	CN(Au)	R(Au)
He	6.5	2.77
1:1	5.3	2.73
2:1	5.7	2.73
1:2	5.2	2.77

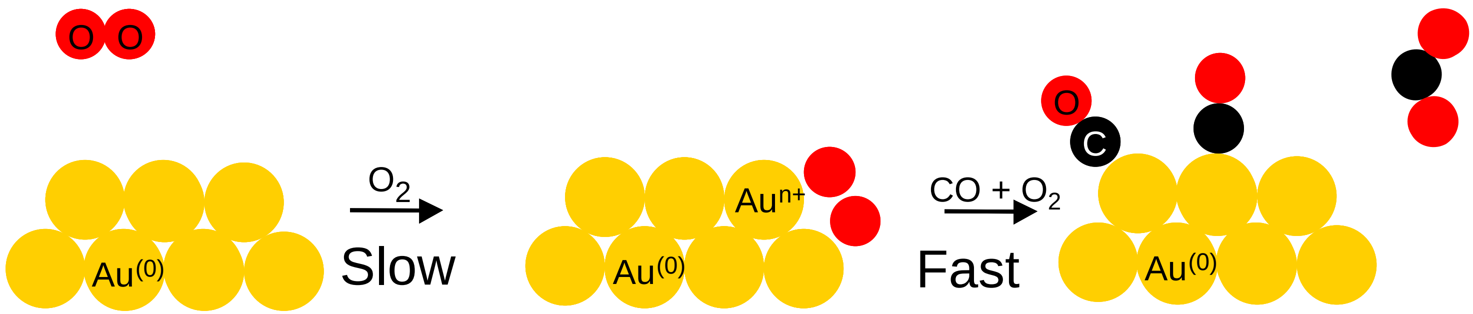
Small oxygen contribution

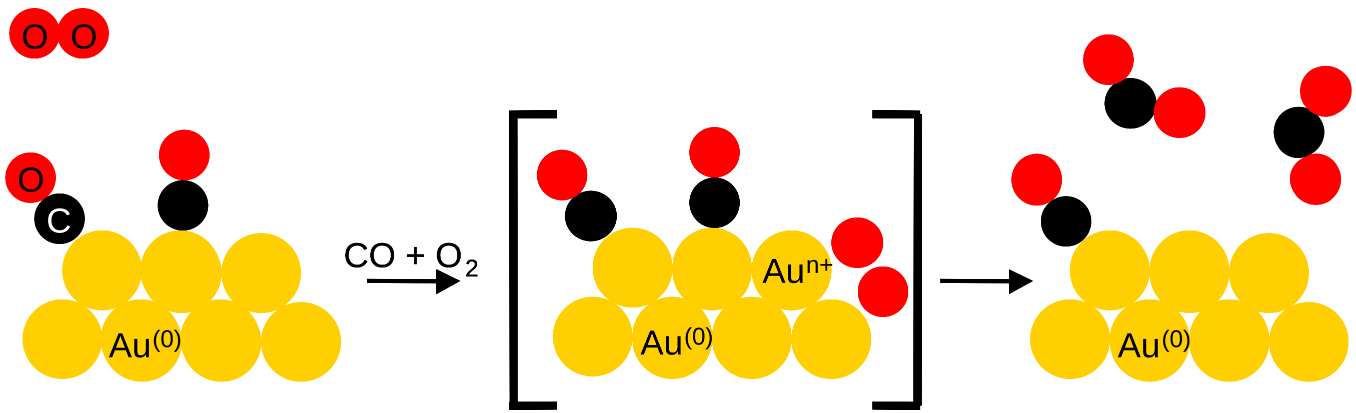
More intense with more CO:
holes in the d-band (anti-bonding states)

Gold catalysts and activation of oxygen

- Under (diluted) O_2: surface oxidation (Au/Al_2O_3 & Au/TiO_2)
- Switch to CO/O_2: CO keeps gold reduced





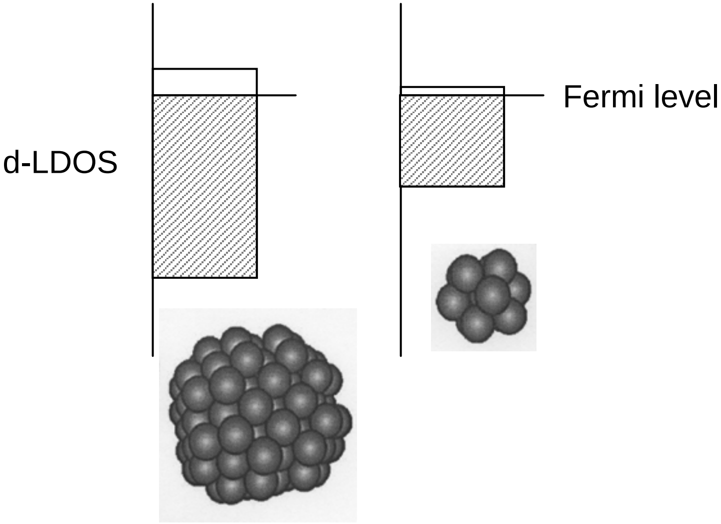


Reduced gold is active phase

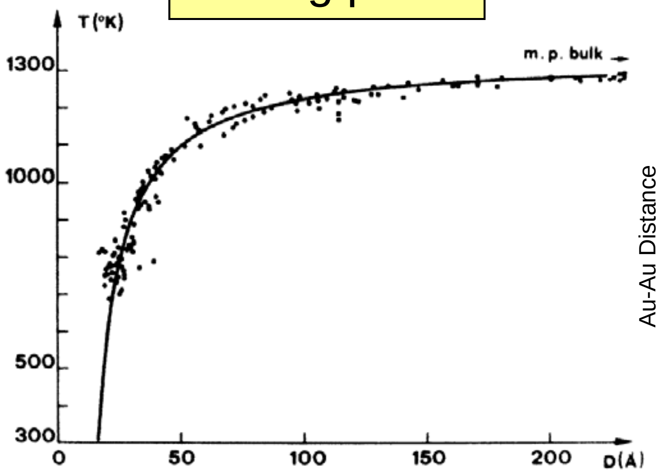
Gold participates in oxygen activation

Van Bokhoven *Angew. Chem. (2006) VIP*

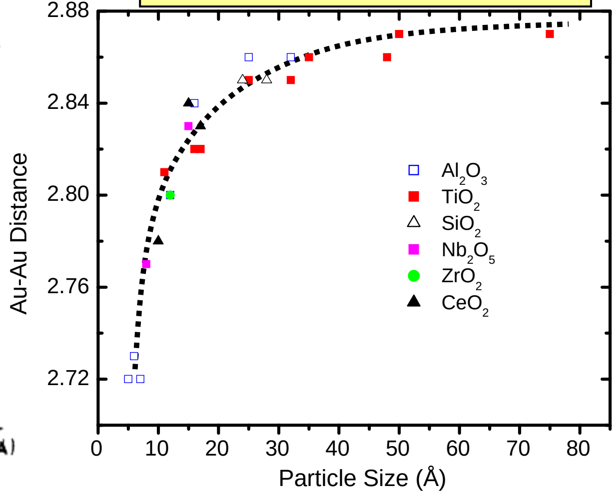
- Rehybridization of spd-orbitals ($5d^{10-x}6sp^{1+x}$)
- Smaller particles have fewer holes in the d-band
- Particle size dominates support-effect
- Oxygen is activated on gold particle



