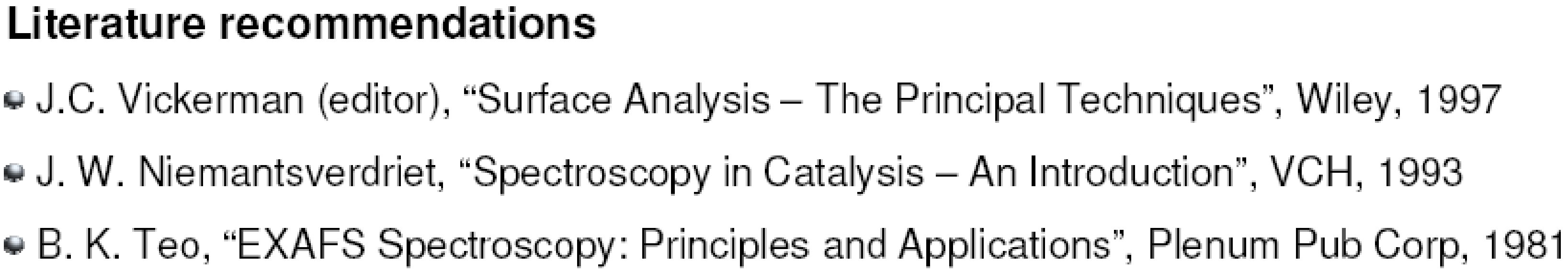
X-ray absorption spectroscopy



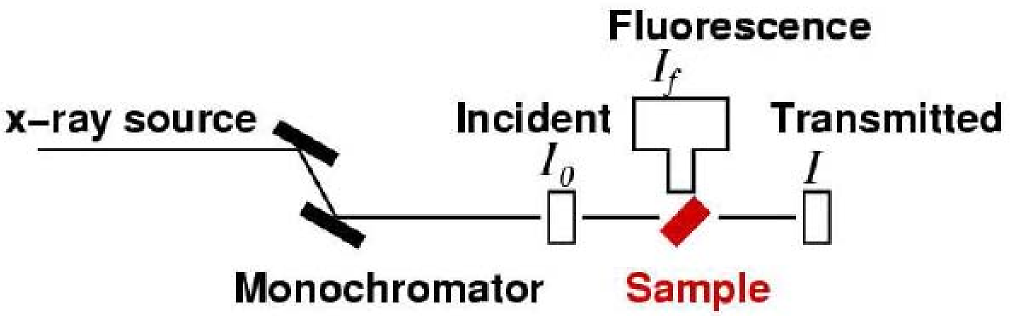
Literature recommendations

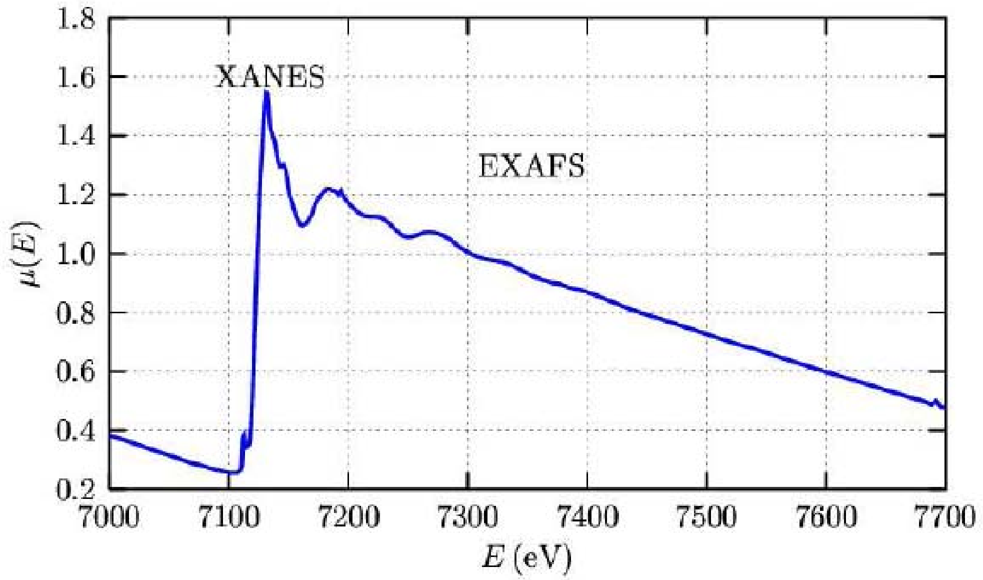
- J.C. Vickerman (editor), “Surface Analysis – The Principal Techniques”, Wiley, 1997
- J. W. Niemantsverdriet, “Spectroscopy in Catalysis – An Introduction”, VCH, 1993
- B. K. Teo, “EXAFS Spectroscopy: Principles and Applications”, Plenum Pub Corp, 1981

Jagdeep Singh

Jeroen A. van Bokhoven

What is XAS?

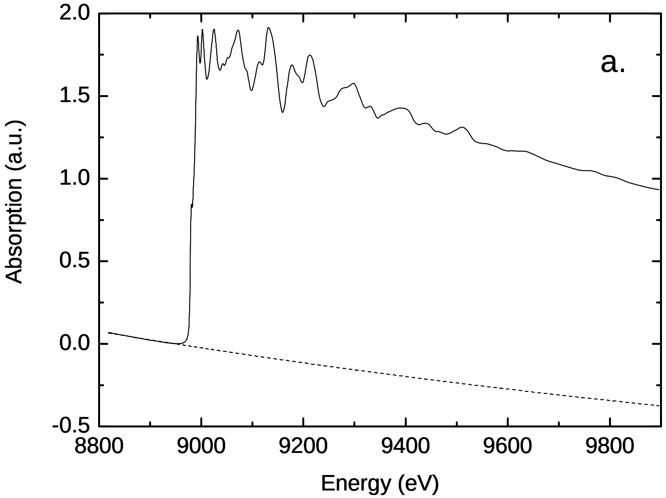




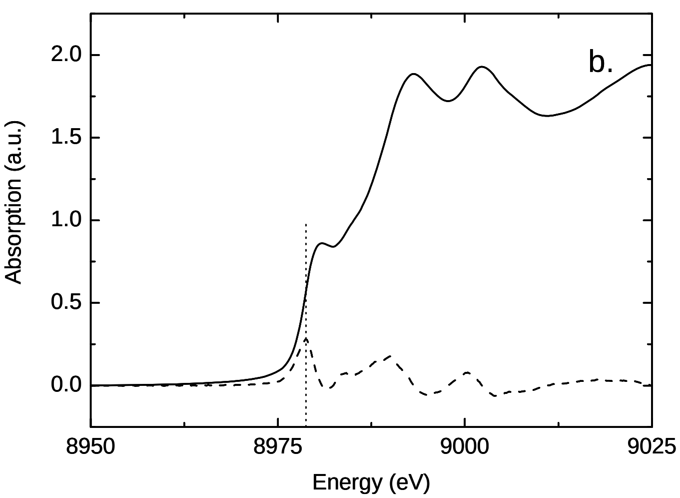
Absorption as function of energy of the x-ray

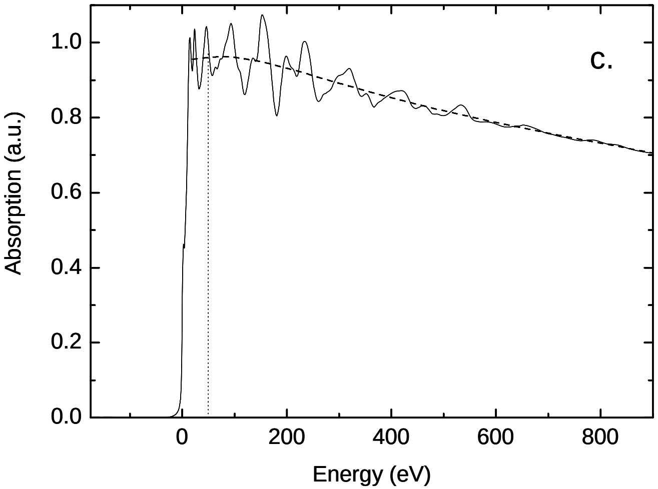
Data-analysis

Pre-edge subtraction

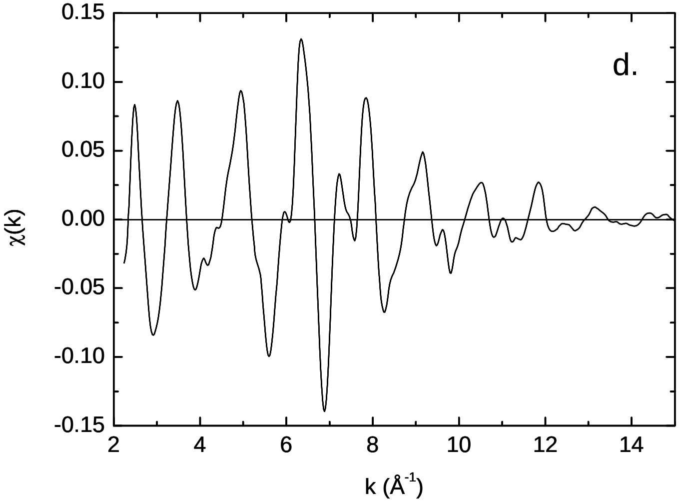


Edge energy determination





Background and Normalization



EXAFS Function

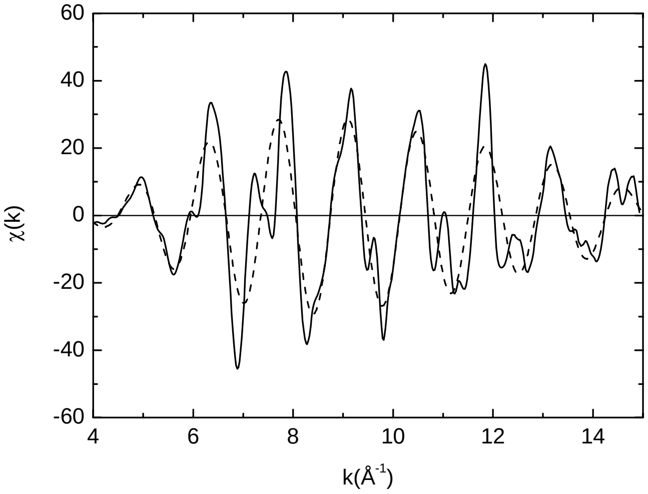
EXAFS formula

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

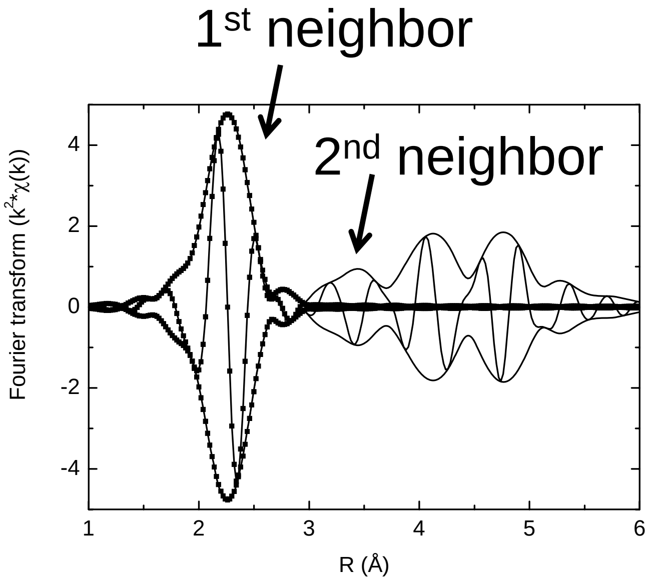
Scatter power

Damping

Disorder



Fourier transformation →


1st neighbor

2nd neighbor

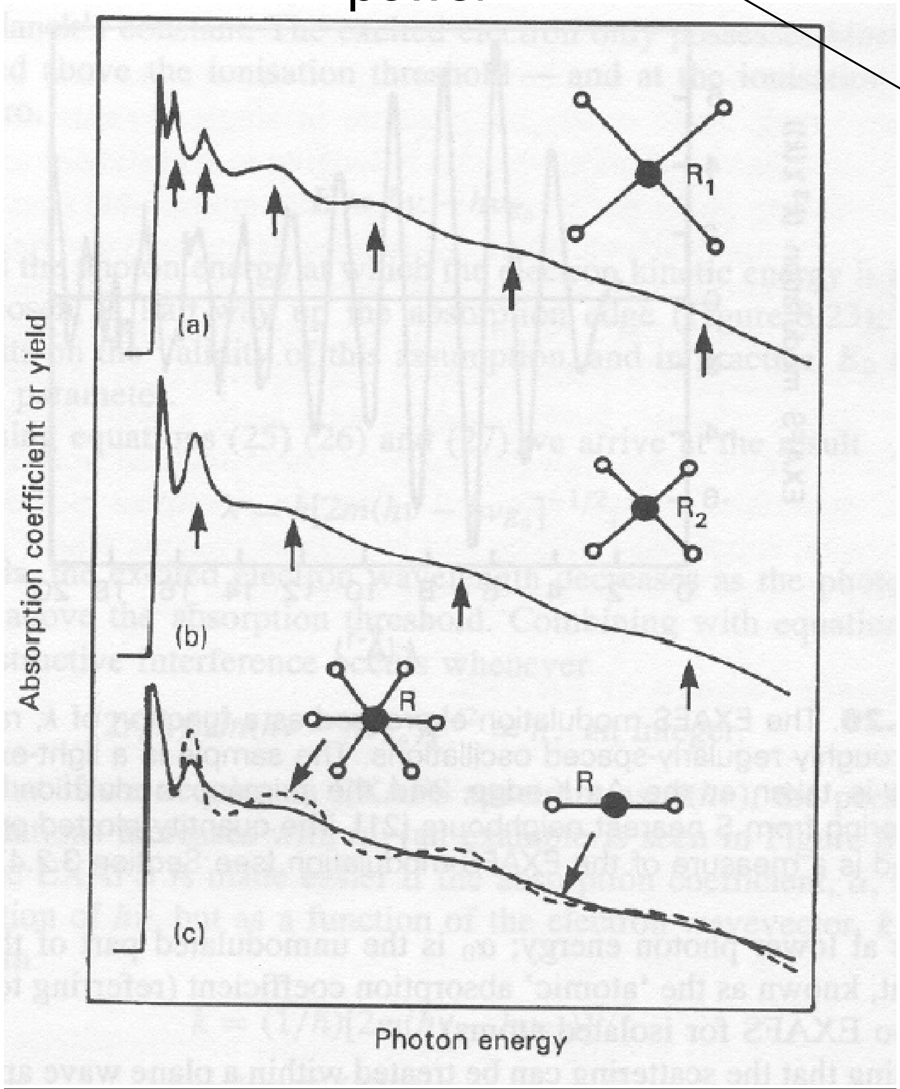
radial distribution function

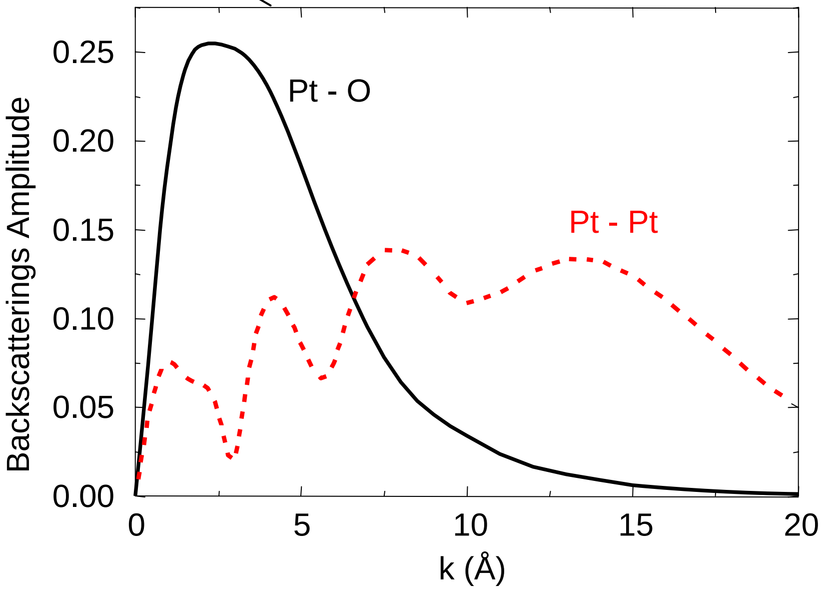
$$\chi(k) = \sum_i N_i F_i(k) \frac{S_0^2}{kR_i^2} \exp\left(\frac{-2R_i}{\lambda}\right) \exp\left(-2\sigma_i^2 k^2\right) \sin\left(2kR_i + \varphi_j(k)\right)$$