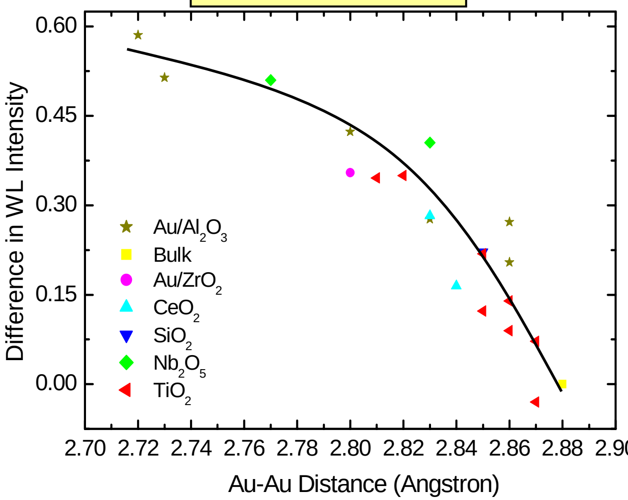
Boiling point



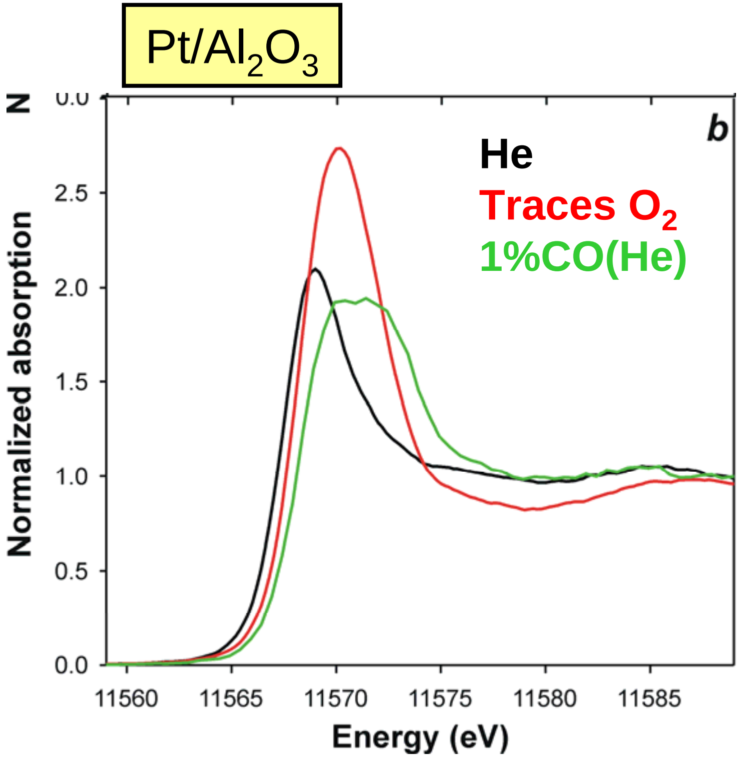
Gold-Gold distance



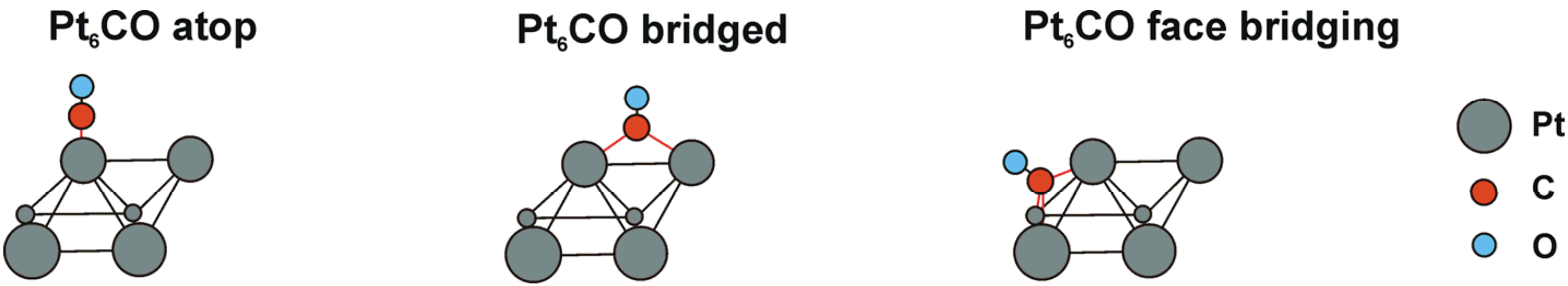
d electrons



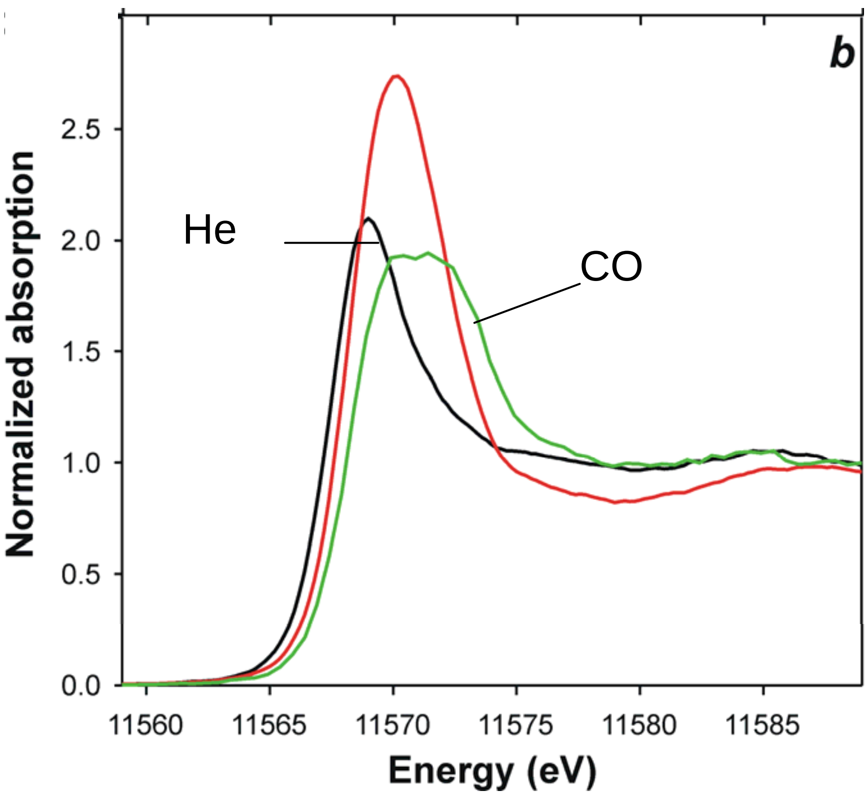
Adsorption sites from XAS

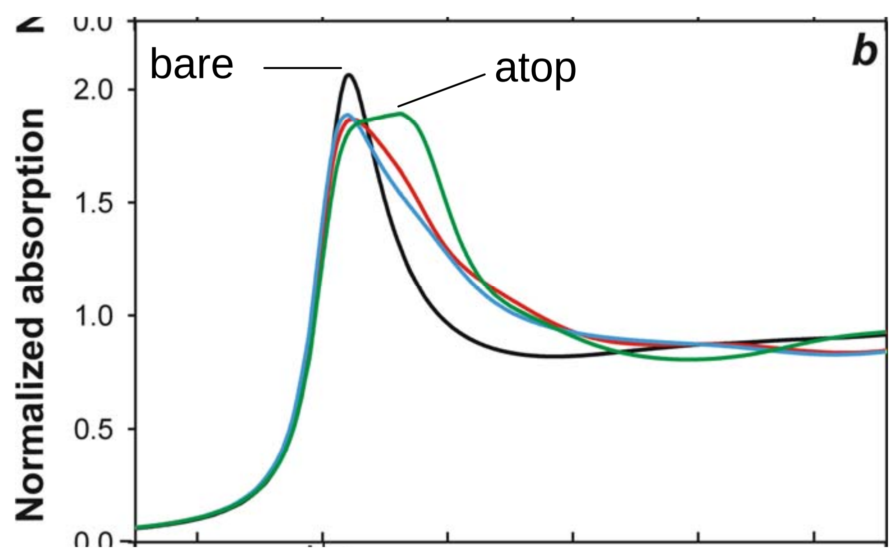


FEFF8 simulation



Experimental



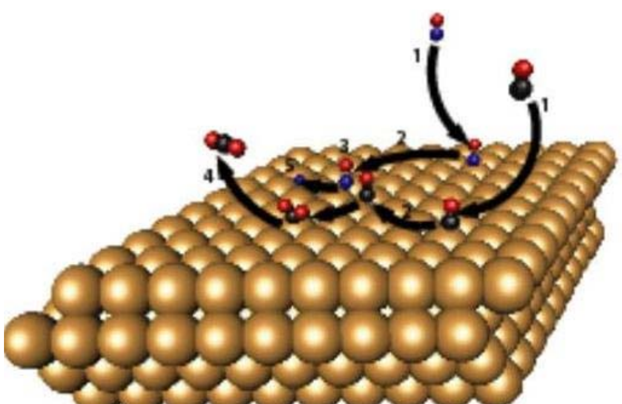


fuel cell (PEM)

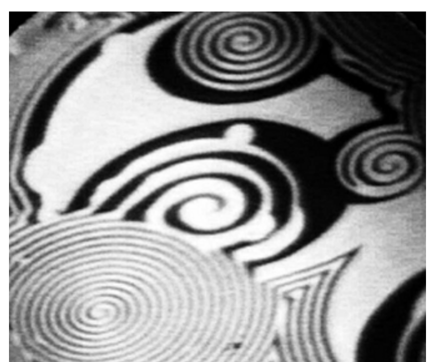
catalytic converter

platinum catalyst

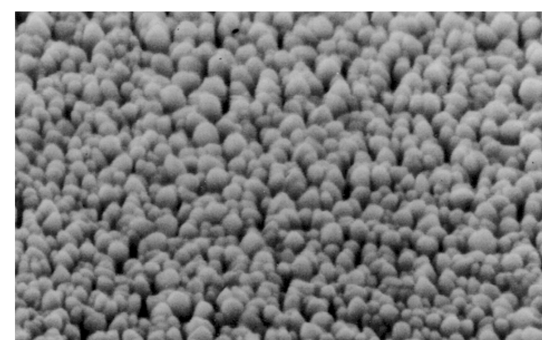
Structure of the active phase?