Scatter power

Damping

Disorder





Temperature effect on EXAFS / XANES

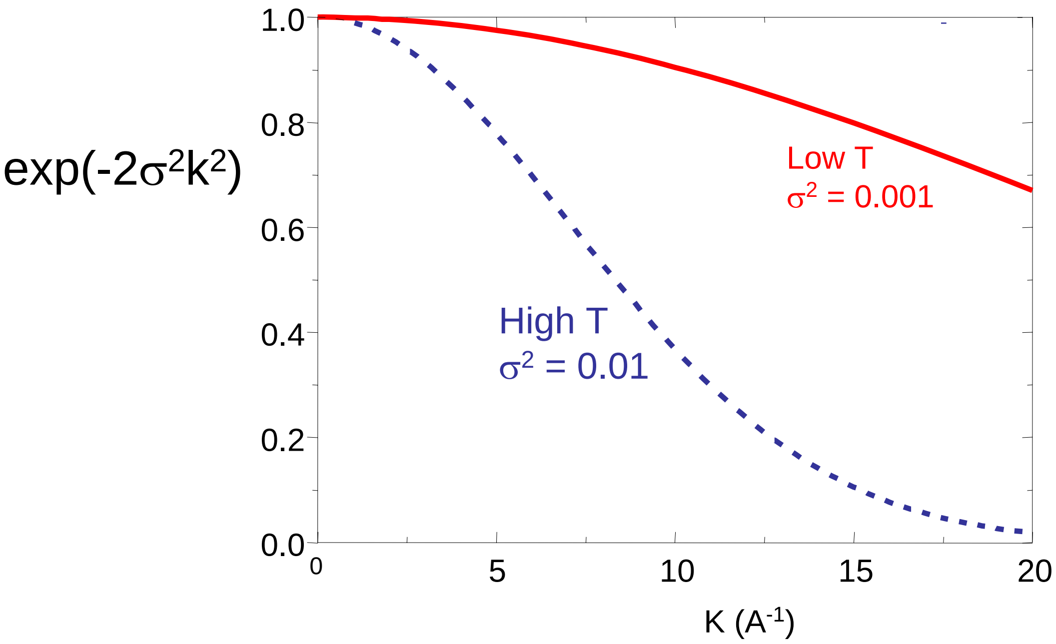
$$\chi(k)=\sum_i N_i F_i(k)\cdot\frac{S_0^2}{kR_i^2}\cdot\exp\left(\frac{-2R_i}{\lambda}\right)\cdot\exp\left(-2\sigma_i^2k^2\right)\cdot\sin\left(2kR_i+\varphi_j(k)\right)$$

Scatter power

Damping

Disorder

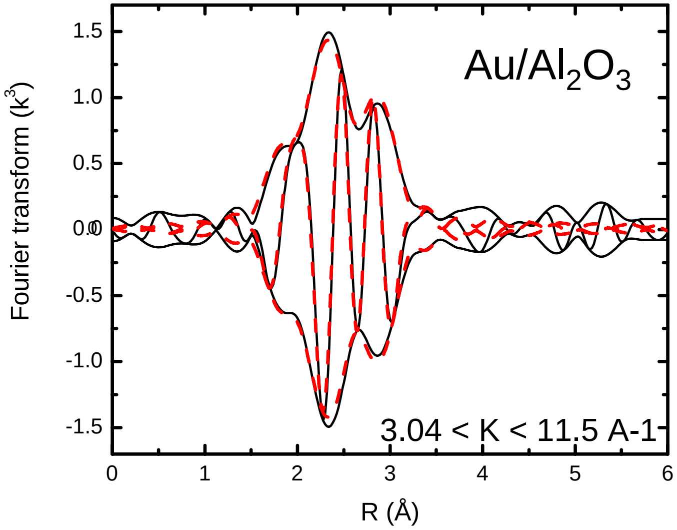
Temperature effect



Getting structural information from EXAFS

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

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



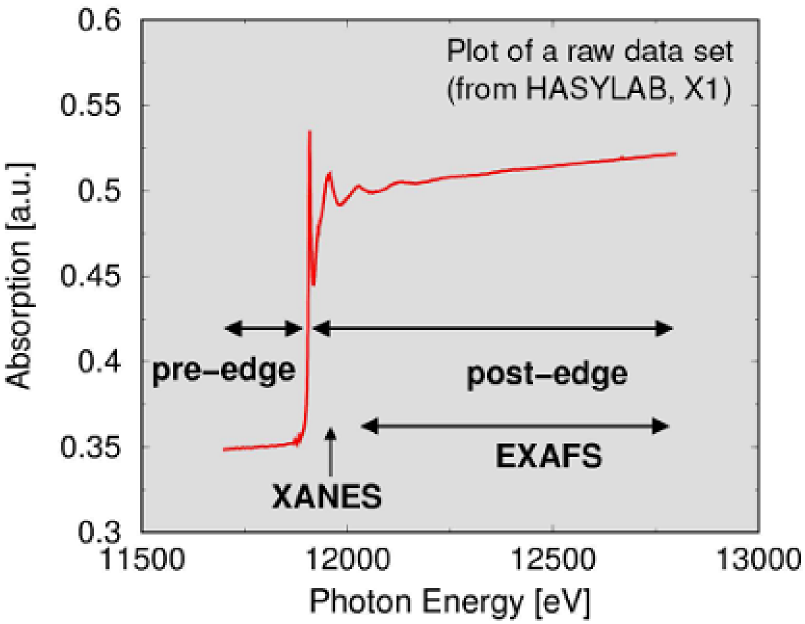
Coordination number	**6.8**
Au-Au distance	**2.76 Å**
ΔDWF	**0.0058**
C3	9 E-6
C4	3E-6

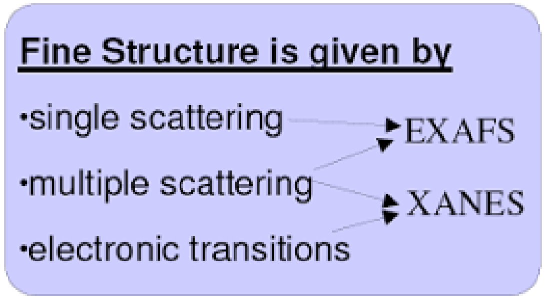
Added parameter: ΔE_0

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

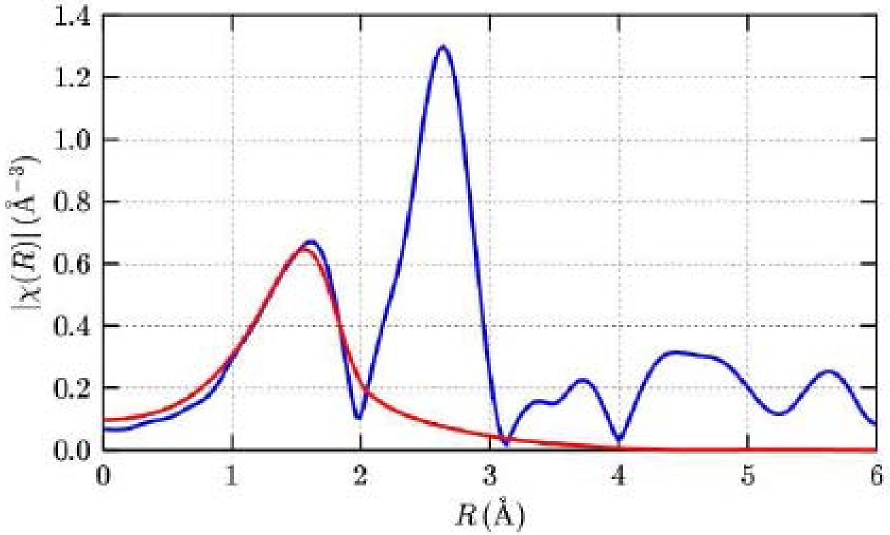
- single scattering → EXAFS
- multiple scattering → EXAFS, XANES
- electronic transitions → XANES

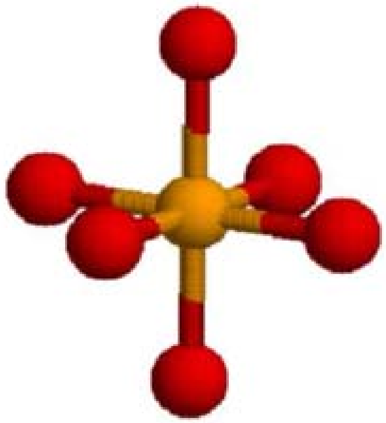
Electronic Information ← → **Structural Information**

- Angular momentum projected DOS
- transition probabilities

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

Data Analysis: Fitting Process 1st coordination shell

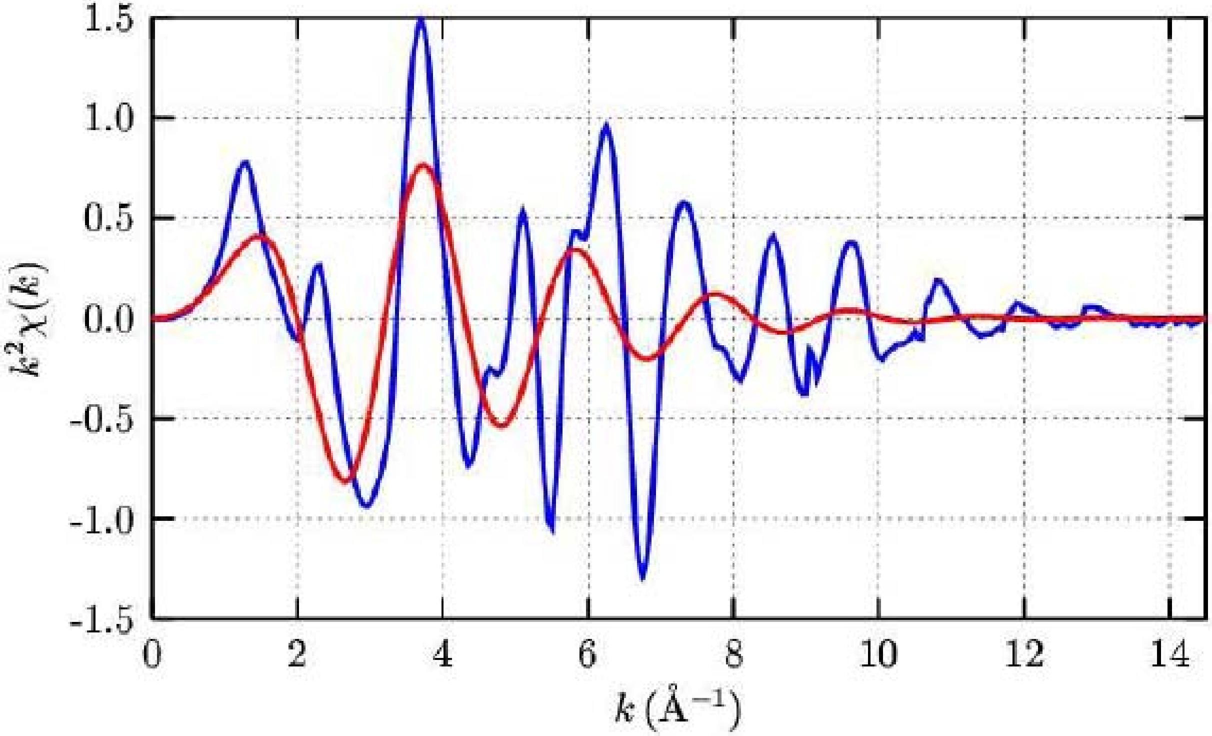




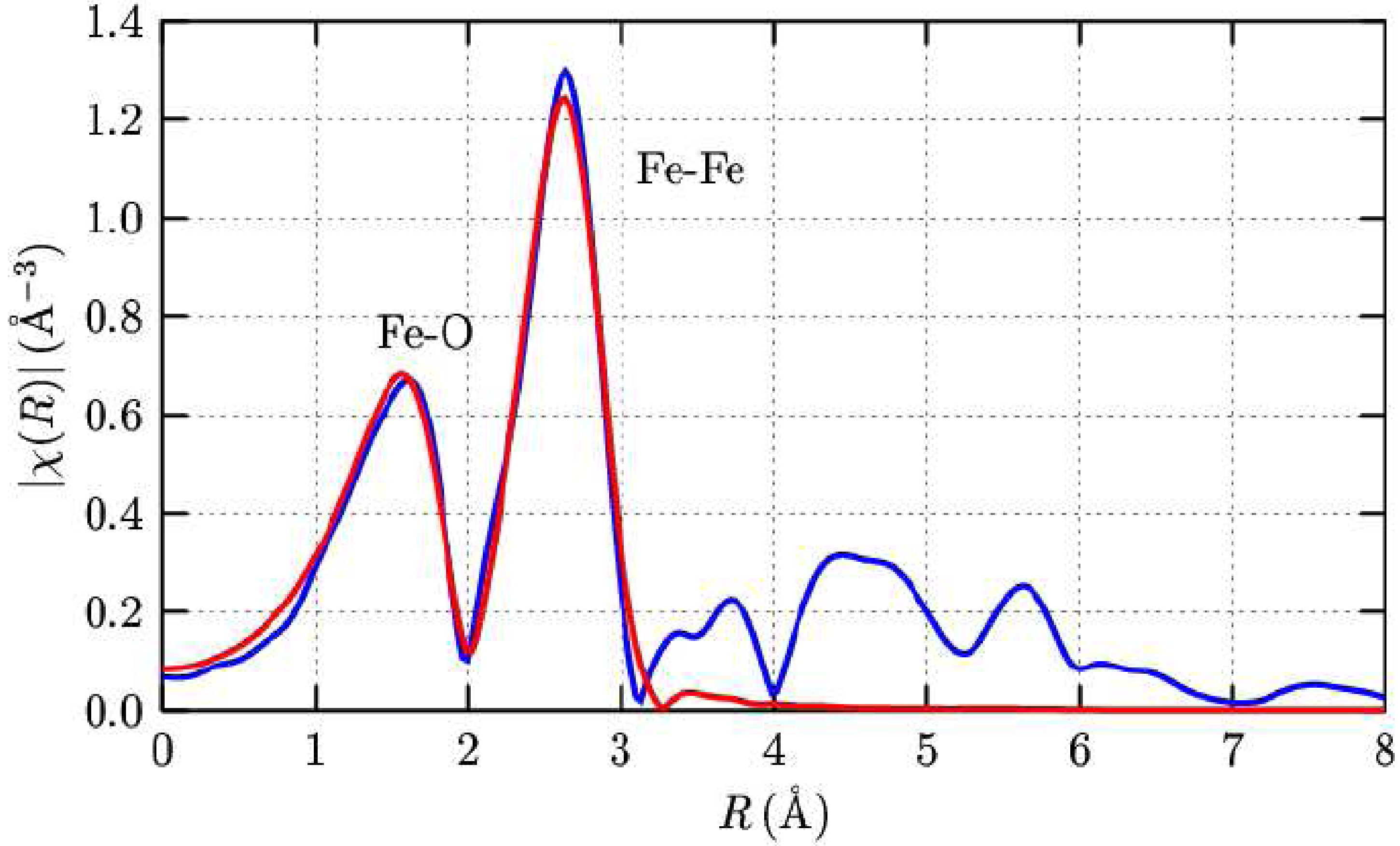
Parameter	Value
N	5.8
R	2.1
ΔE_0	-3.1
σ^2	0.015

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

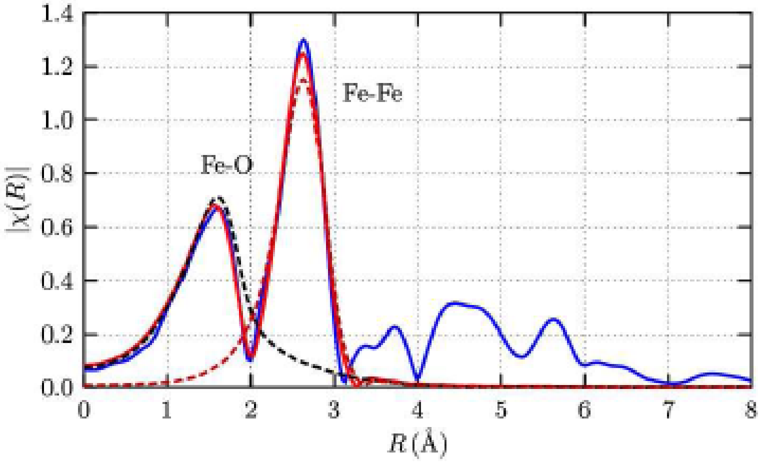
Data Analysis: 1st coordination shell in k-space

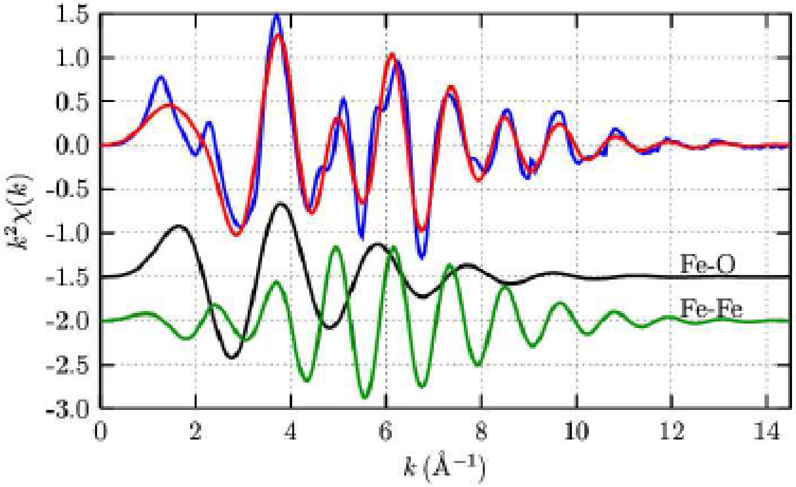


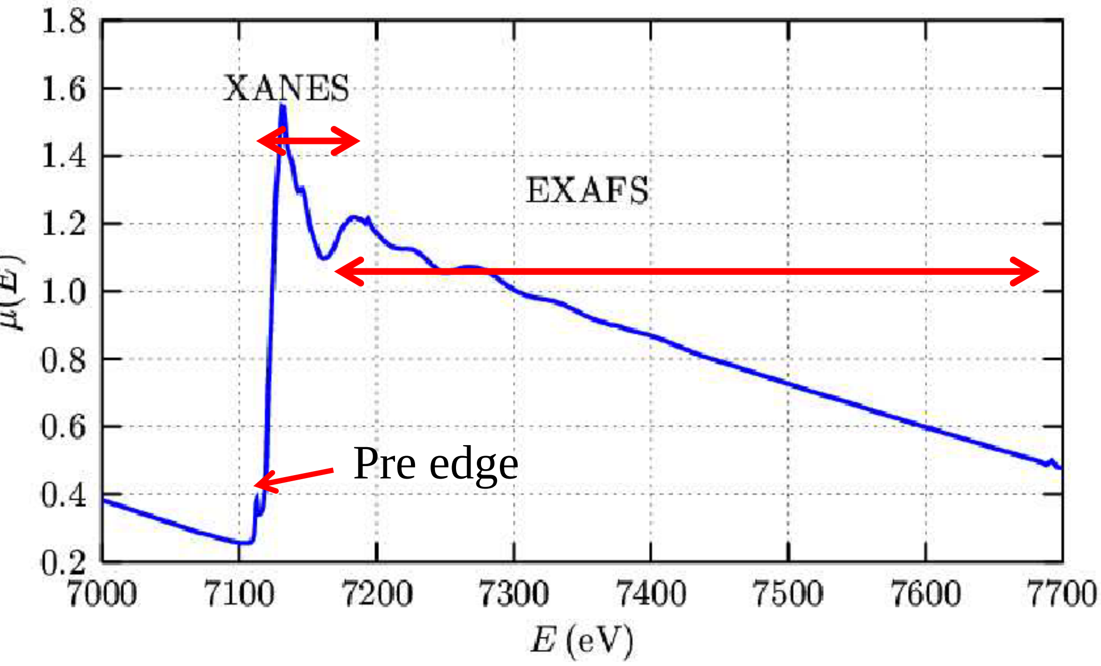
Data Analysis: Adding the 2nd coordination shell

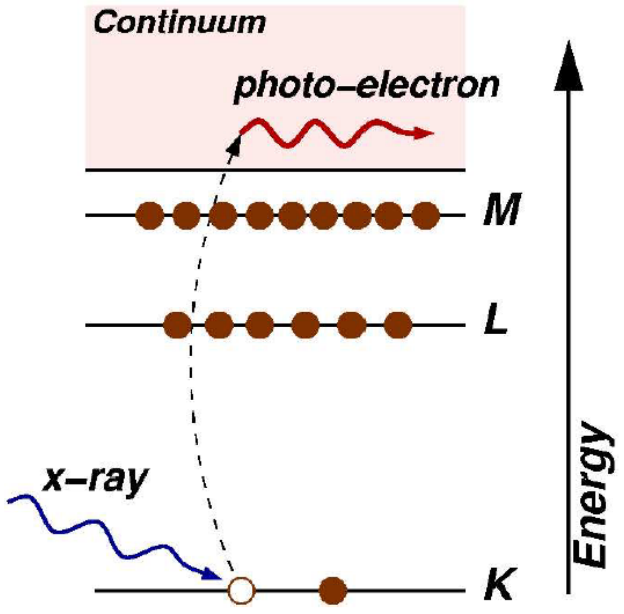


Data Analysis: Other ways of looking at the fit







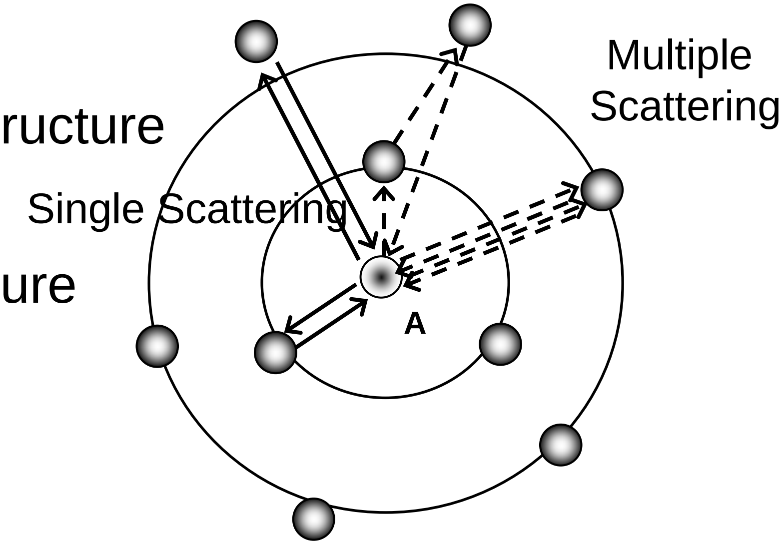


EXAFS (χ) Extended X-ray Absorption Fine-Structure

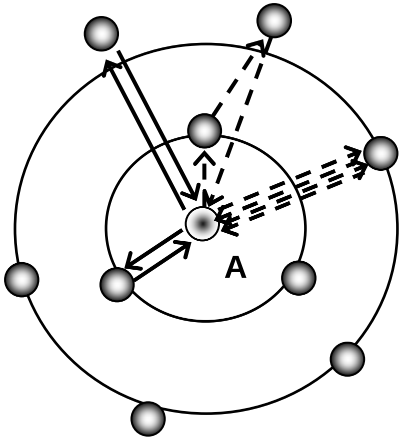
Single scattering

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

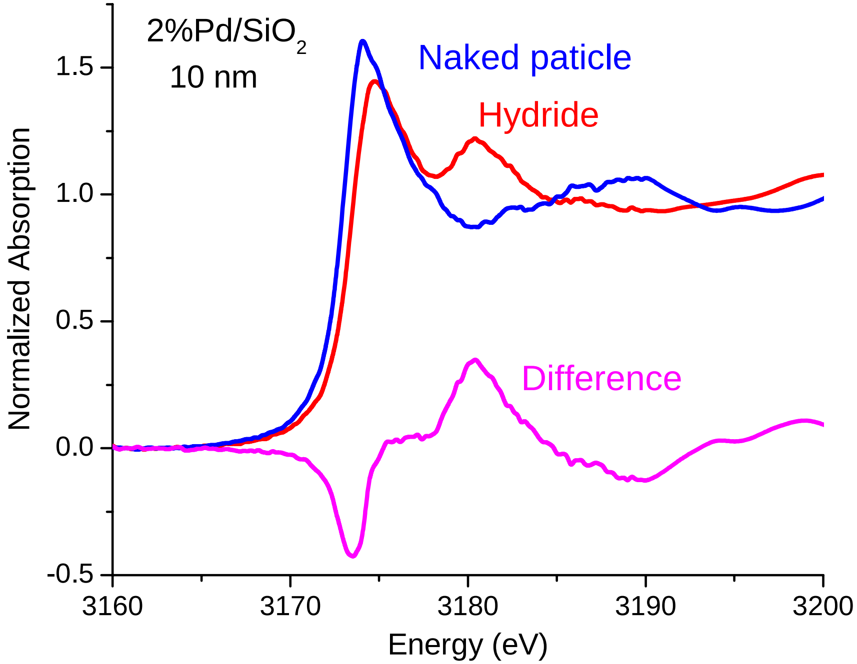
deactivation

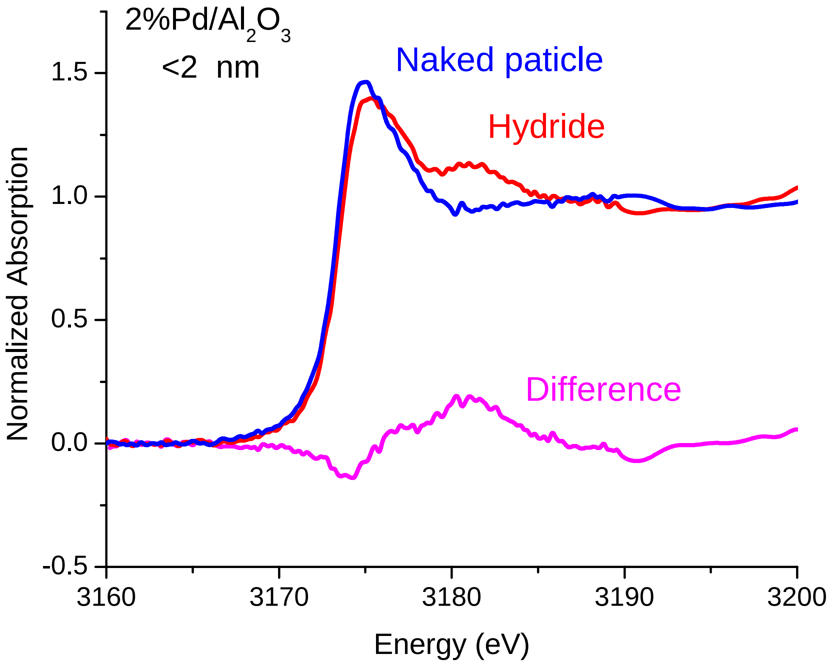
time-resolution (few msec)

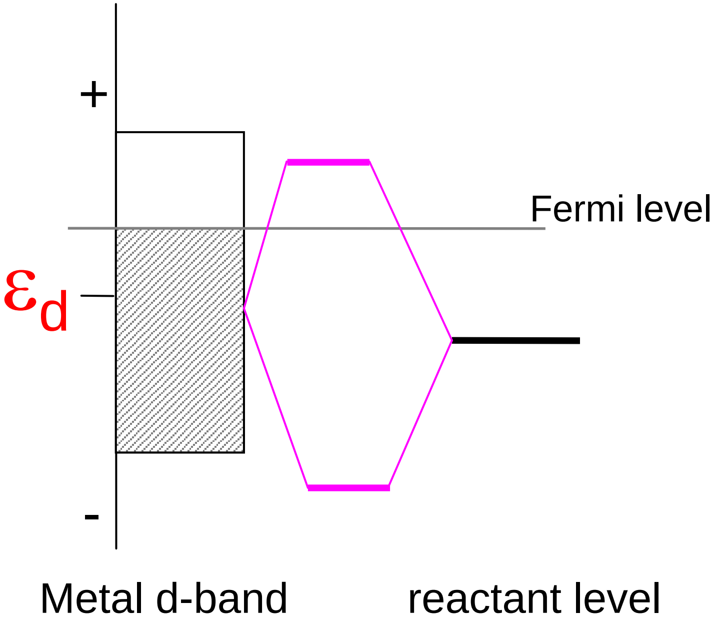
space-resolution (few μm)

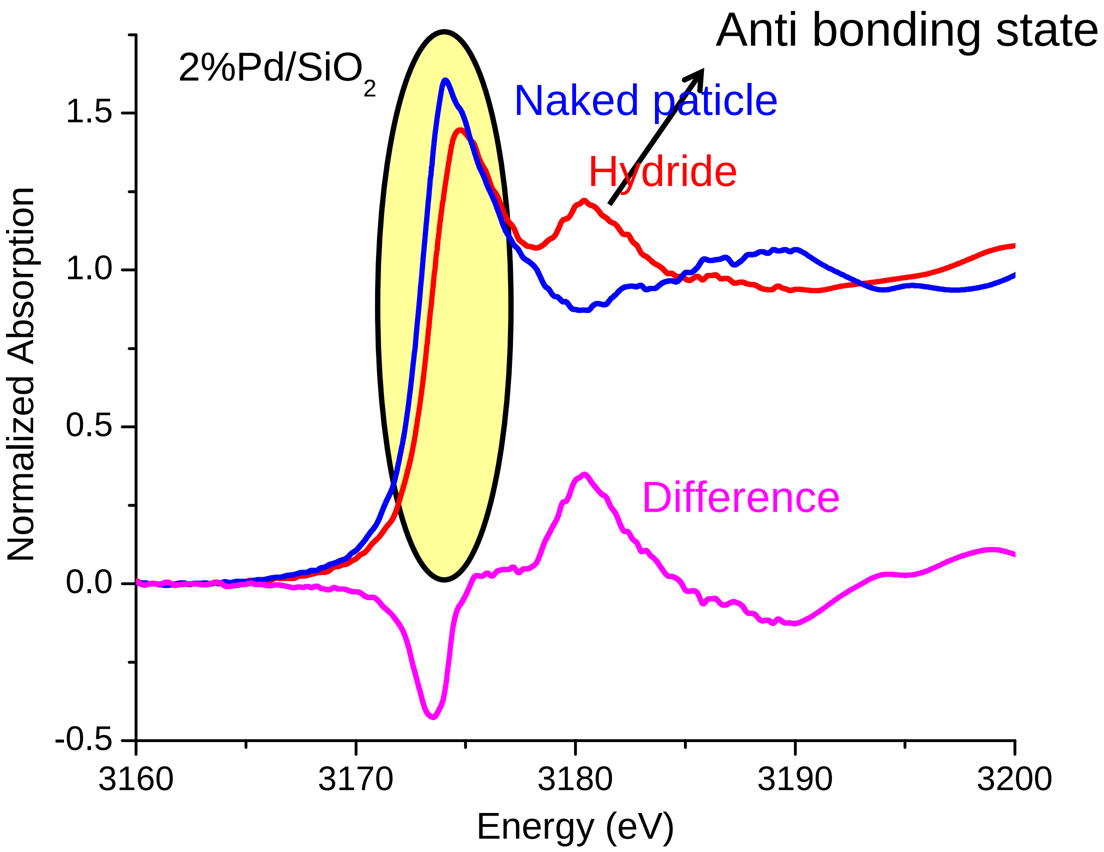
… … .