surface reaction



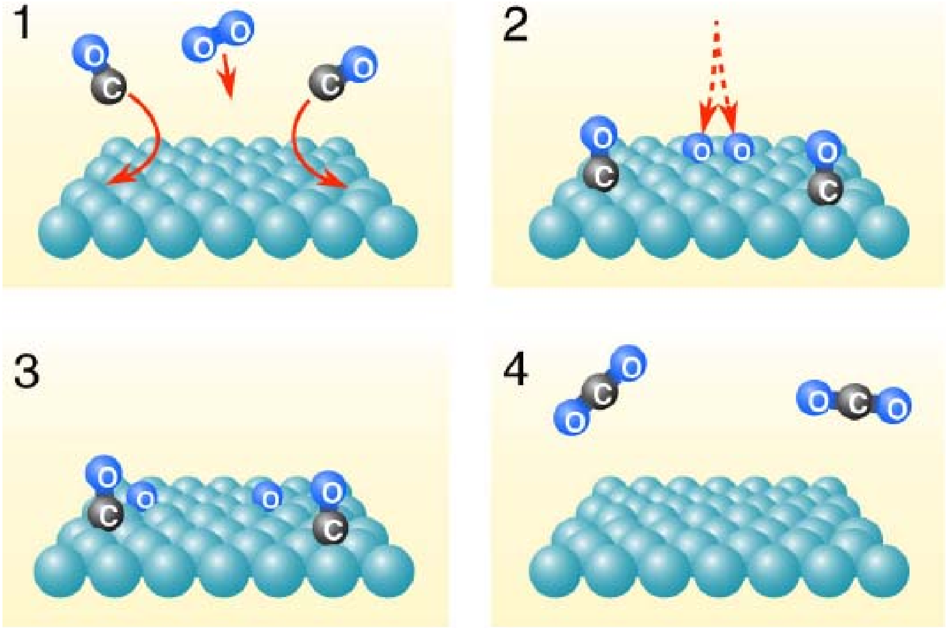
surface patterns



surface roughening

Single Crystals

UHV conditions

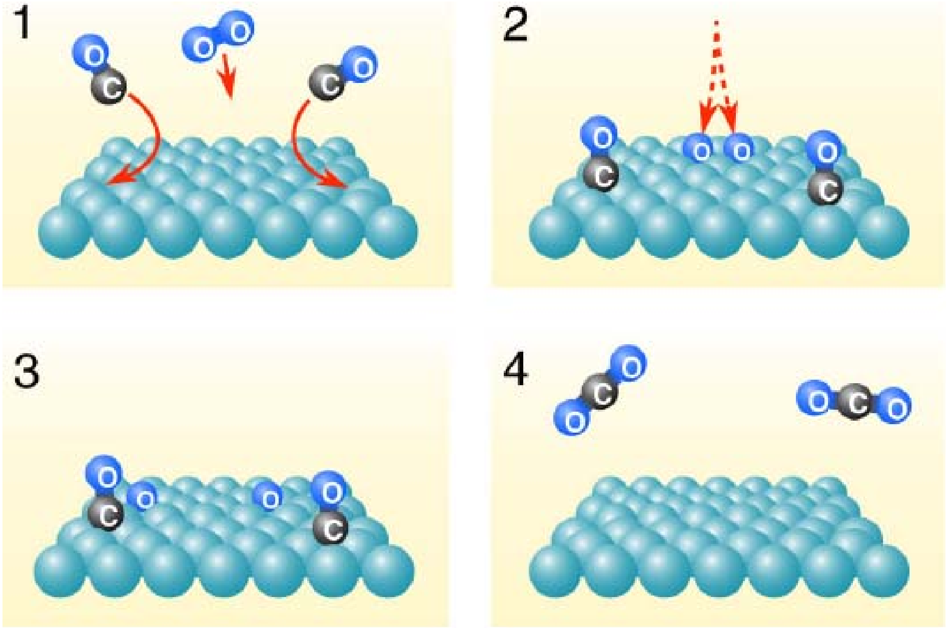


Langmuir-Hinshelwood

Single Crystals

UHV conditions

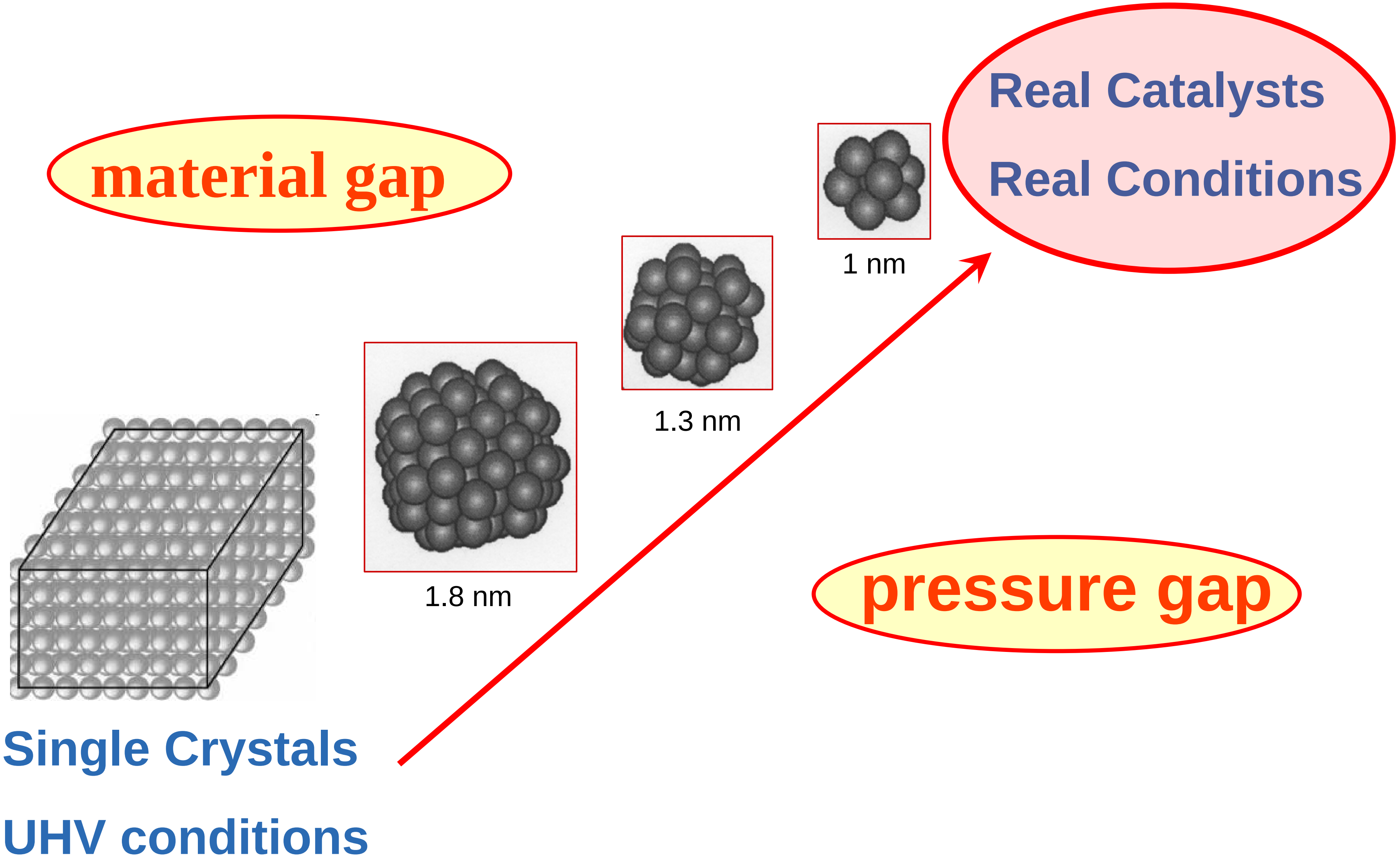
high pressure



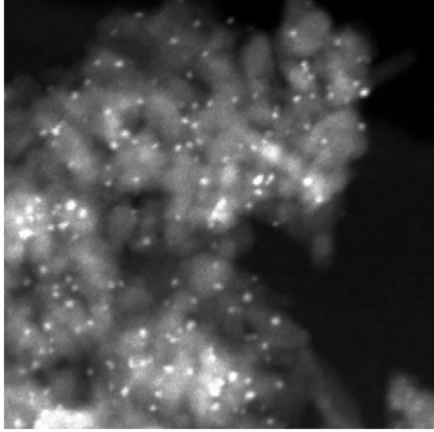
Langmuir-Hinshelwood

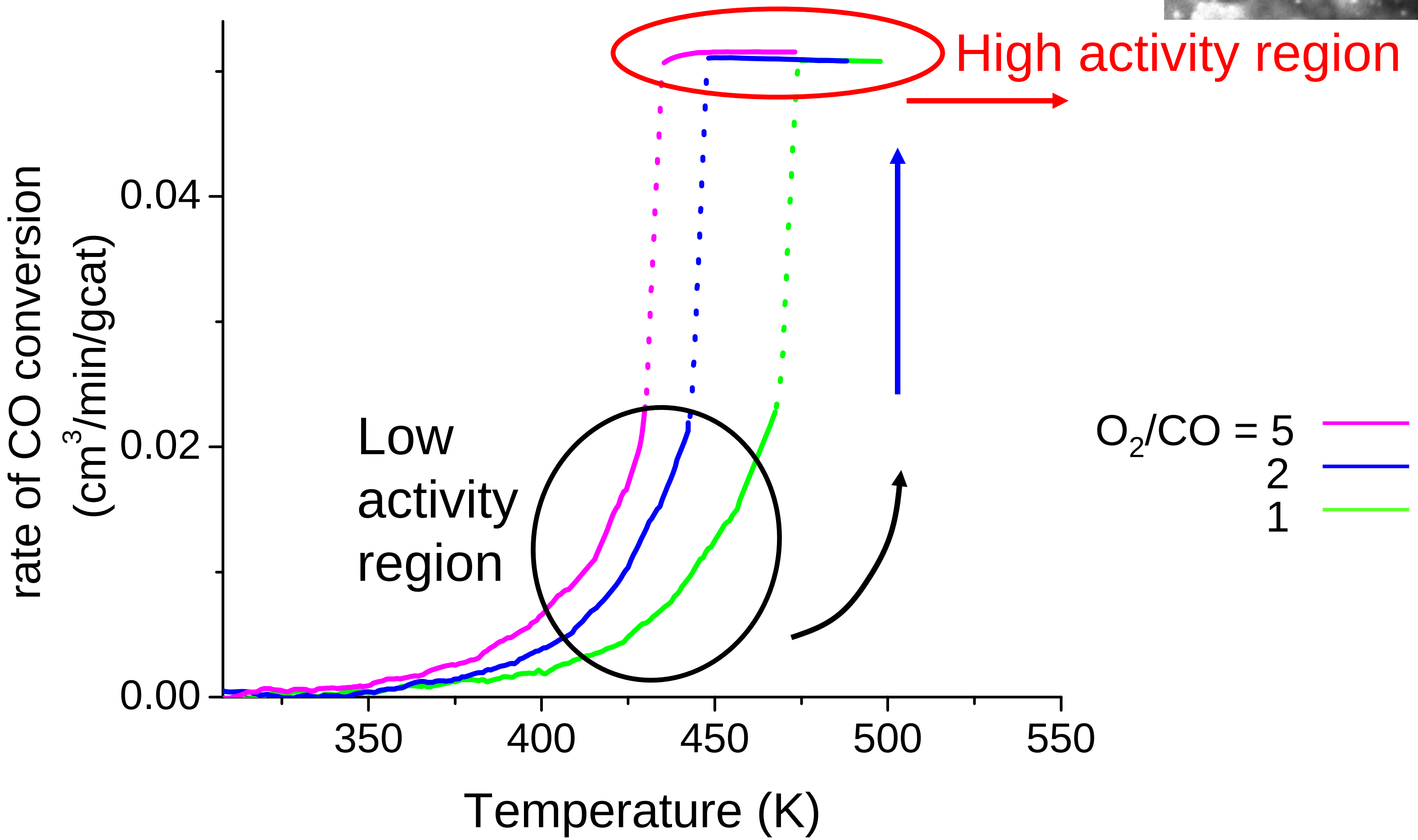
Two reaction regimes

- Low activity – CO poisoning
- High activity **???**


material gap
Real Catalysts
Real Conditions
1 nm
1.3 nm
1.8 nm
pressure gap
Single Crystals
UHV conditions

Conversion data

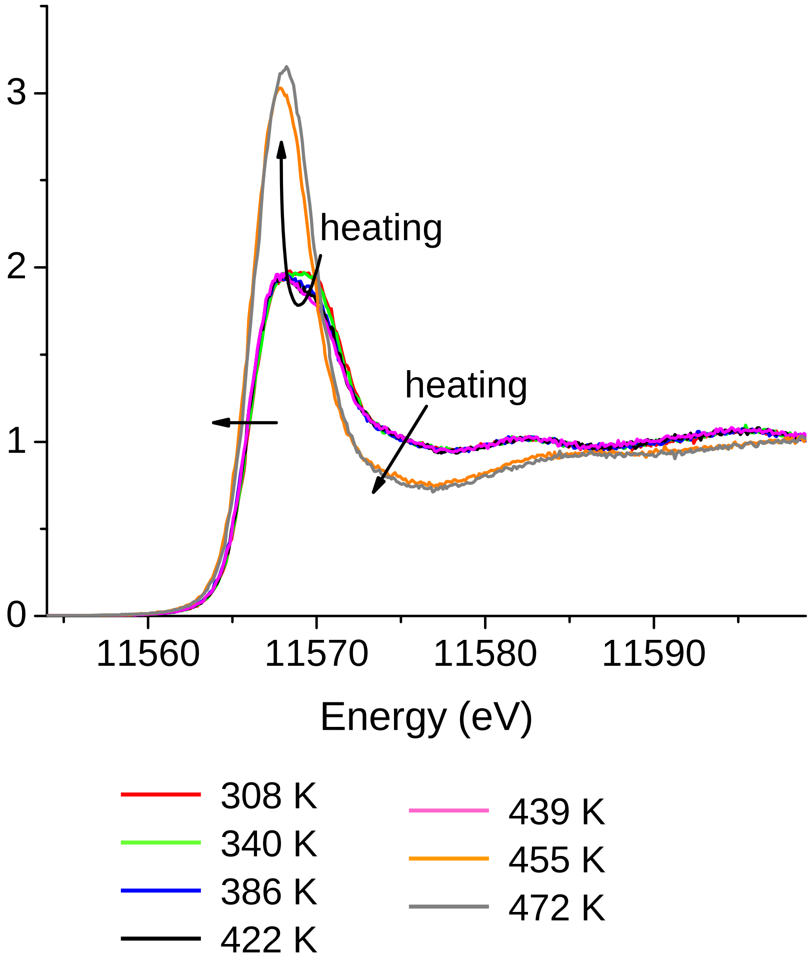




Conversion data

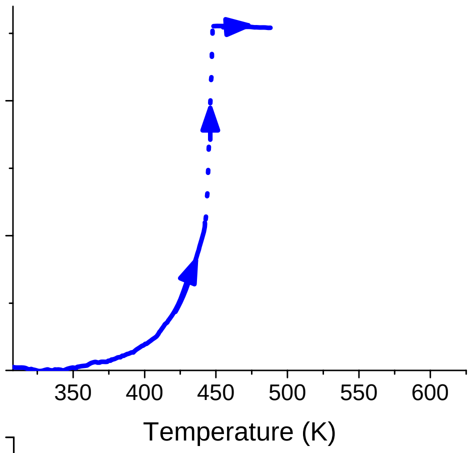
O_2/CO ratio	ignition or extinction temperature (K)		hysteresis	temperature for onset of conversion (K)
	heating	cooling		
1	472	456	yes	340
2	445	440	yes	338
5	433	421	yes	329

XAS

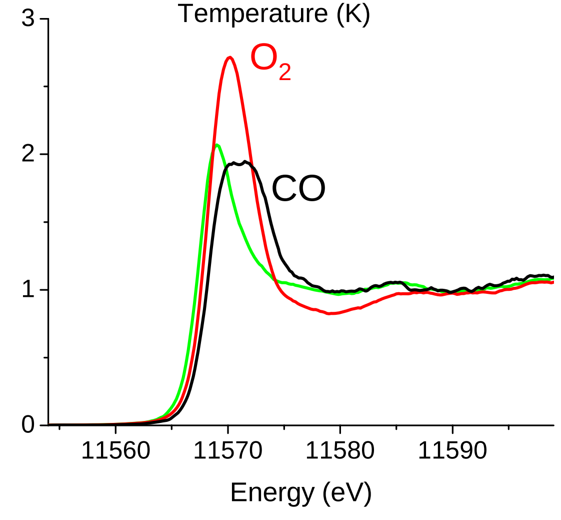


3
2
1
0
heating
heating
11560
11570
11580
11590
Energy (eV)
308 K
340 K
386 K
422 K
439 K
455 K
472 K