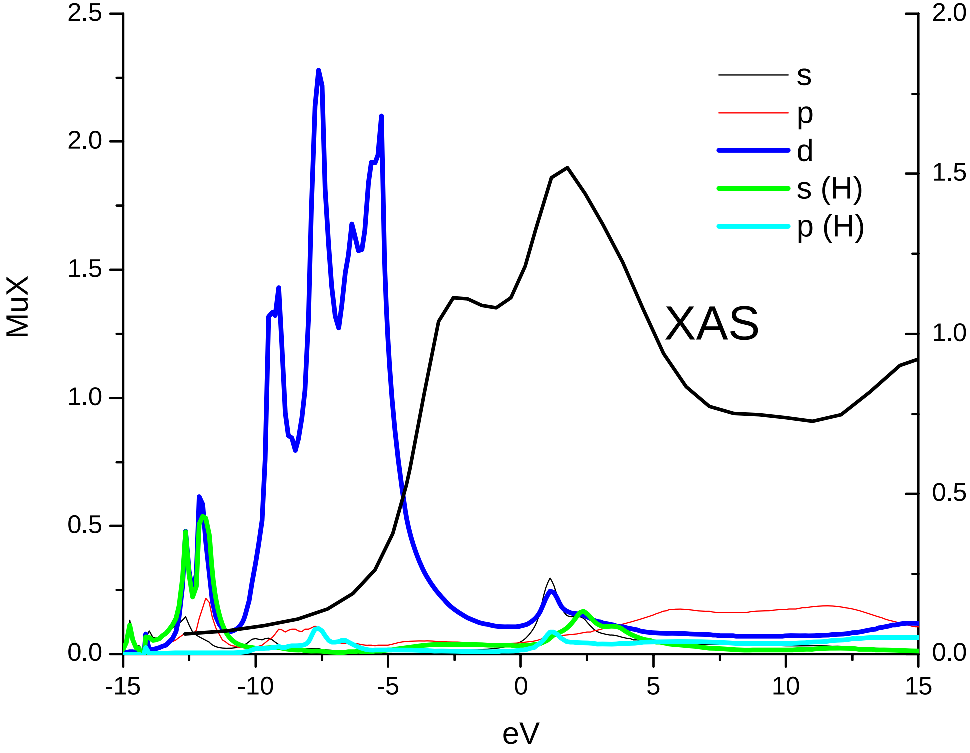
Palladium hydride formation



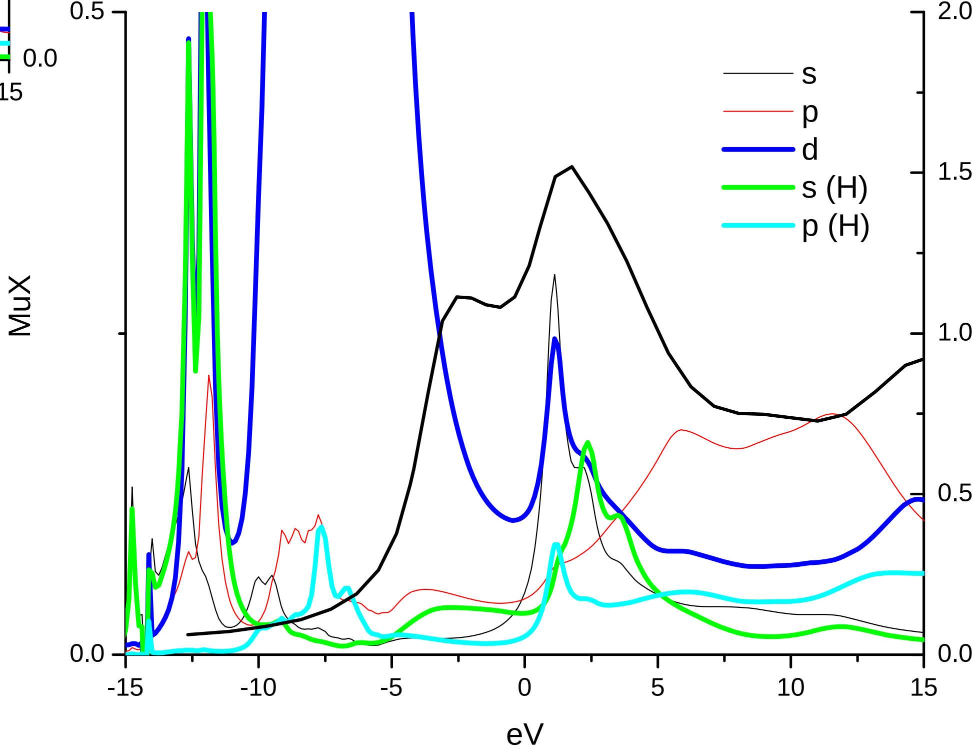



+
Fermi level
ε_d
-
Metal d-band
reactant level


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)



DOS vs XANES for PdH$_{0.64}$ (93 atoms)

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

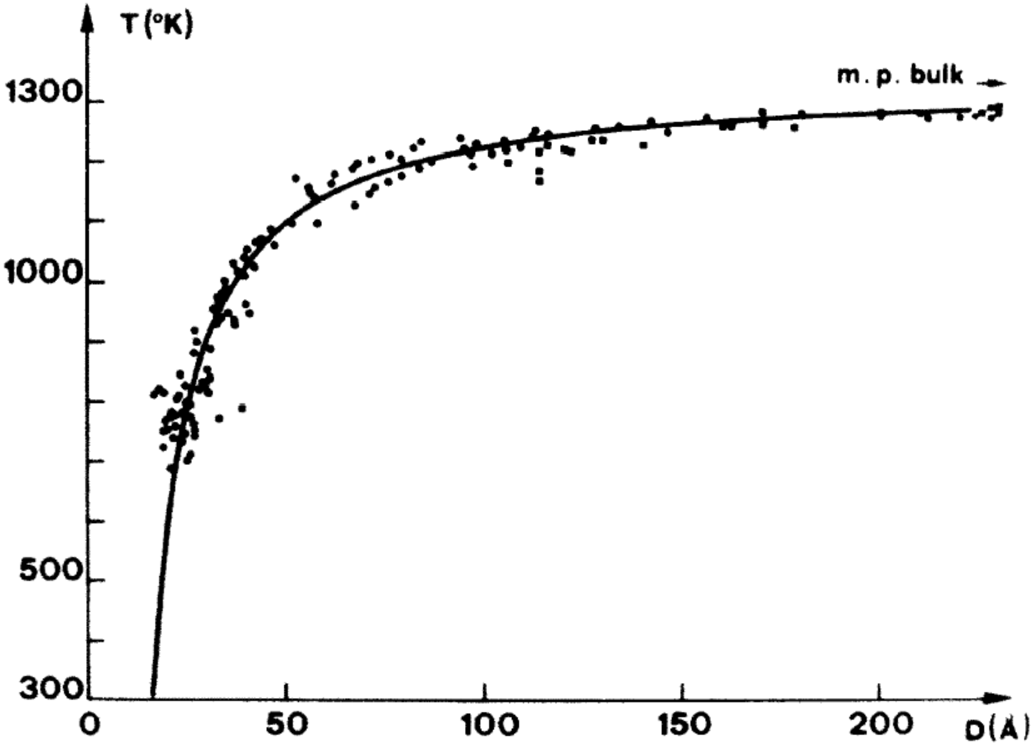
highly active in presence of H_2: Haruta Catal. Today 36 (1997) 153

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



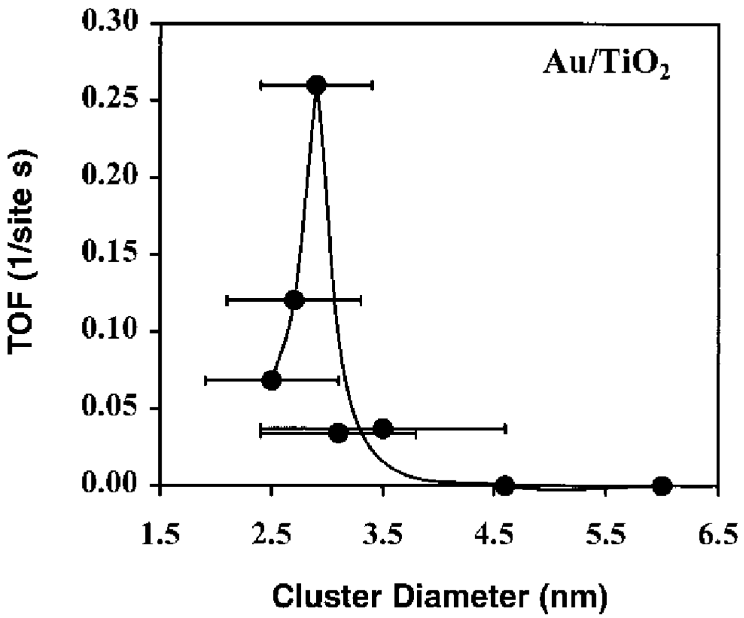
Buffat Phys. Rev. A 13 (1976) 2287

Catalysis by Gold

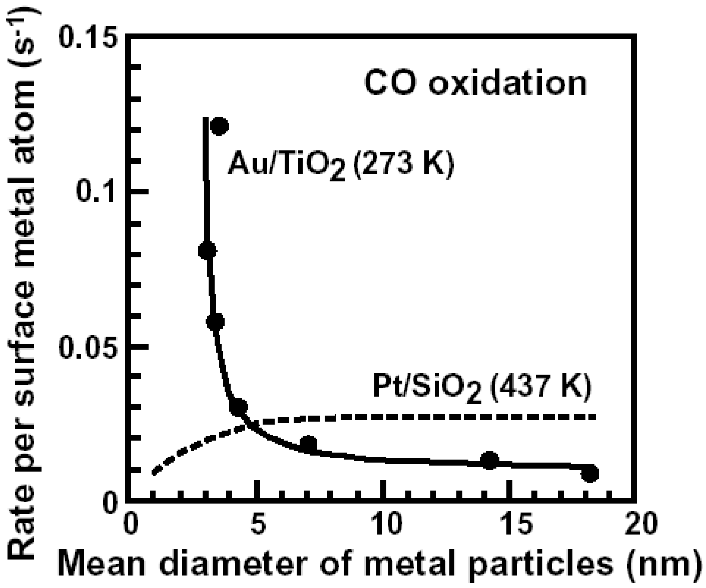
Physical properties

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

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

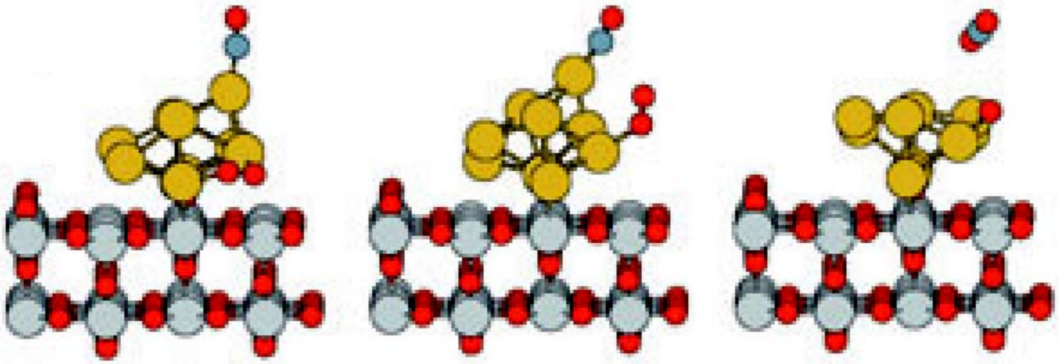
Oxidation state

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

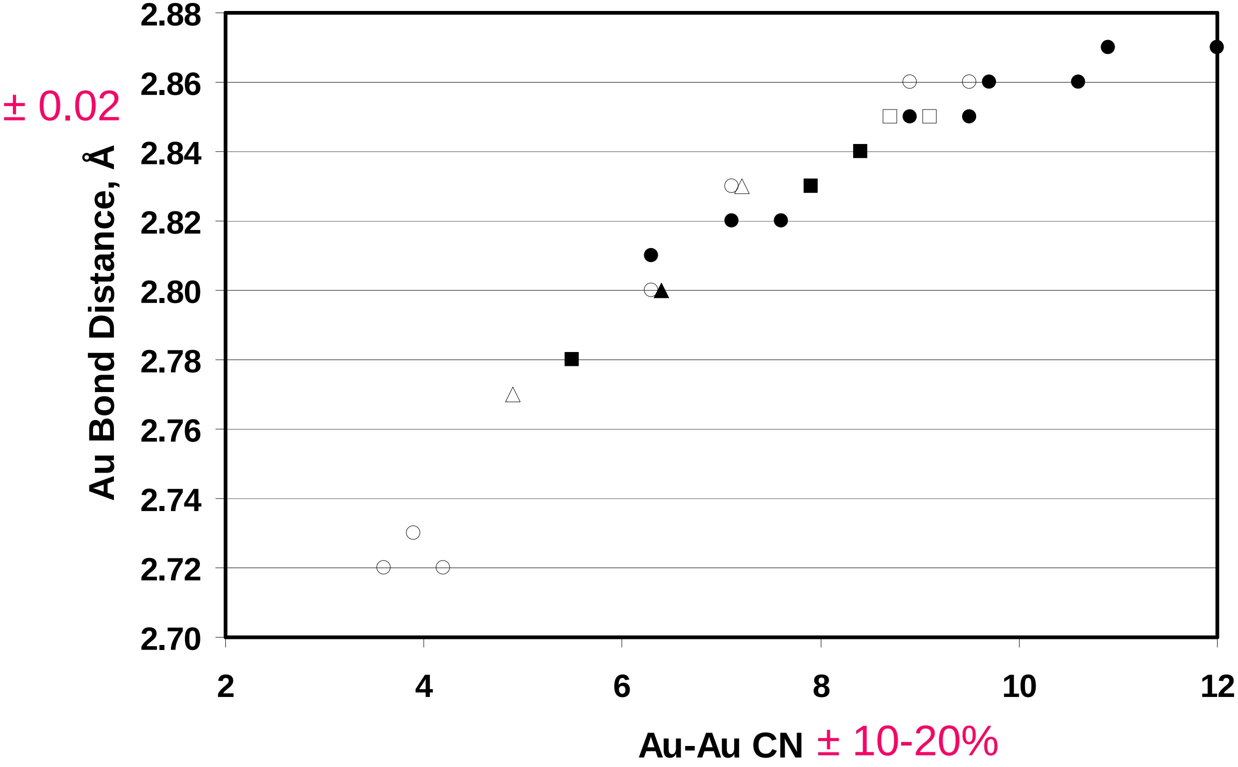
- Deposition precipitation $HAuCl_4$ adjusted pH
- Washing with a base to remove chlorine
- Reduction in hydrogen

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

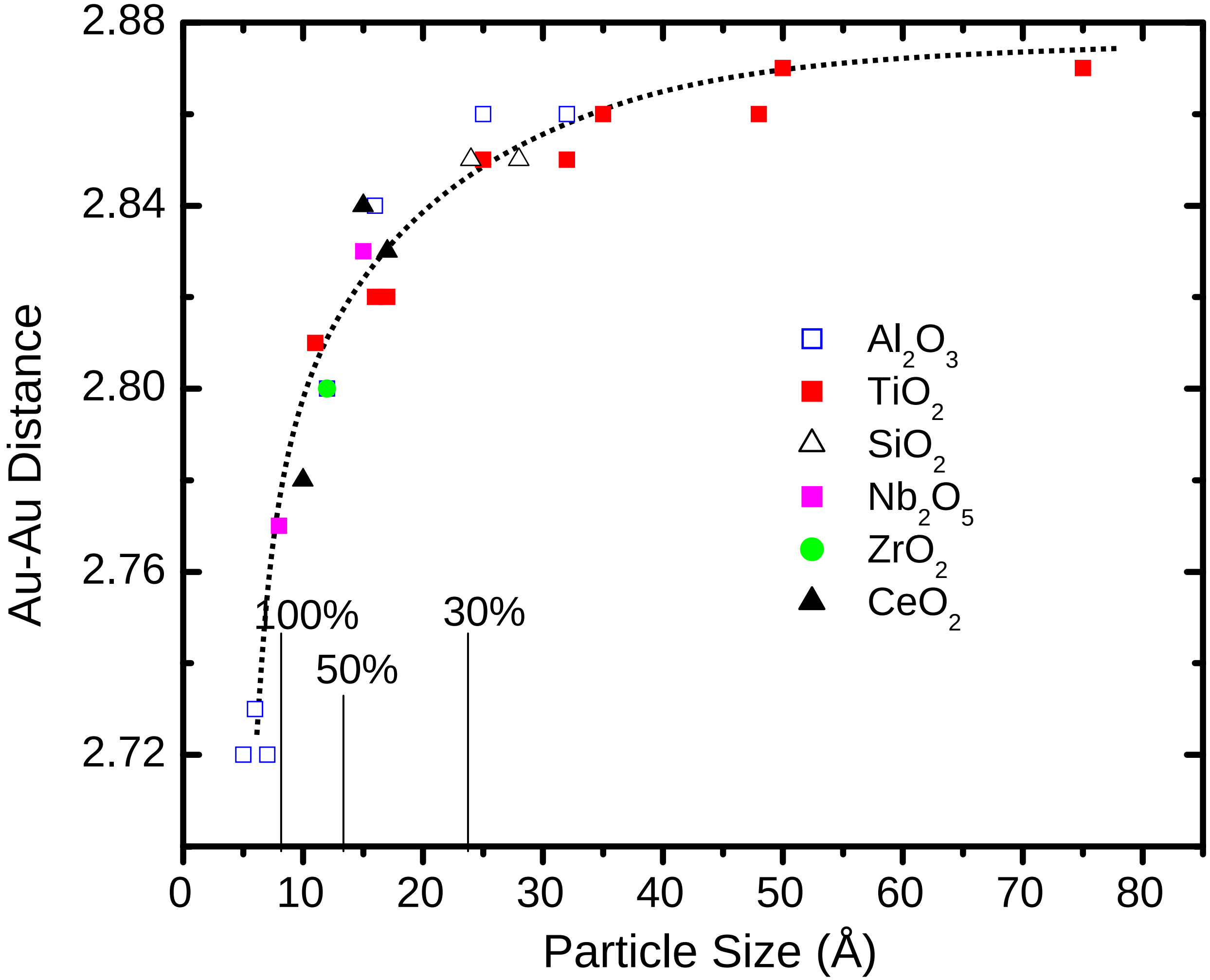


± 0.02

± 10-20%

Bulk value
2.88 Å

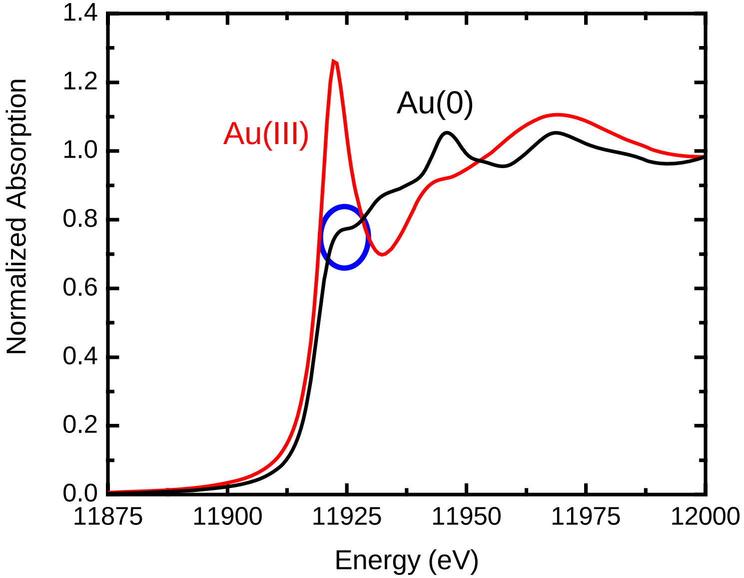
EXAFS Fitting Results of Reduced Catalysts



Strong reduction in Au-Au distance with particle size

No visible influence of support

Electronic structure from L_{III} XANES



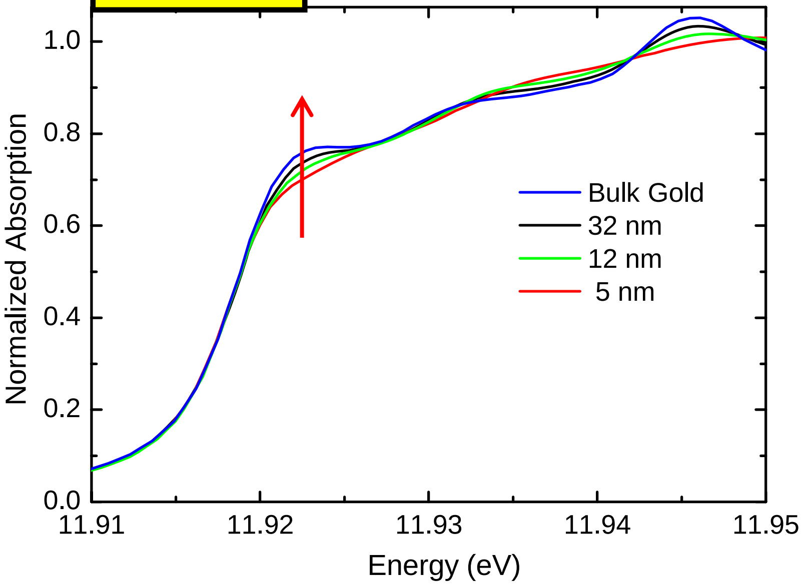
Whitelines reflect number of holes in the d-band

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

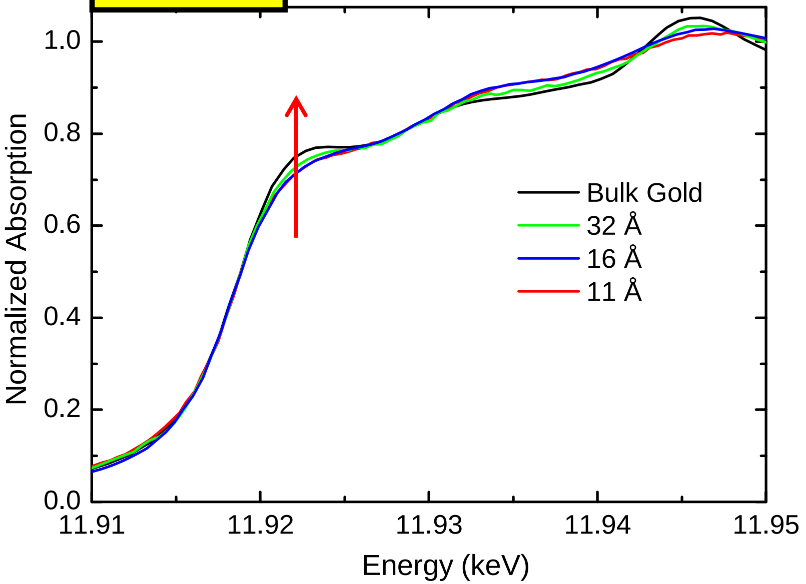
Mattheiss, L.F. *et al. Phys. Rev. B* **1980**, *22*, 1663