$O_2/CO = 2$

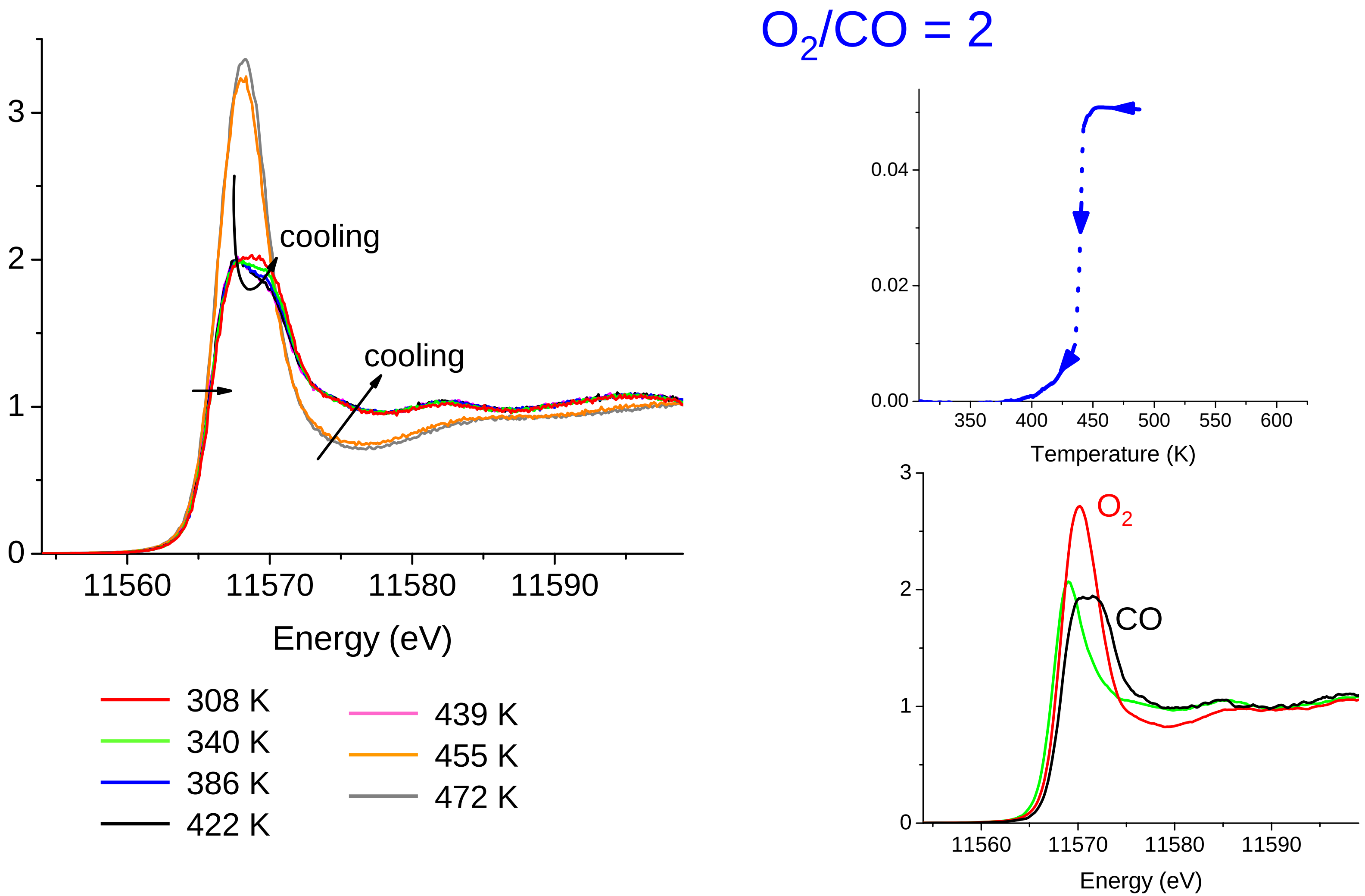


350
400
450
500
550
600
Temperature (K)



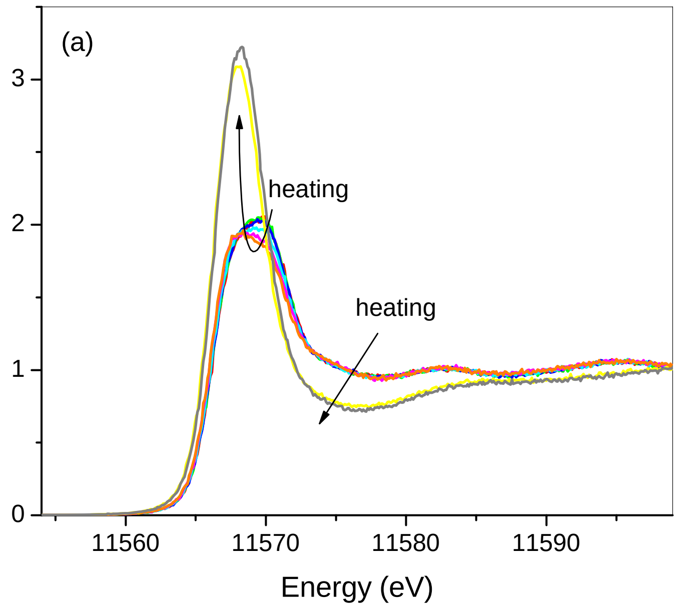
3
2
1
0
O_2
CO
11560
11570
11580
11590
Energy (eV)

XAS

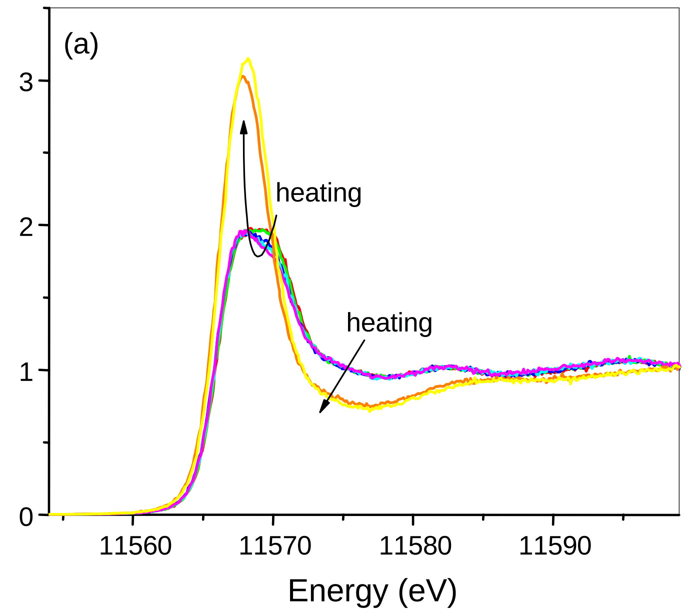


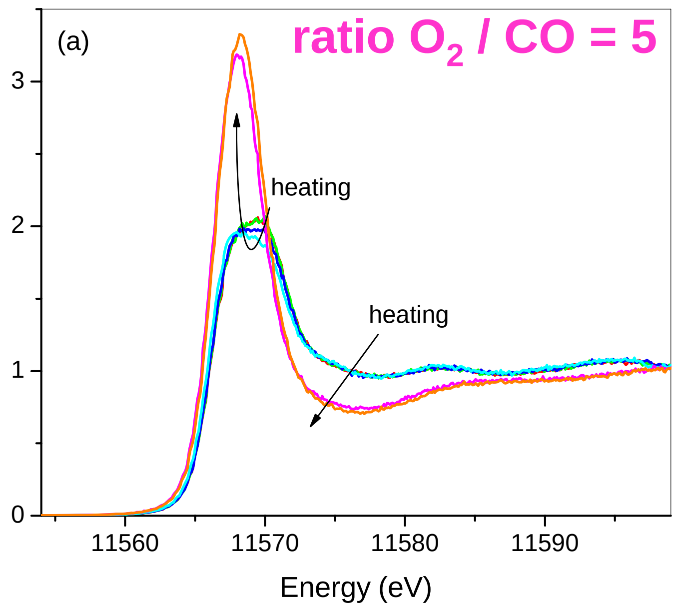
3
2
1
0
11560
11570
11580
11590
Energy (eV)
cooling
cooling
308 K
340 K
386 K
422 K
439 K
455 K
472 K
O2/CO = 2
0.04
0.02
0.00
350
400
450
500
550
600
Temperature (K)
3
2
1
0
11560
11570
11580
11590
Energy (eV)
O2
CO