Whitelines reflect number of holes in the d-band

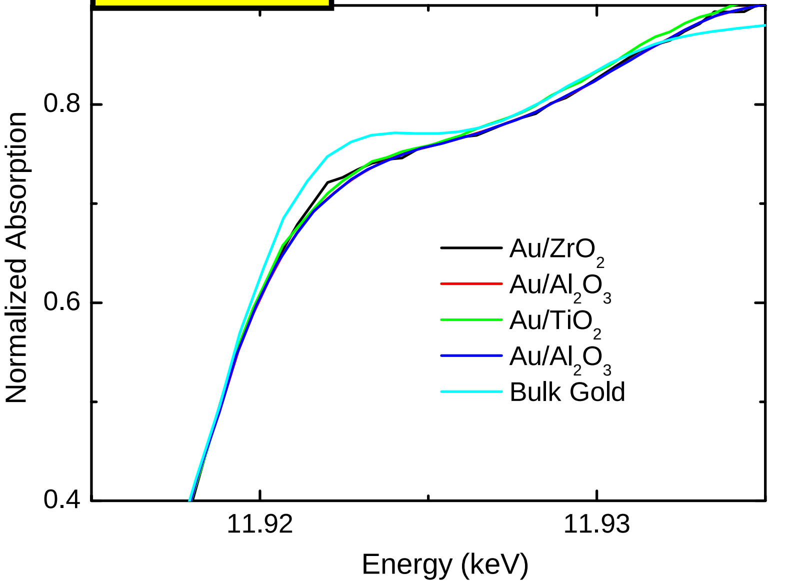
Au/Al_2O_3



Au/TiO_2



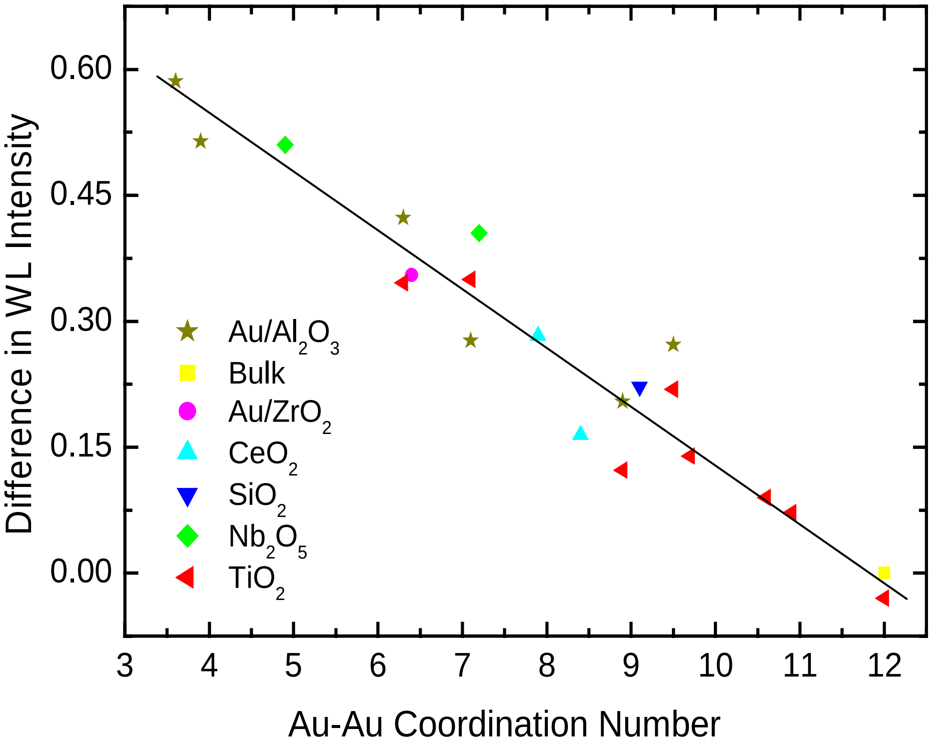
1.1 nm Au

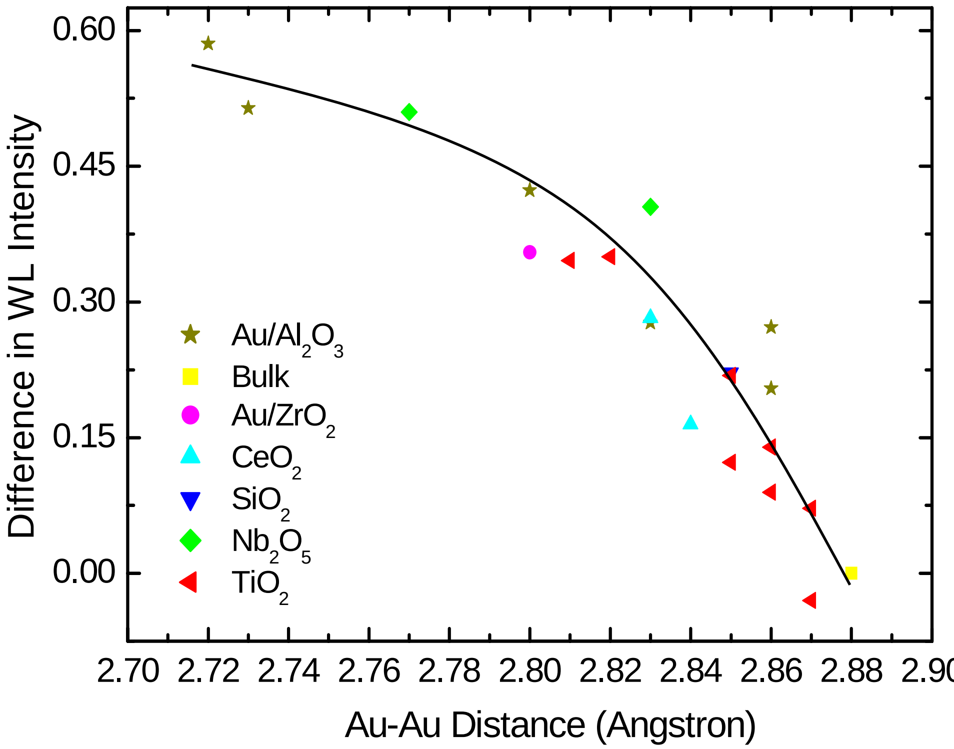


Whiteline is particle-size dependent

Whiteline intensity versus particle size

Difference intensity with bulk

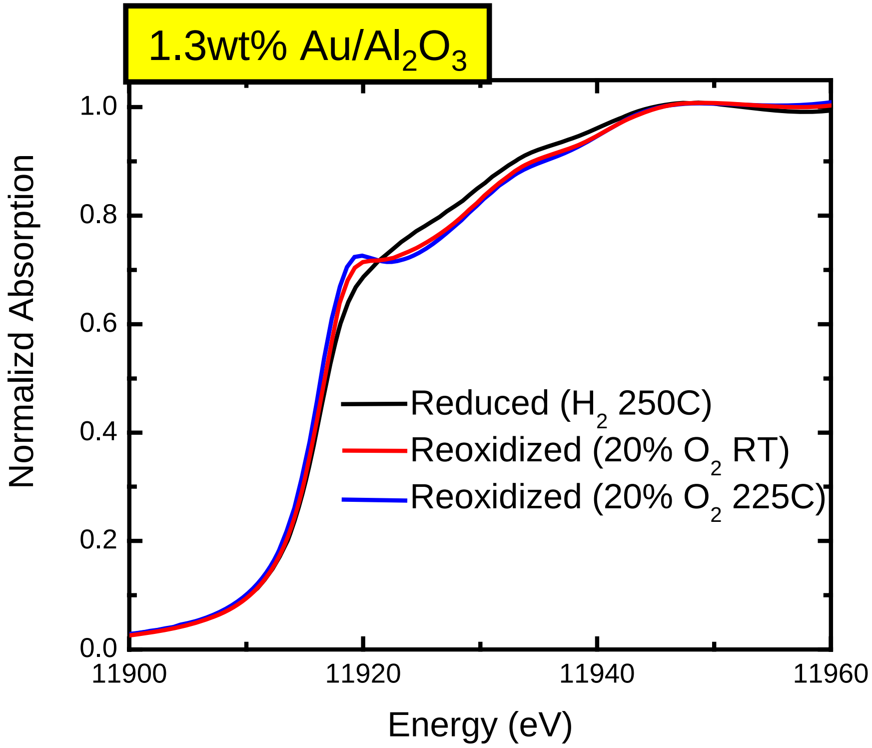


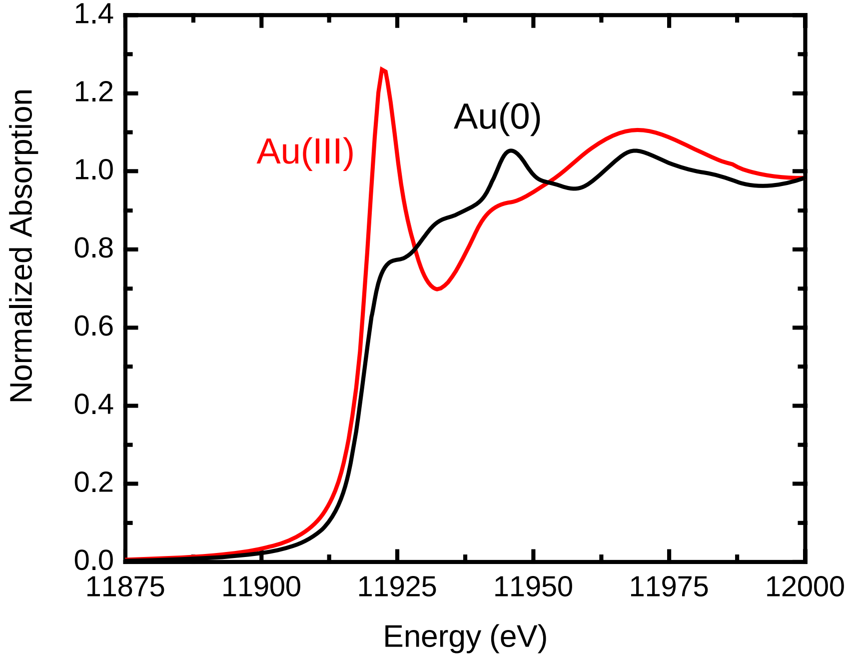


Six supports, one trend

Larger particles fewer d-electrons

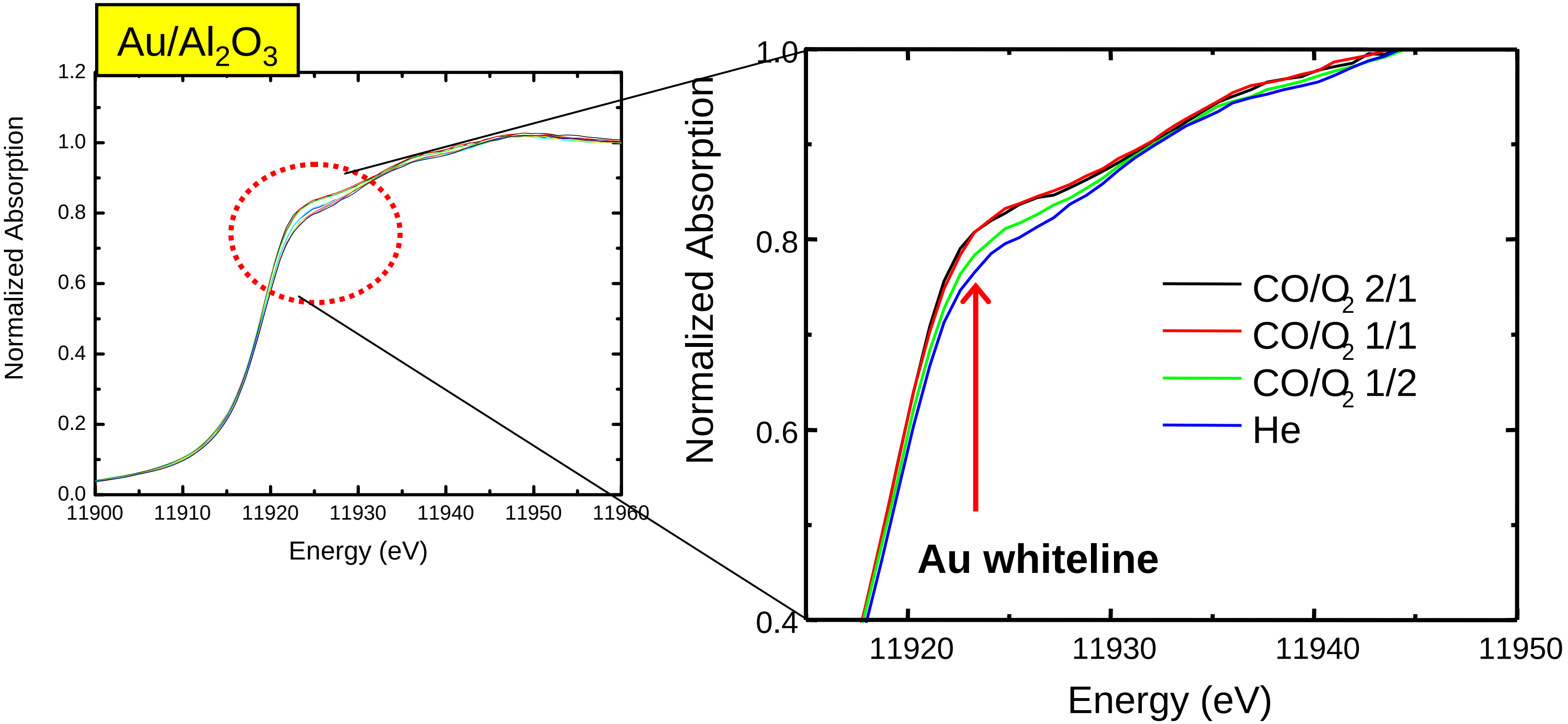
Exposure to 20% O_2





	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



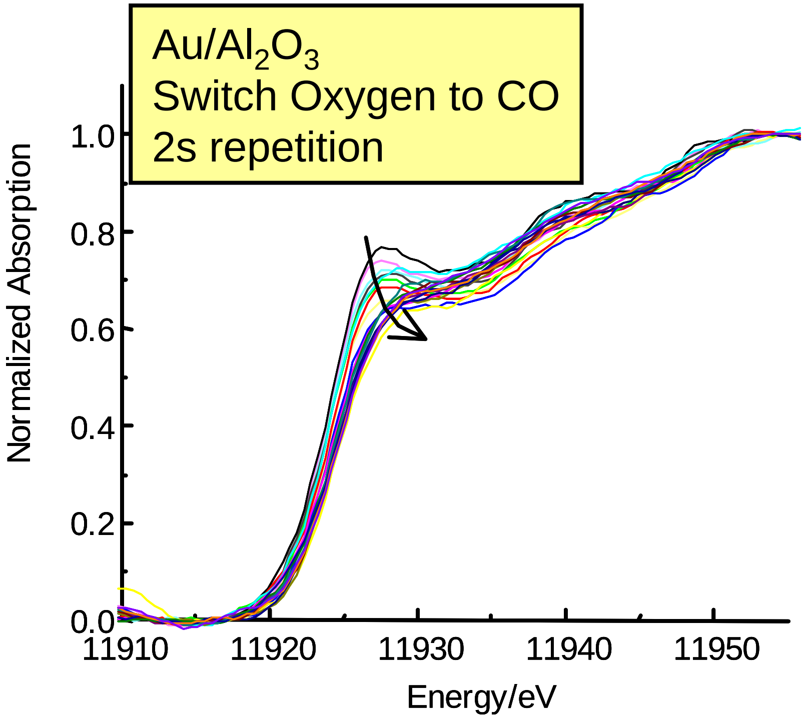
	CN(Au)	**R(Au)**
He	6.5	2.77
1:1	5.3	2.73
2:1	5.7	2.73
1:2	5.2	2.77

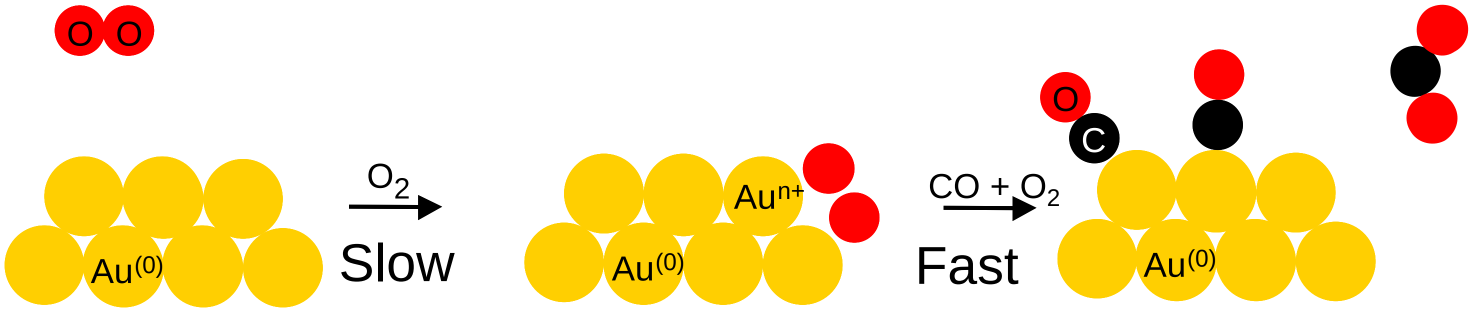
Small oxygen contribution

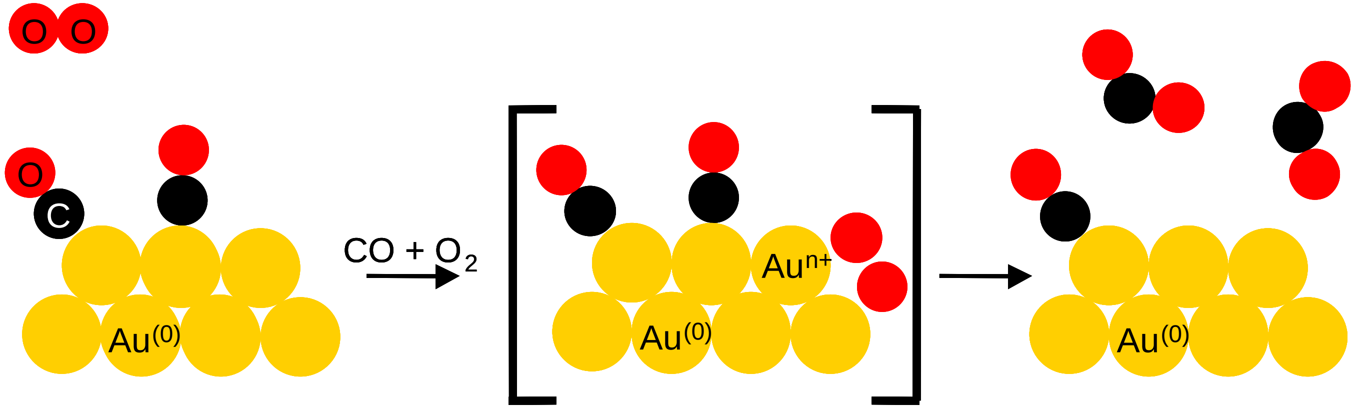
More intense with more CO:
holes in the d-band (anti-bonding states)

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





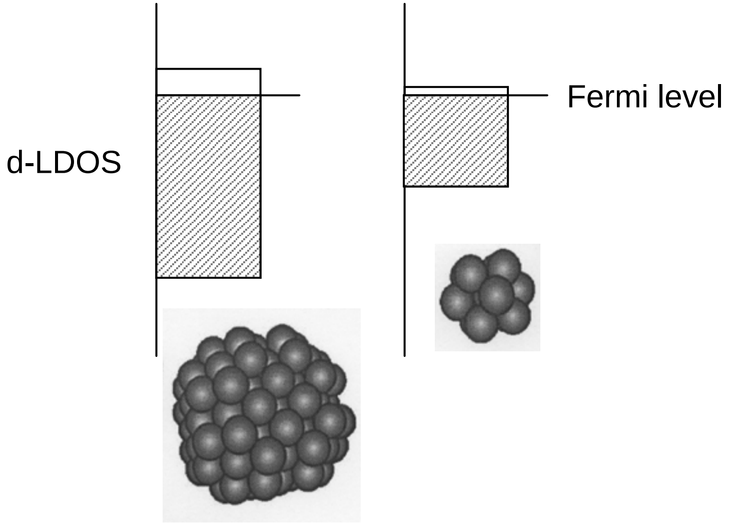


Reduced gold is active phase

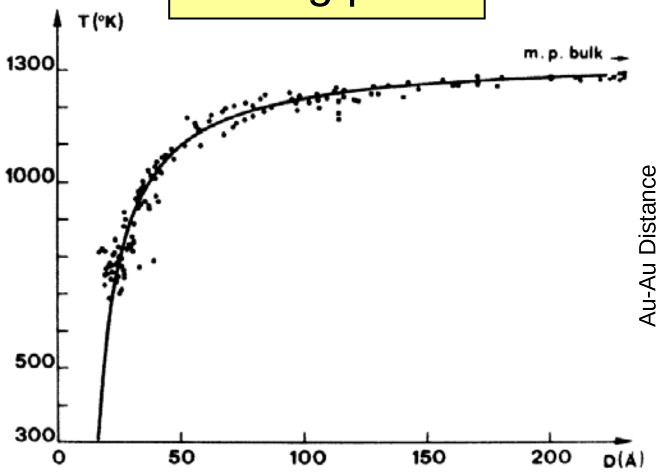
Gold participates in oxygen activation

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

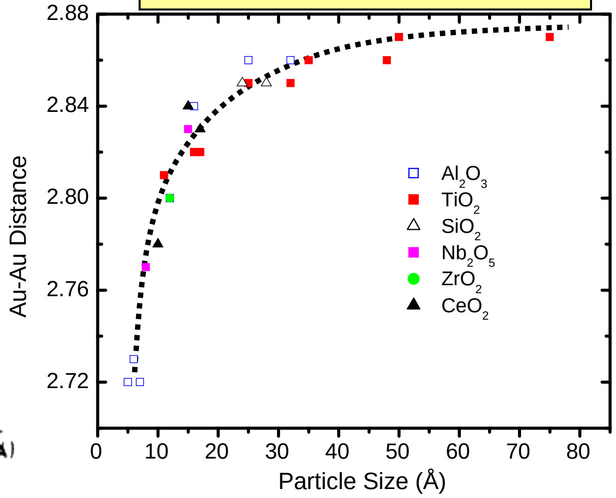
- Rehybridization of spd-orbitals ($5d^{10-x}6sp^{1+x}$)
- Smaller particles have fewer holes in the d-band
- Particle size dominates support-effect
- Oxygen is activated on gold particle



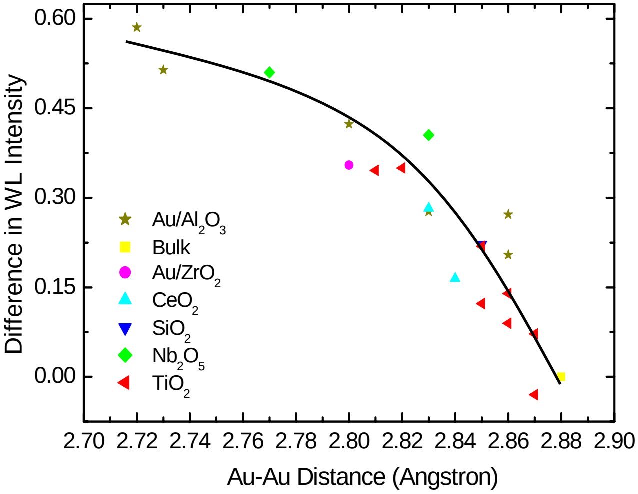
Boiling point



Gold-Gold distance

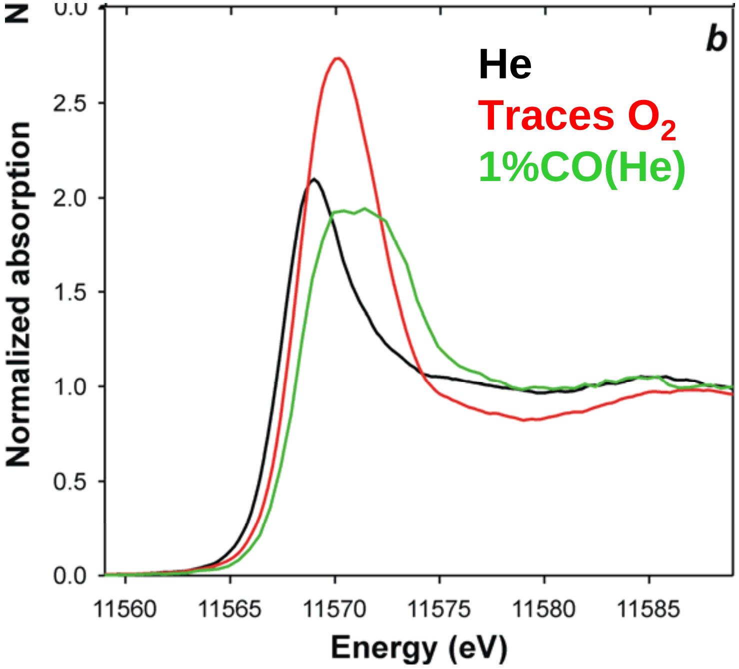


d electrons

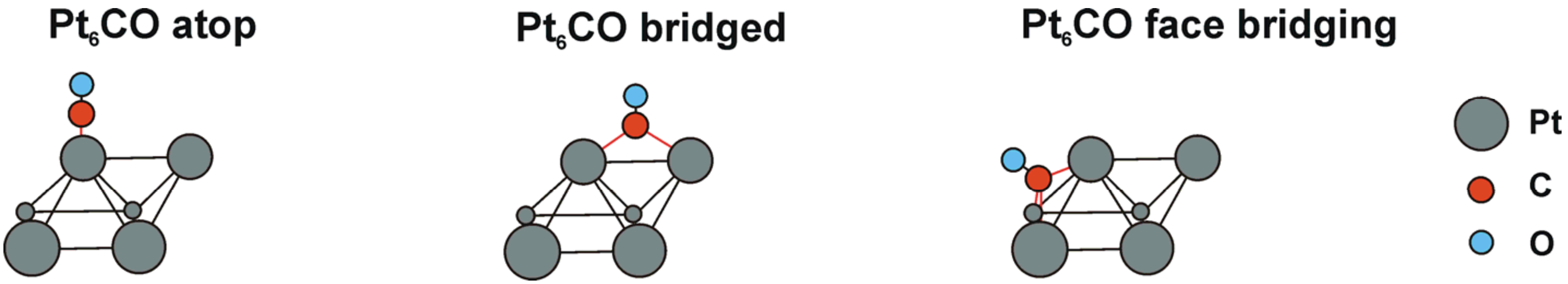


Adsorption sites from XAS

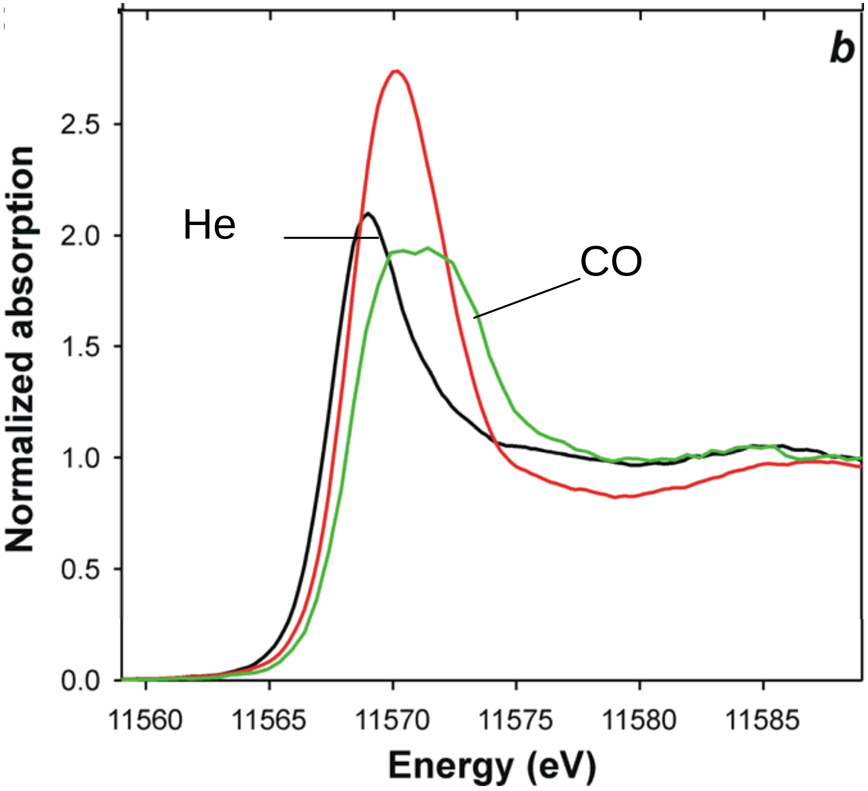
Pt/Al_2O_3

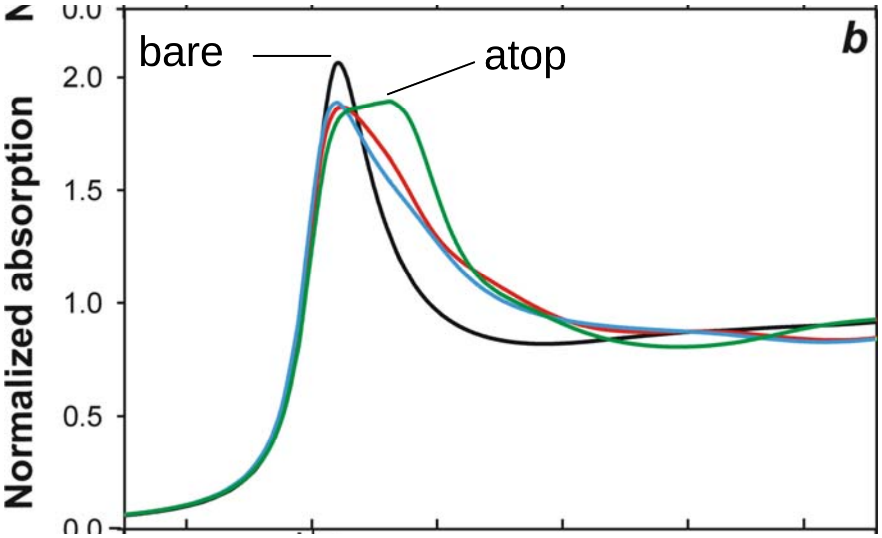


FEFF8 simulation



Experimental



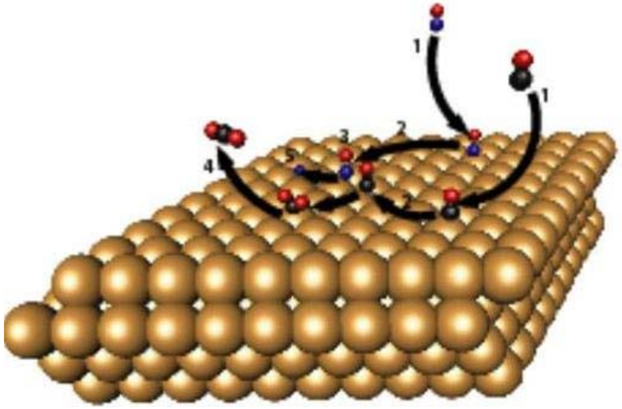


fuel cell (PEM)

catalytic converter

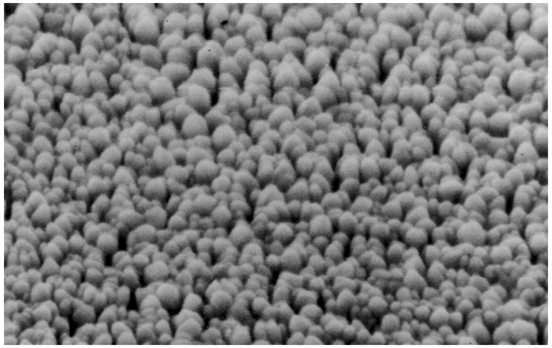
platinum catalyst

Structure of the active phase?