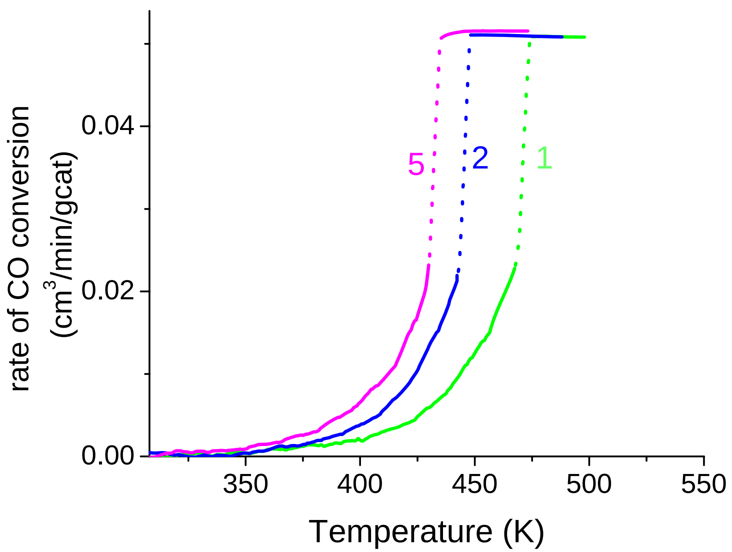
ratio O_2 / CO = 1



ratio O_2 / CO = 2

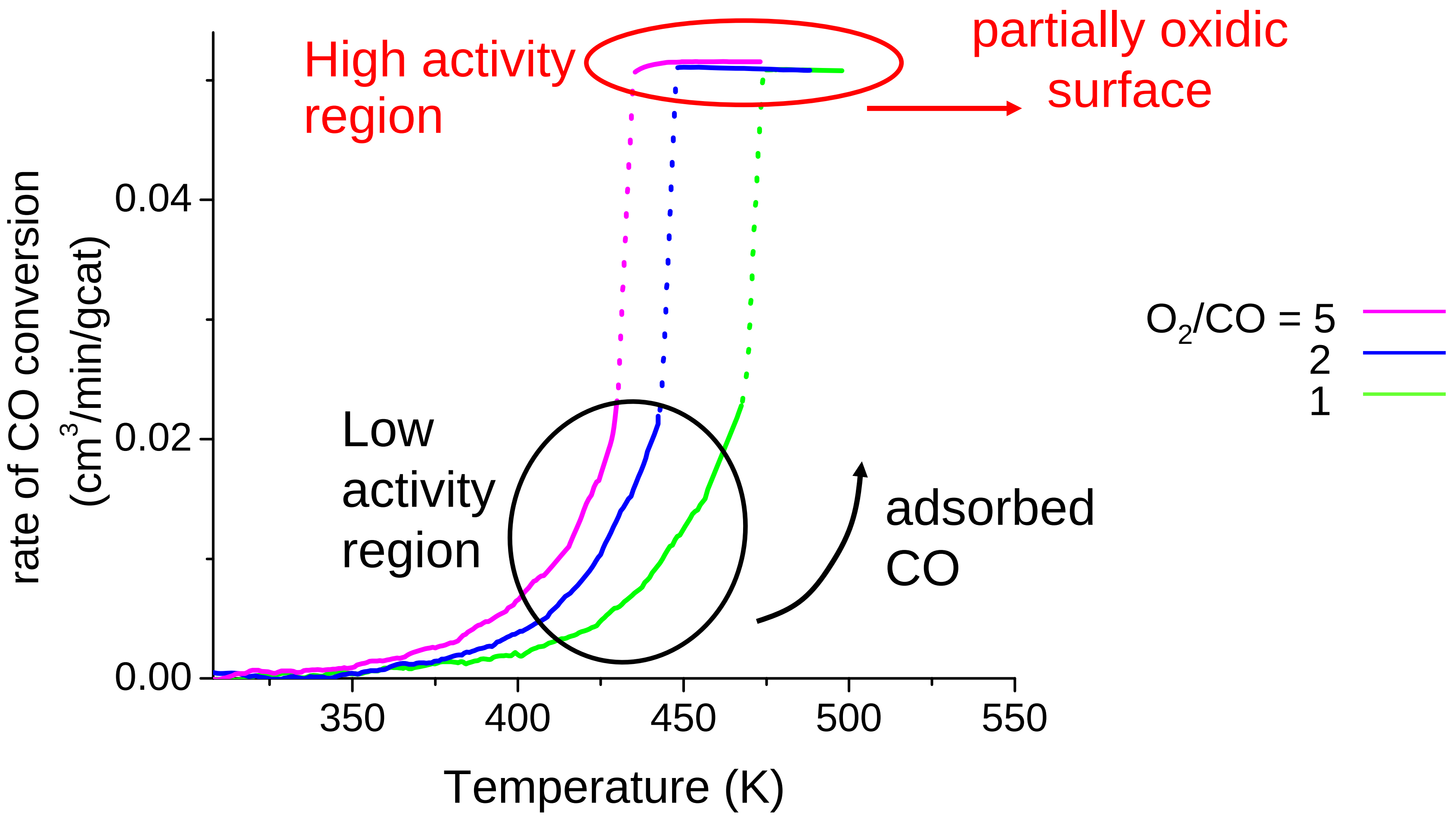




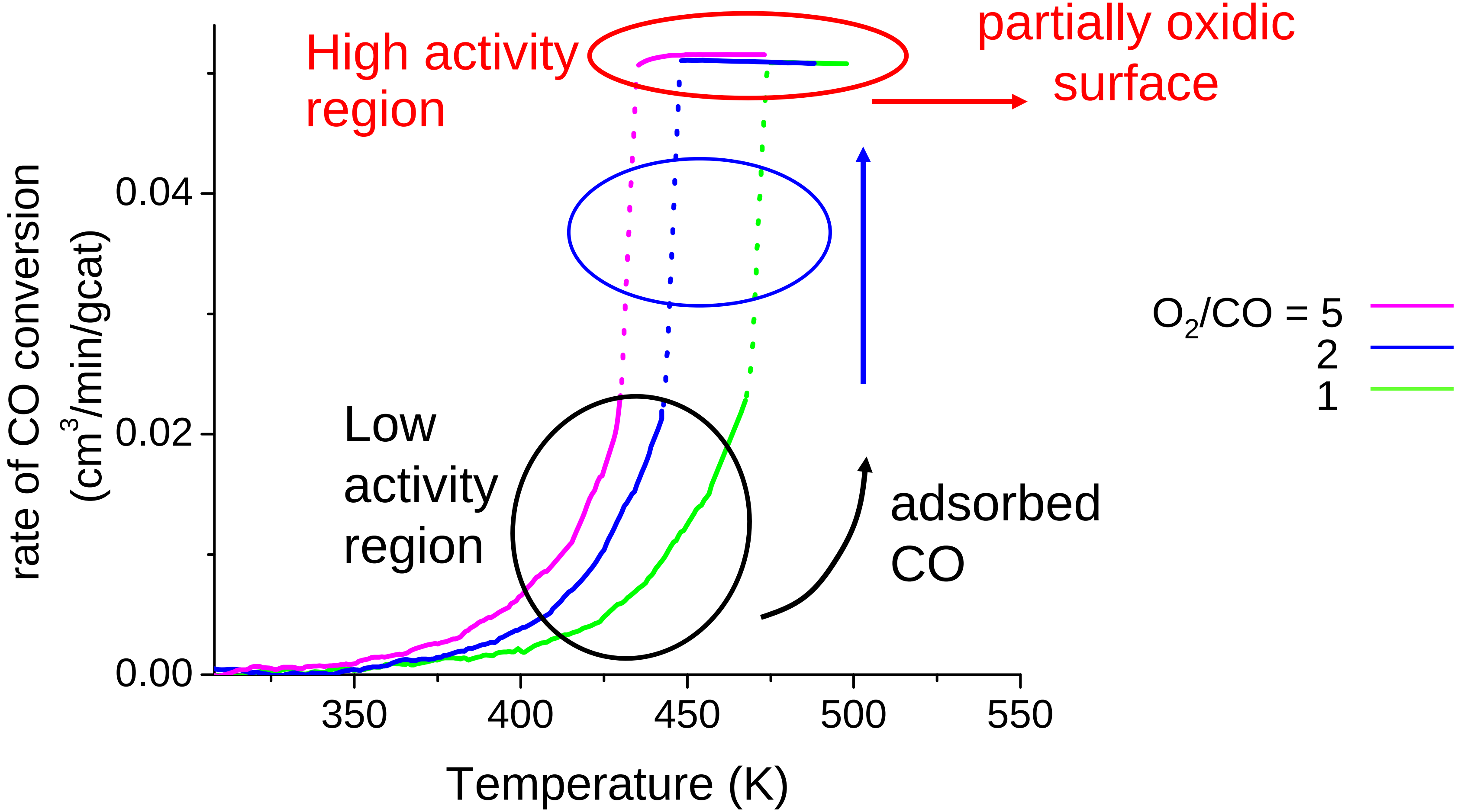


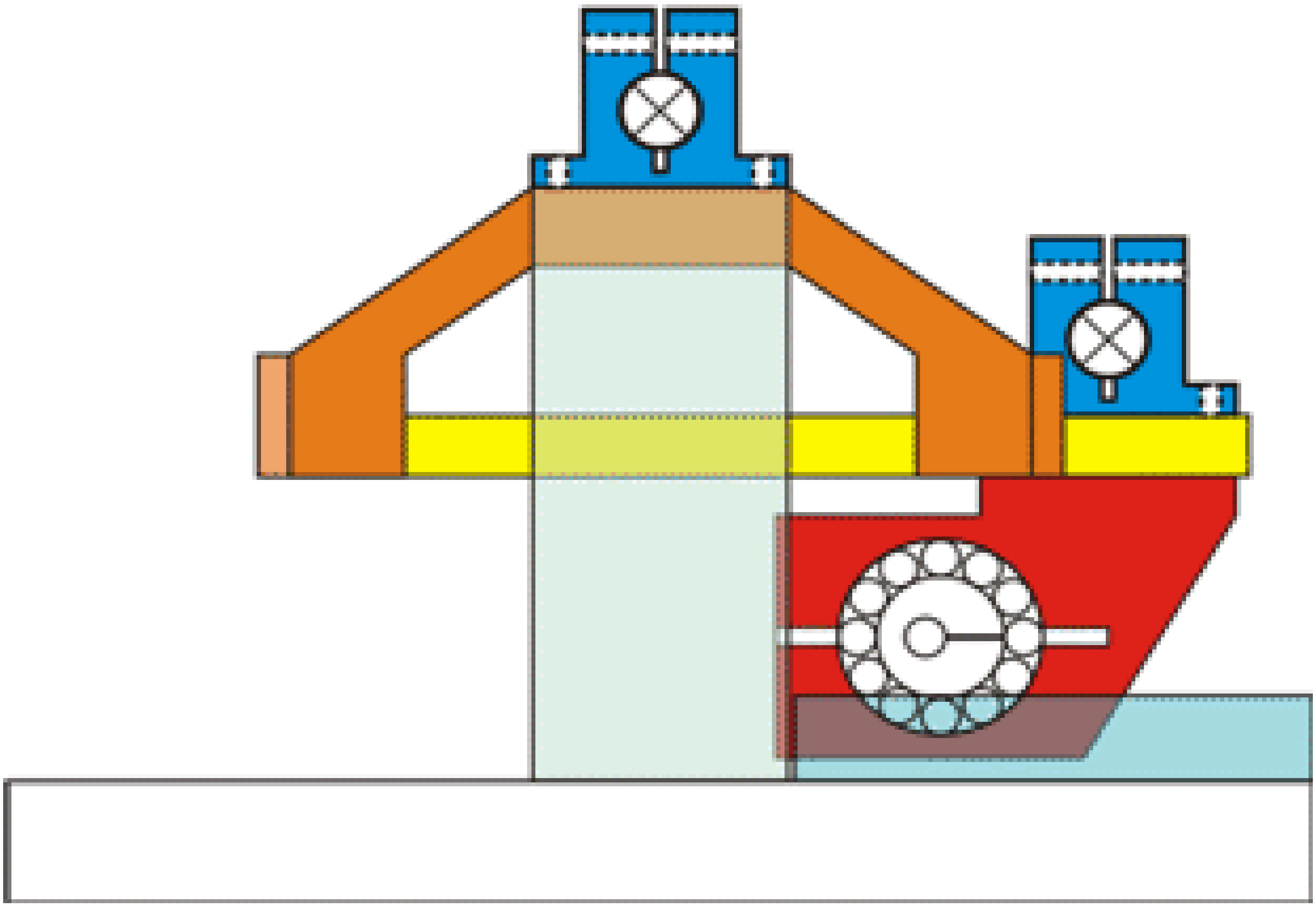
oxidation parallels ignition

Kinetics and XAS



Kinetics and XAS

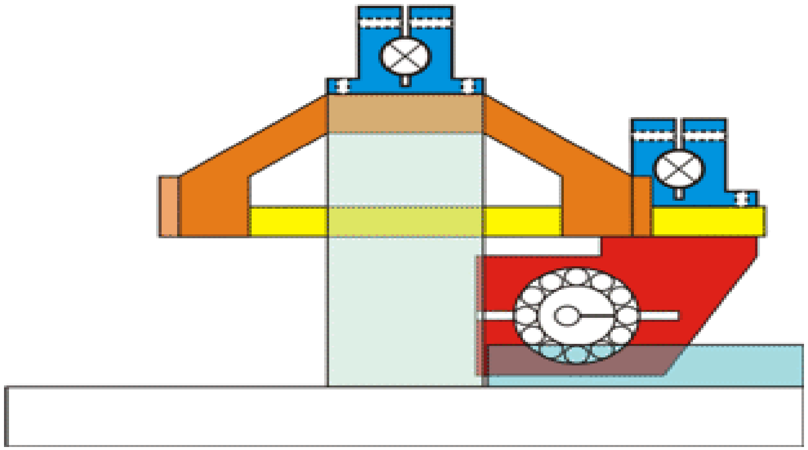


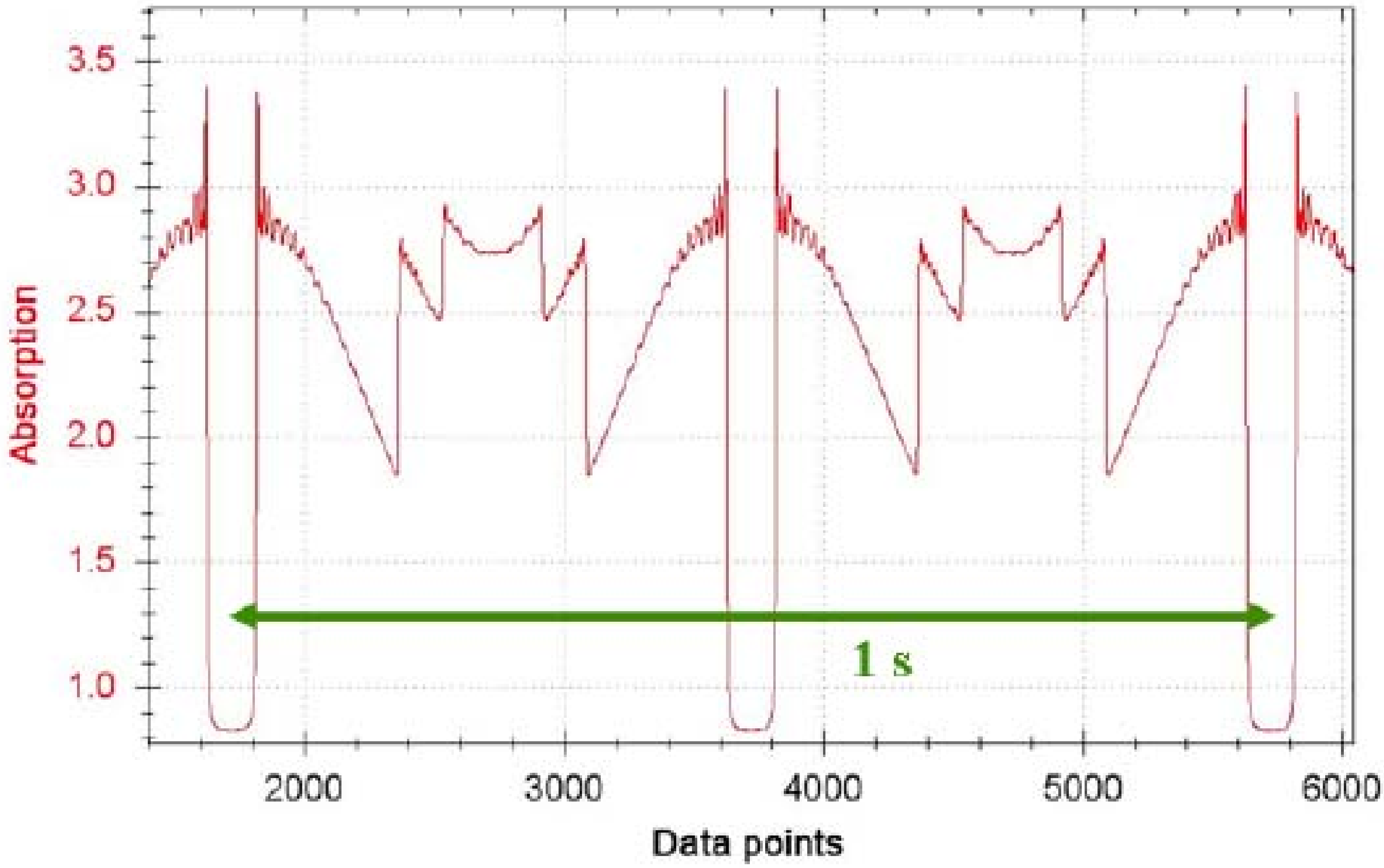


Qexafs signals

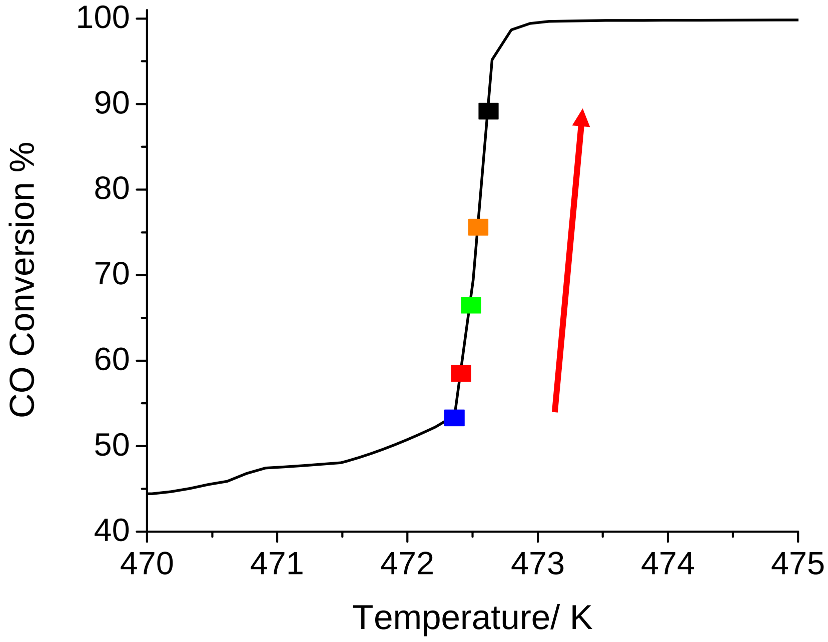
Pt foil

L_3, L_2, L_1 edges

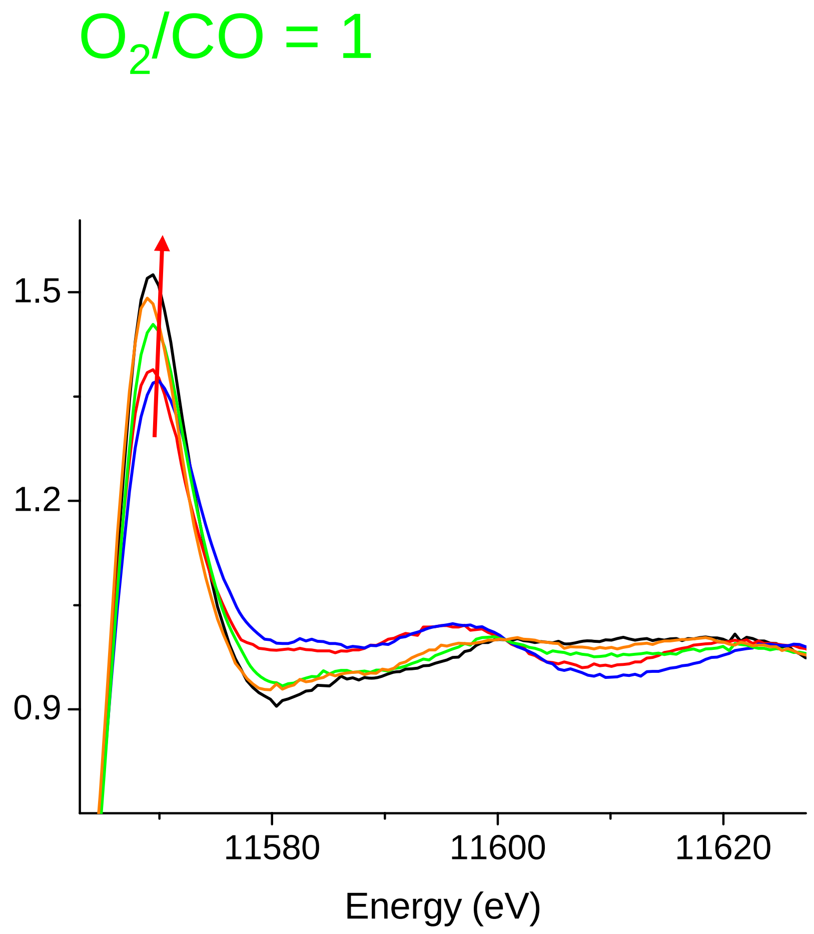




XAS (QEXAFS)

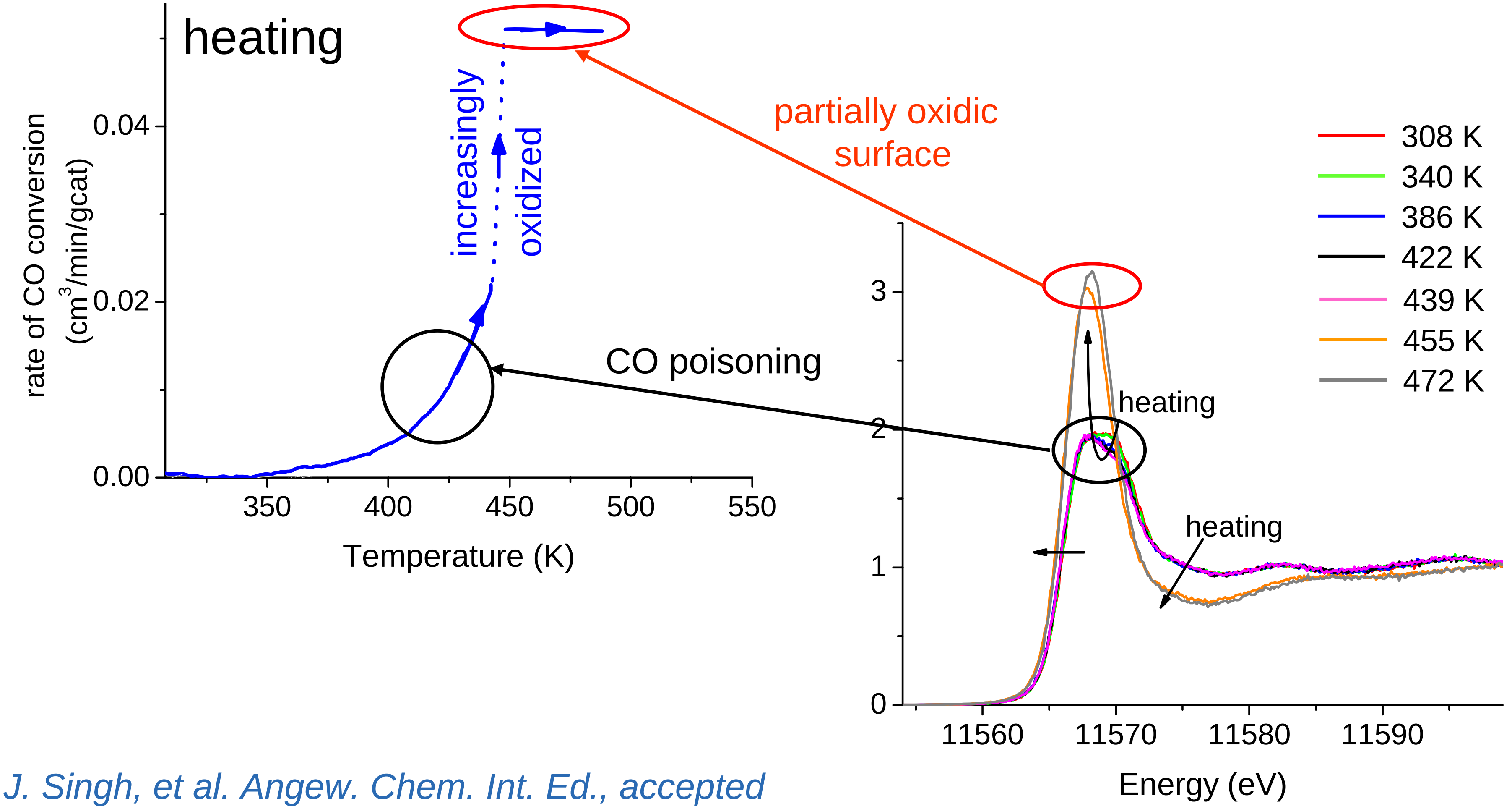


100
90
80
70
60
50
40
CO Conversion %
470
471
472
473
474
475
Temperature/ K



O2/CO = 1
1.5
1.2
0.9
11580
11600
11620
Energy (eV)

Kinetics and XAS

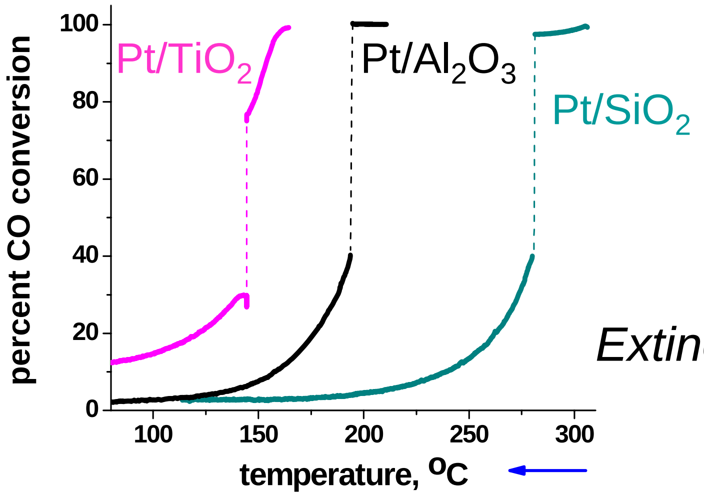


J. Singh, et al. Angew. Chem. Int. Ed., accepted

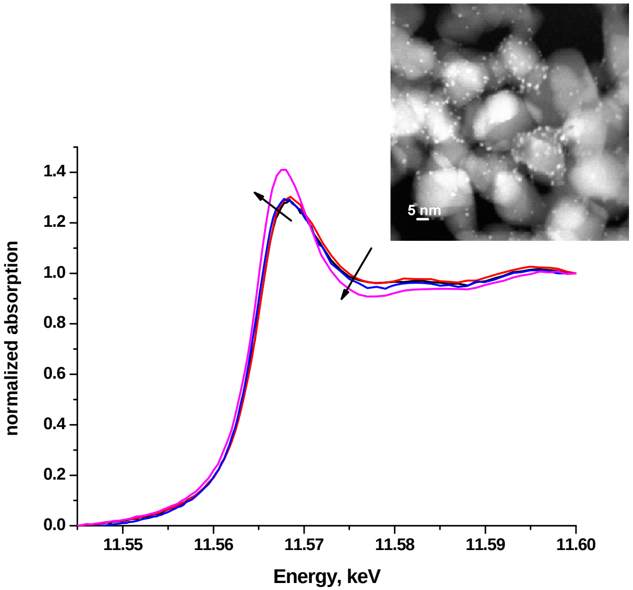
Conclusions

- a highly active state of the catalyst is discovered
- the catalyst shows different structure in low- and high-activity regime; low-activity region : CO adsorbed on platinum, high-activity region: partially oxidized platinum
- the catalyst increasingly oxidizes during the ignition
- high temperature and a high oxygen concentration benefit the formation of the more active partially oxidic catalyst.

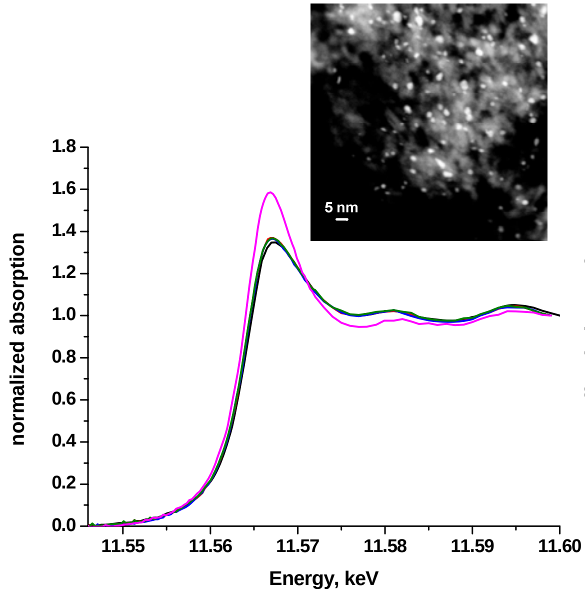
Other supports
(normal XAS)



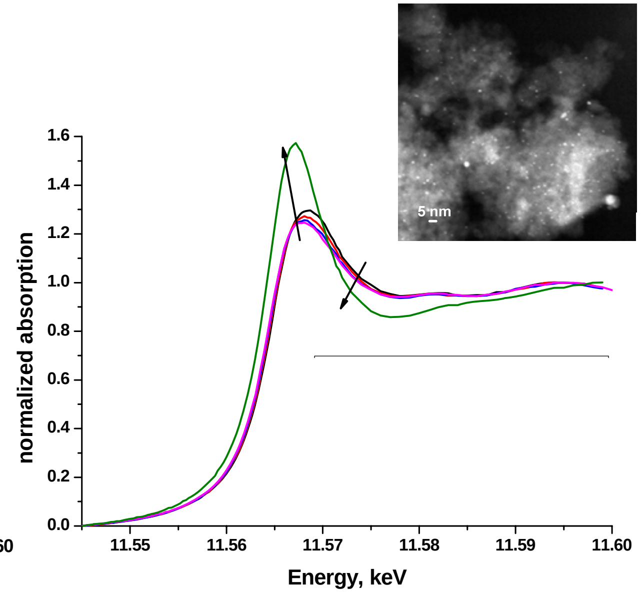
Extinction plots



TiO_2, 1.3 nm

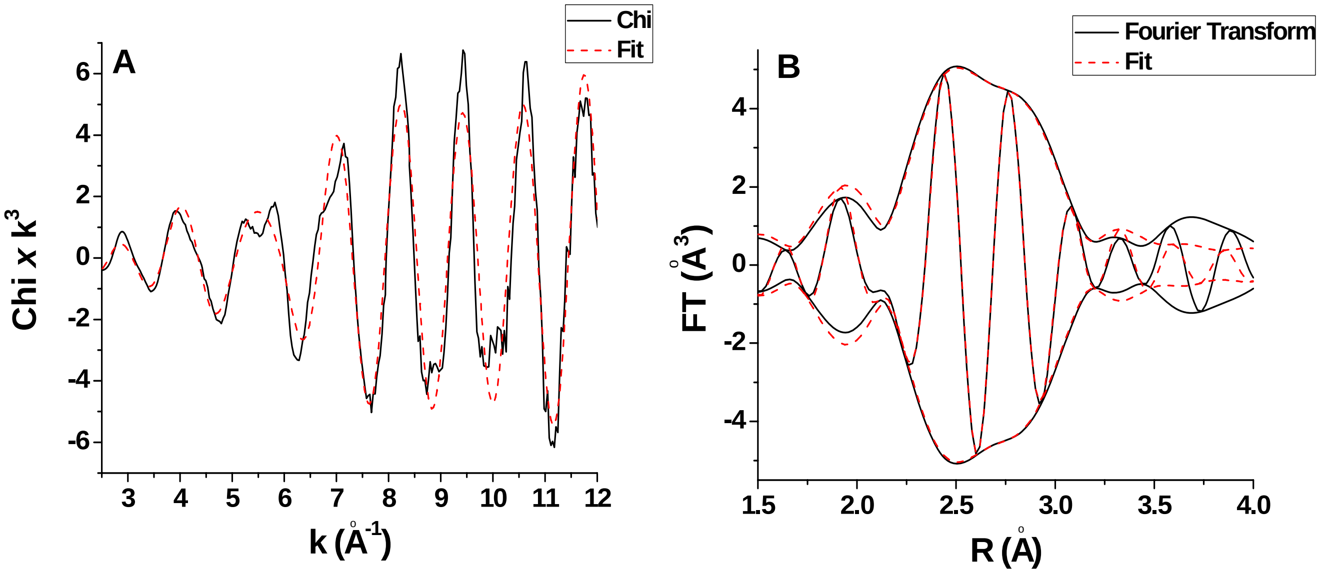


Pt/Al_2O_3L, 2 nm



SiO_2, 1.5-3 nm

EXAFS analysis
Below and above temperature of ignition

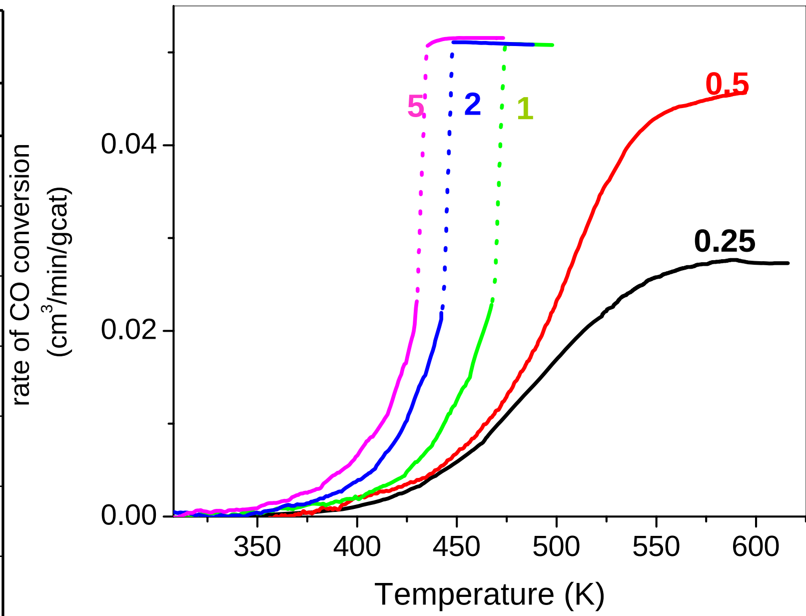


K^3 weighted CHI and Fourier transform
2.5 < k < 12 Å^{-1}
Pt/Al_2O_3L reduced, hydrogen removed; He (RT)

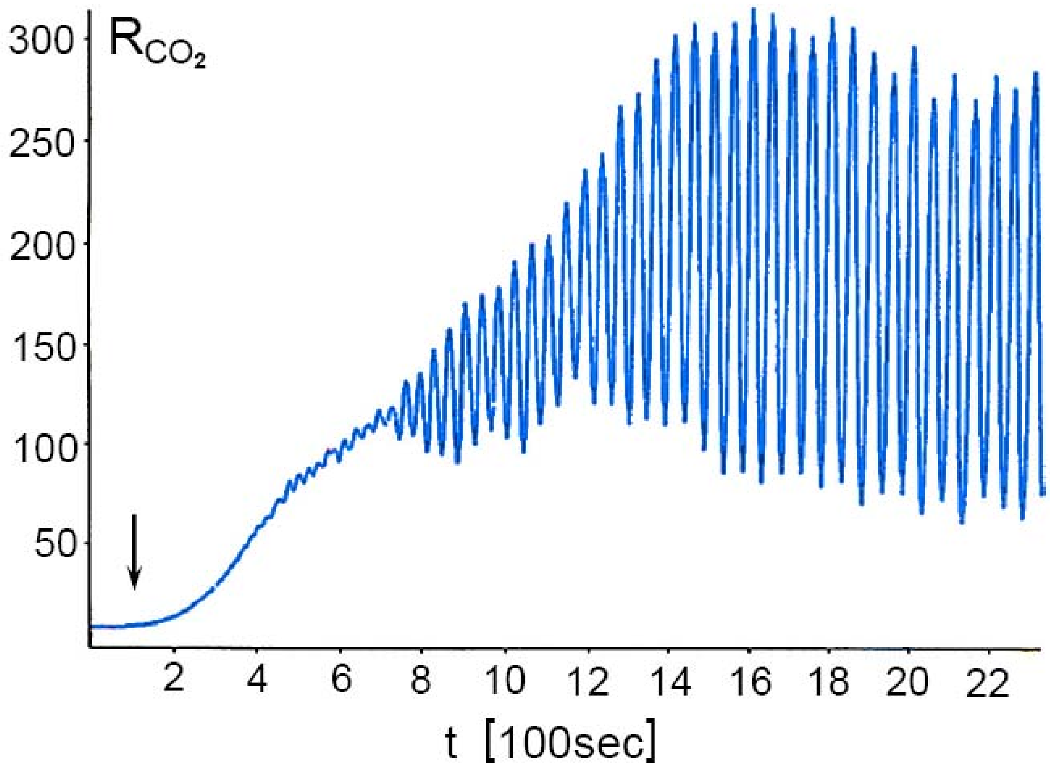
EXAFS analysis

Pt /Al_2O_3 small particles

Conditions	atom	N	DW	R(Å)	Eo
RT, He	Pt	5.7	0.0042	2.72	1.68
below ignition	Pt	6.2	0.0054	2.77	0.58
above ignition	O	2.4	0.0021	1.99	4.36
	Pt	3.0	0.0065	2.61	7.19
RT, O_2/CO	Pt	5.6	0.0039	2.76	1.87



Kinetic oscillations – Single Crystals

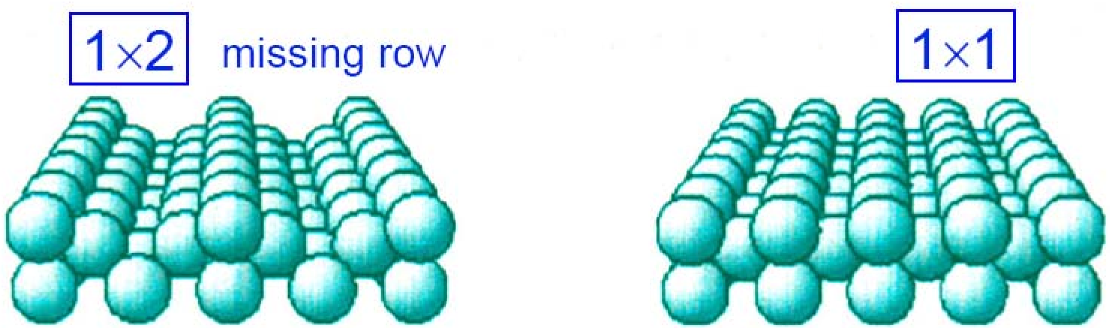


T = 470K
p_{CO}= 3×10^{-5}mbar
p_{O2}= 2.0→2.7×10^{-4}mbar

Pt (110)

M. Eiswirth and G. Ertl, Surface Sci. ***177*** *(1986), 90*

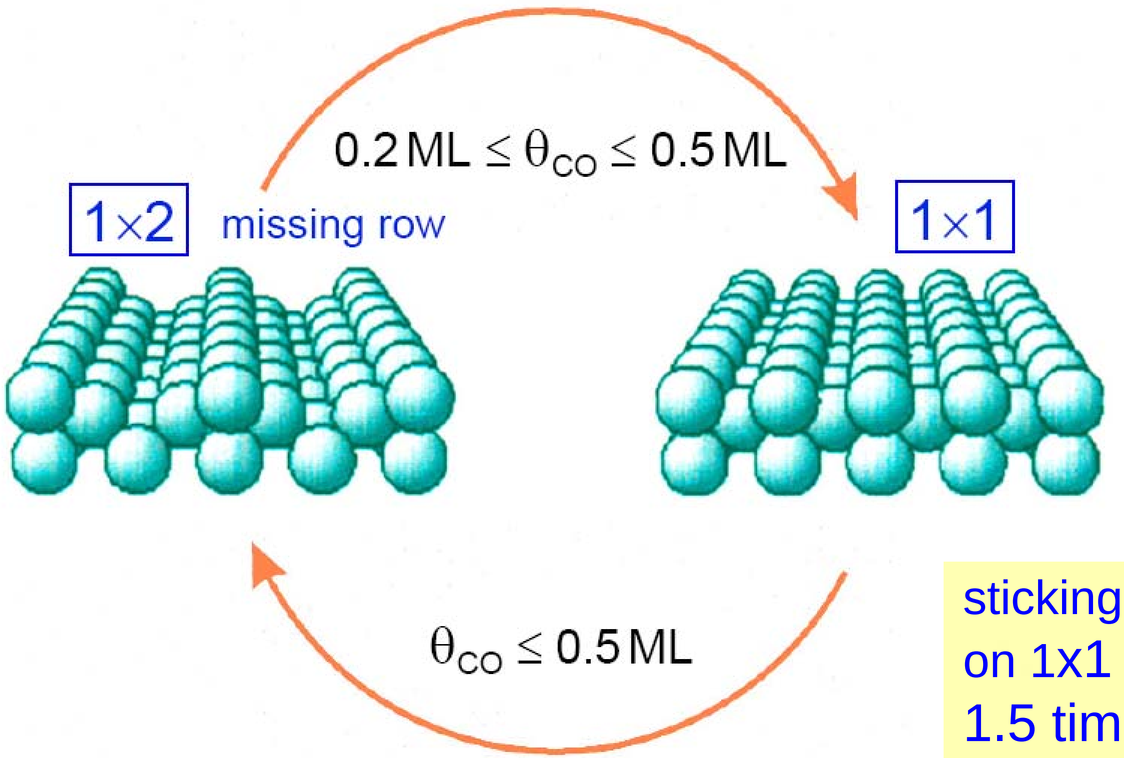
Kinetic oscillations – Single Crystals



bulk crystal plane

Pt (110)

Kinetic oscillations – Single Crystals



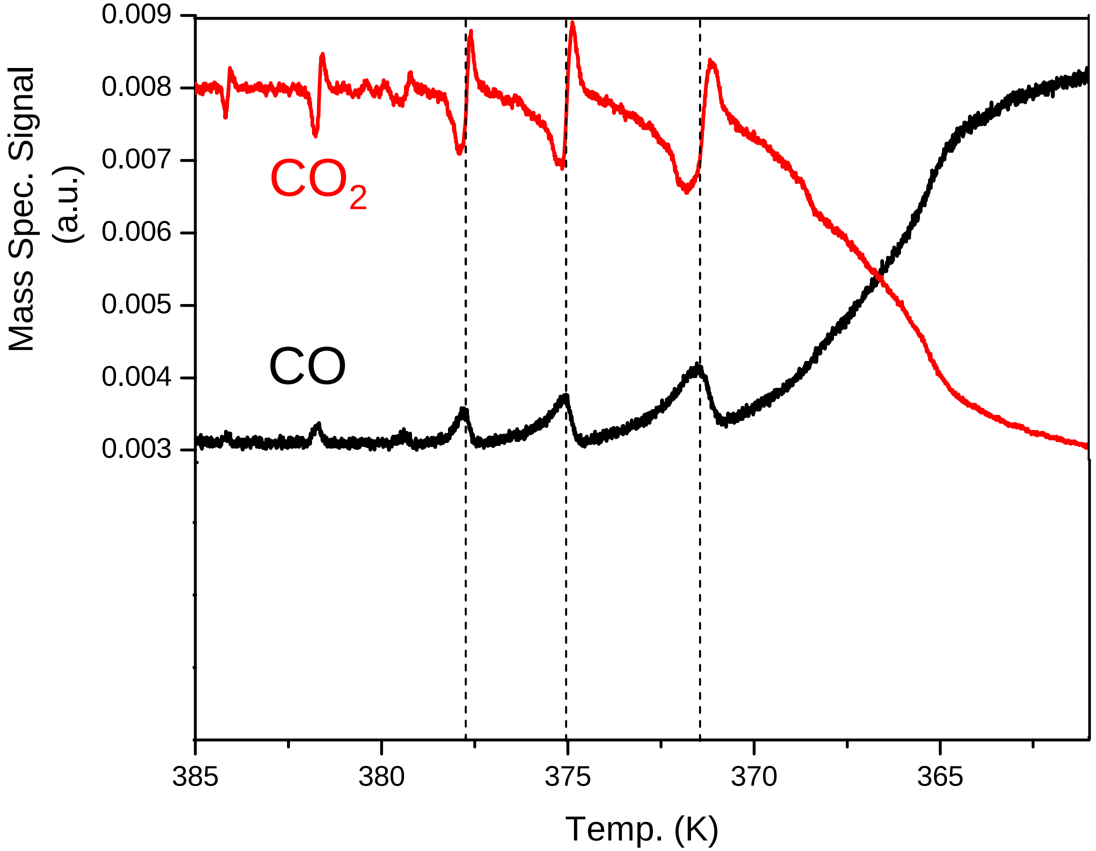
lower adsorption energy of CO

higher adsorption energy of CO

sticking coefficient of O on 1x1 is about 1.5 times than on 1x2

T. Gritsch et al. Phys. Rev. Lett. ***63*** *(1989) 1086*
N. Freyer et al. Surface Sci. ***166*** *(1986) 206*

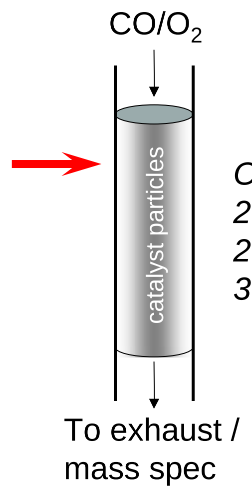
Kinetic oscillations - 2wt% Pt/Al_2O_3



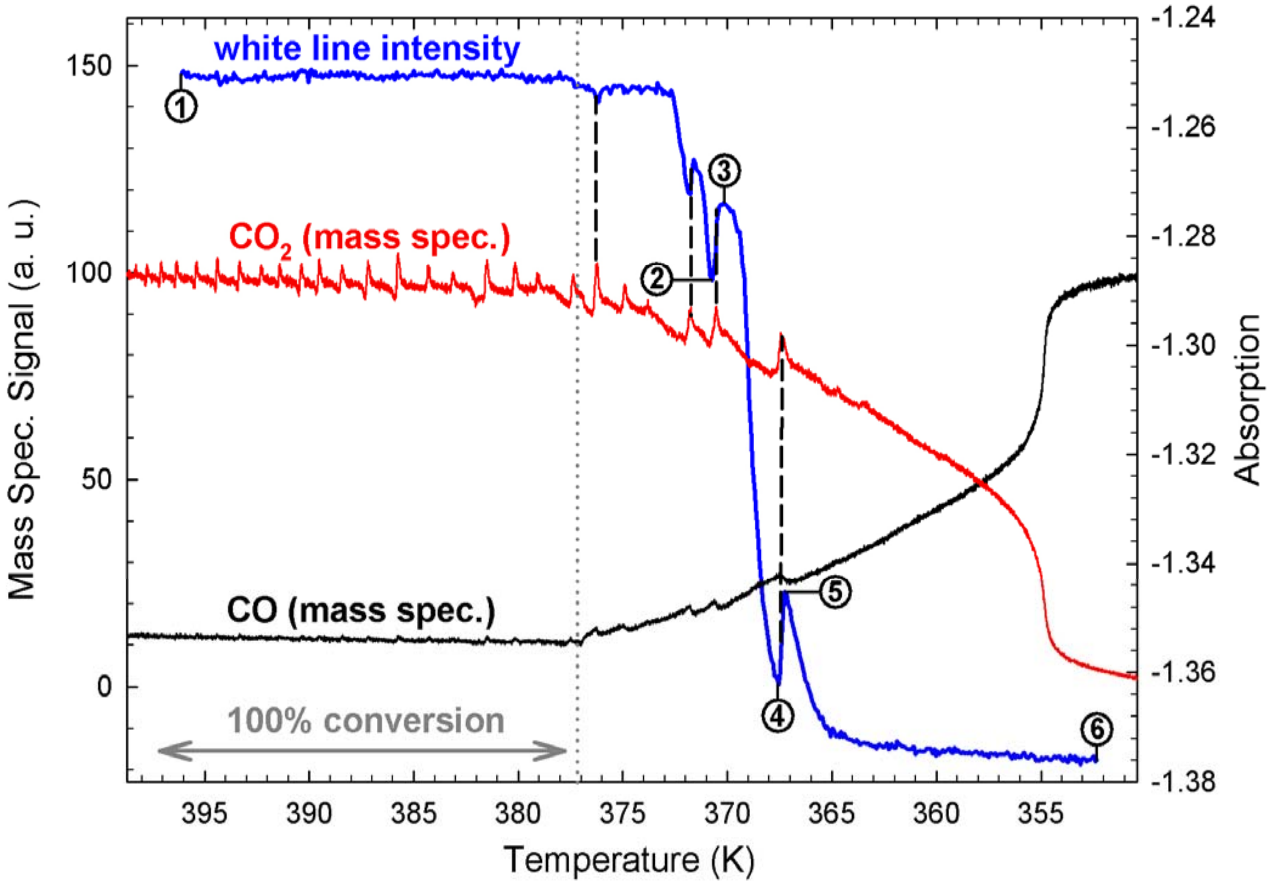
- storage of CO that is released in sudden spike of CO_2

- CO poisoning; activity inversely proportional to adsorbed CO

Kinetic Oscillations and QEXAFS



O_2 : CO = 19
2 wt% Pt/Al_2O_3
20 mg catalyst
30 ml/min



- activity loss due to reduction of active (oxidized) surface
- sudden increase in activity parallels oxidation of surface

kinetic oscillations originate from

the reduction and re-oxidation

of the surface

Best of luck for your exams ☺

Data Analysis: Statistical Considerations

R-Factor	Absolute misfit between data and theory
χ^2	Function minimised in fitting algorithms
red χ^2	minimised function scaled by degrees of freedom

$$N_{ind} = \frac{2 \cdot \Delta k \, \Delta R}{\pi} + 1$$

EXAFS error margins:

N ± 0.5 20%

R ± 0.01 – 0.03

σ^2 ± 20%