surface reaction

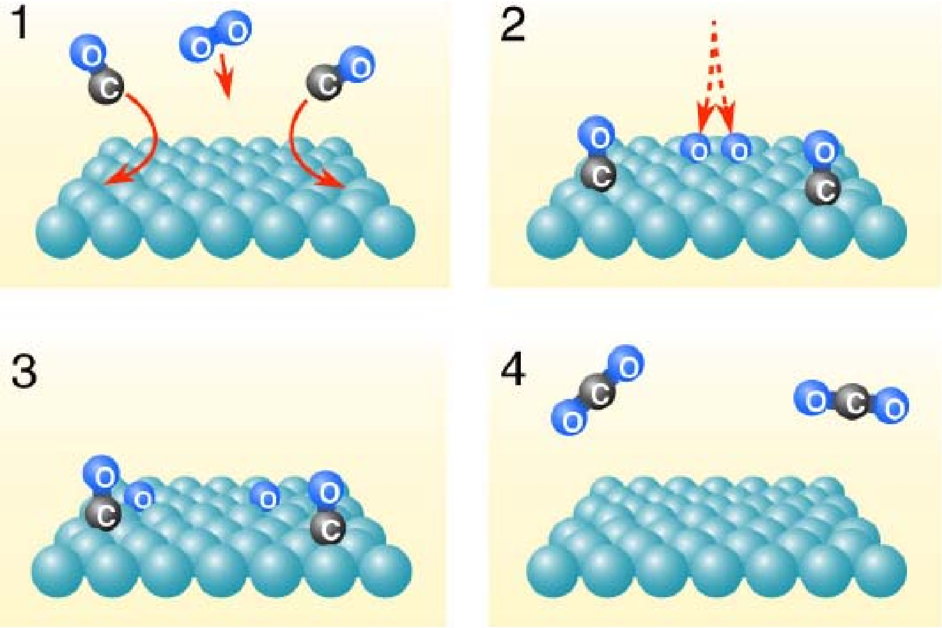
surface patterns



surface roughening

Single Crystals

UHV conditions

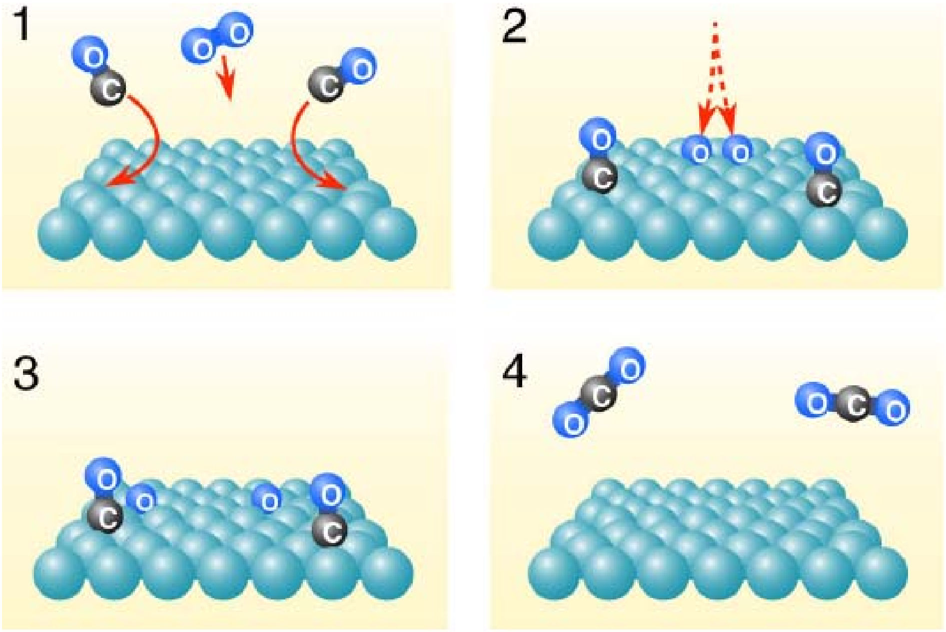


Langmuir-Hinshelwood

Single Crystals

UHV conditions

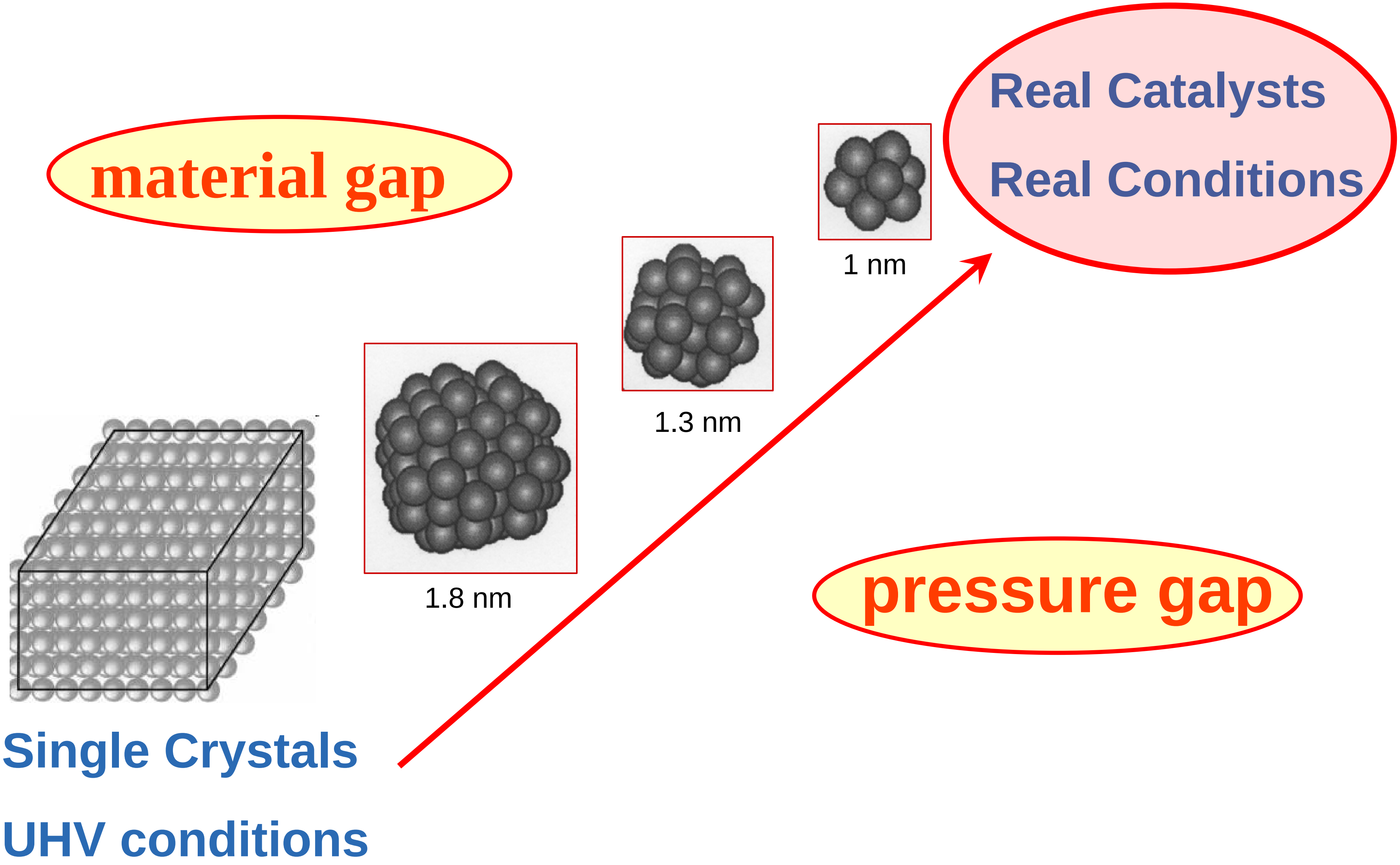
high pressure



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

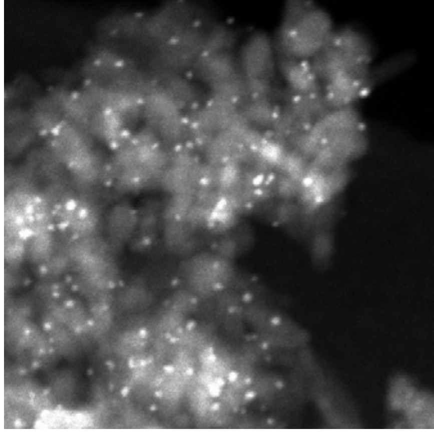
pressure gap

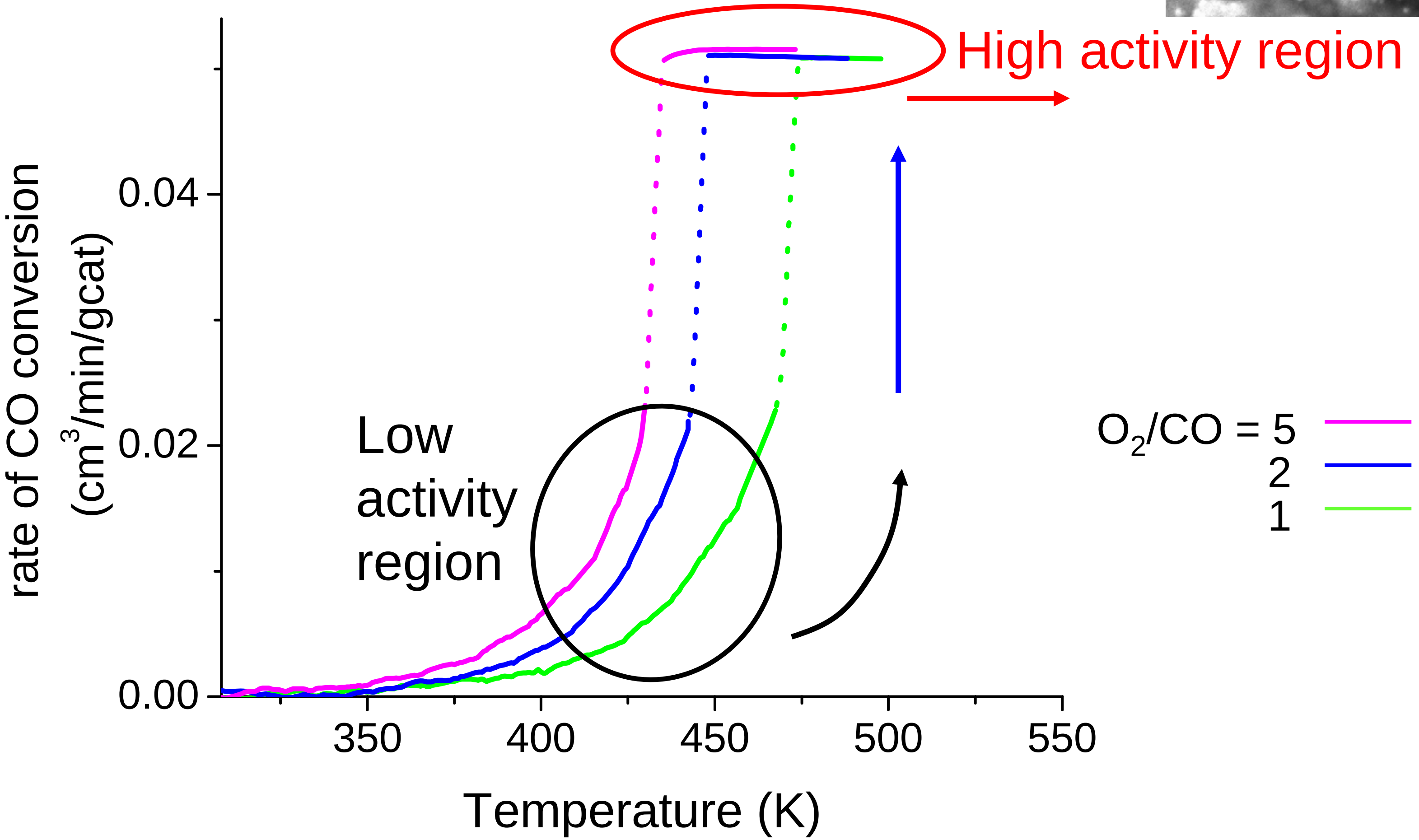
Single Crystals

UHV conditions

Conversion data

$2wt\%Pt/Al_2O_3$





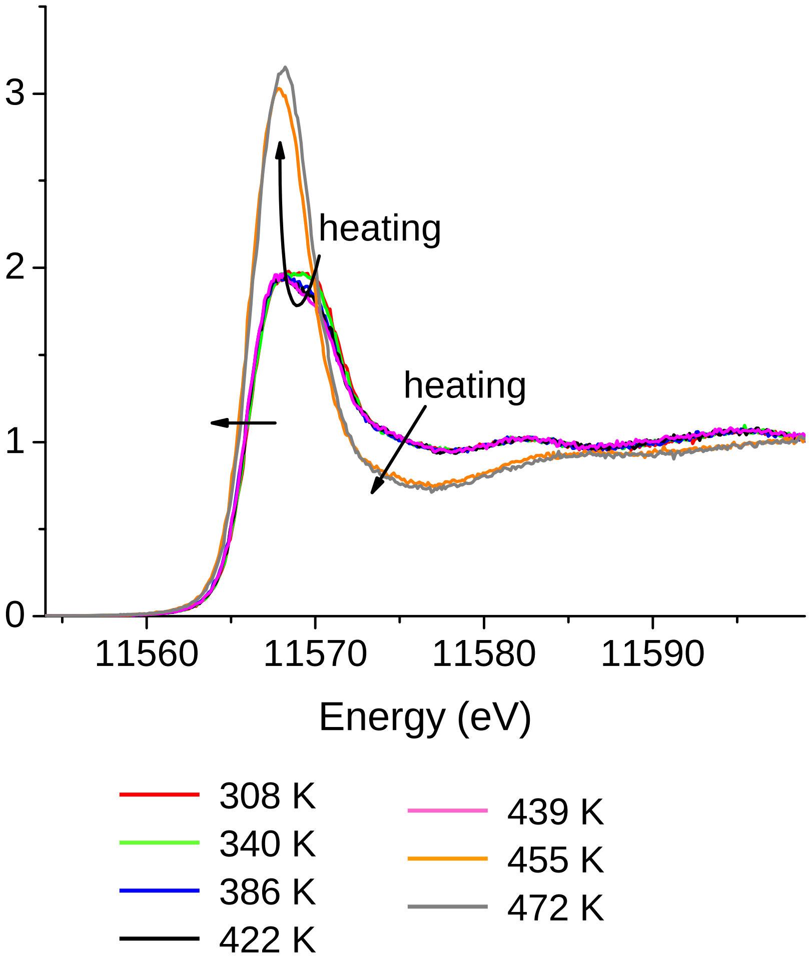
High activity region

Low activity region

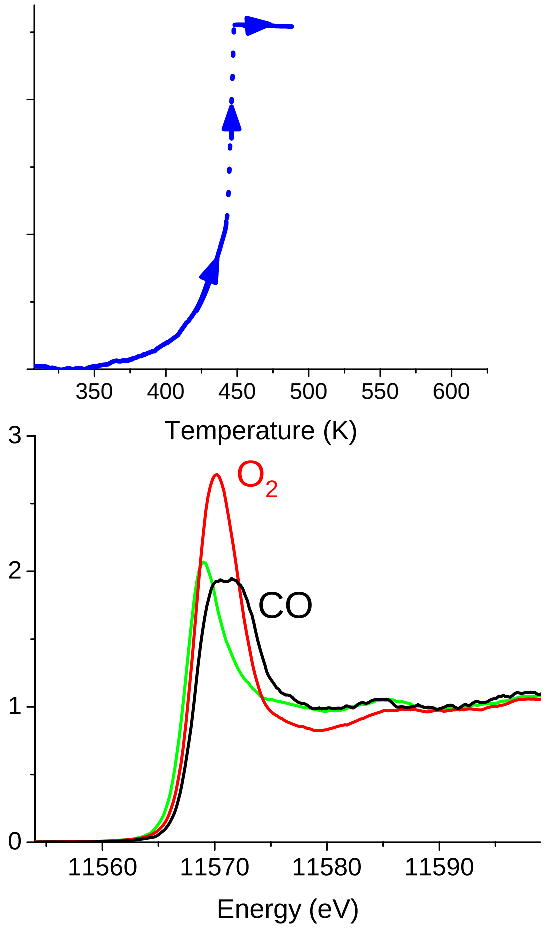
Conversion data

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

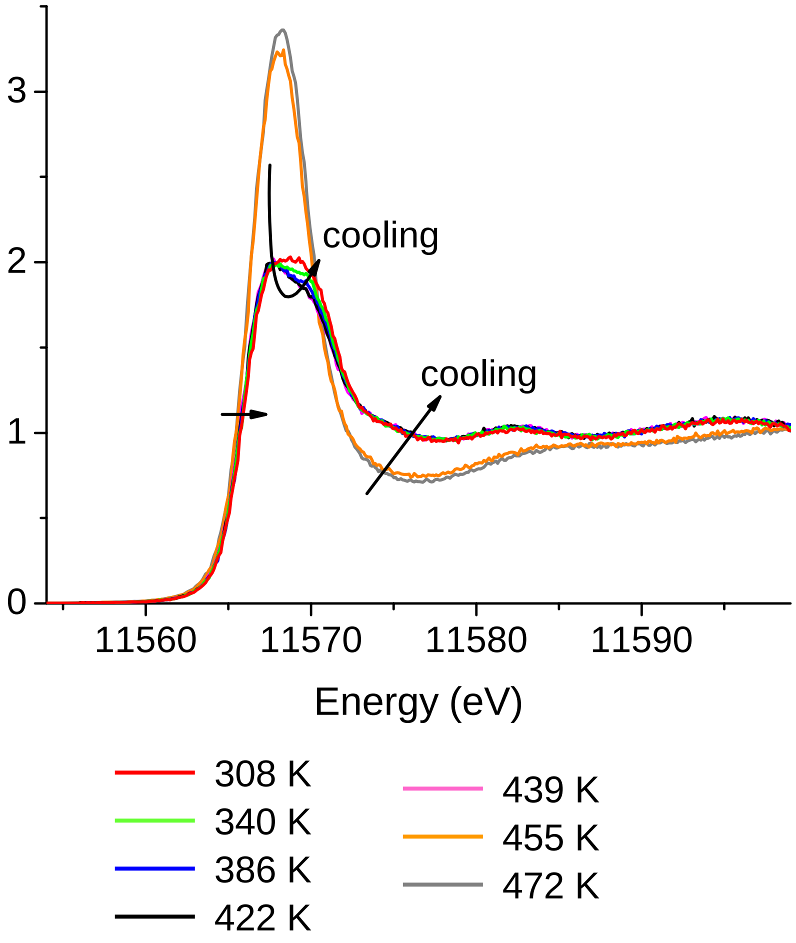
XAS


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

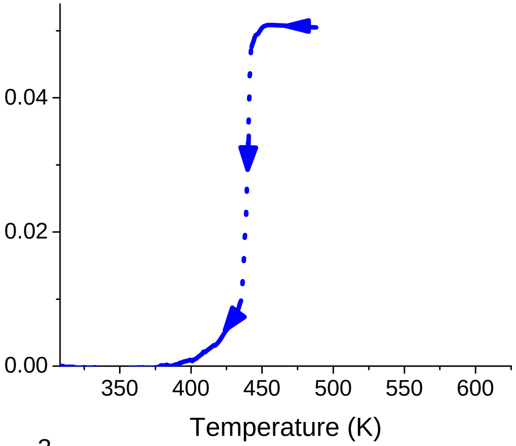
$O_2/CO = 2$

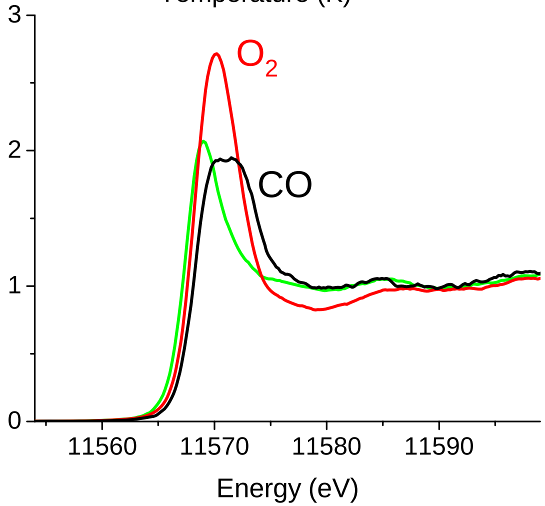

350
400
450
500
550
600
Temperature (K)
3
2
1
0
O_2
CO
11560
11570
11580
11590
Energy (eV)

XAS

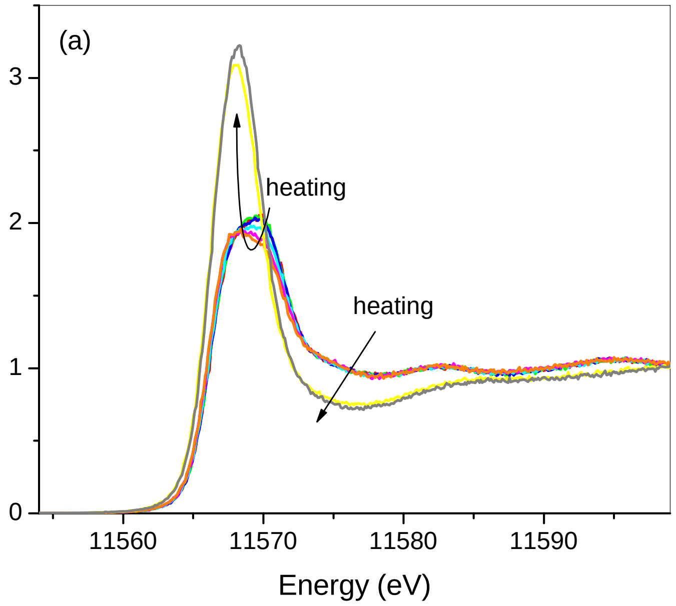

3
2
1
0
cooling
cooling
11560
11570
11580
11590
Energy (eV)
308 K
340 K
386 K
422 K
439 K
455 K
472 K

$O_2/CO = 2$

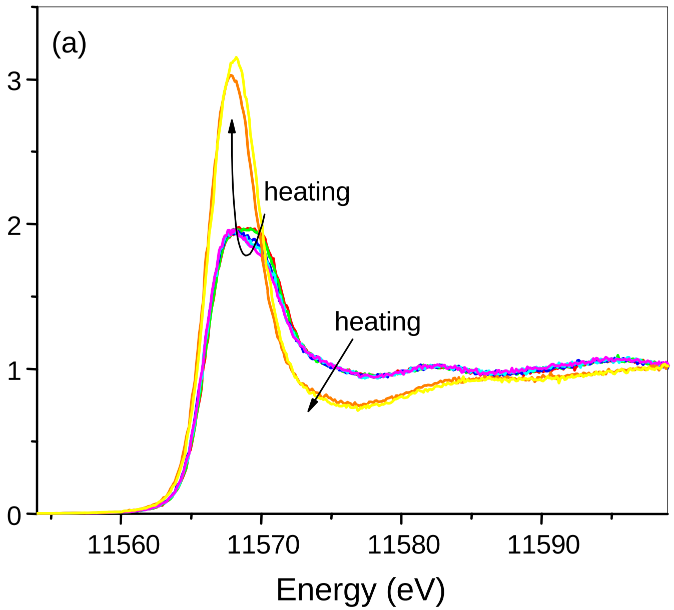

0.04
0.02
0.00
350
400
450
500
550
600
Temperature (K)

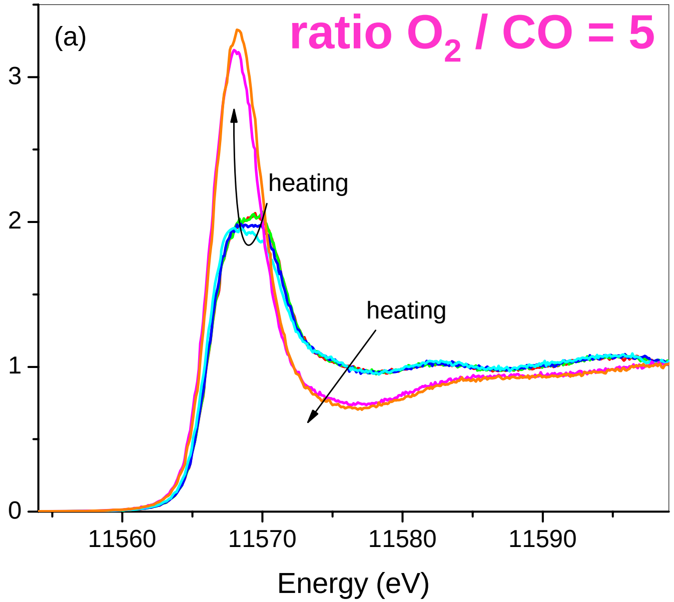

3
2
1
0
O_2
CO
11560
11570
11580
11590
Energy (eV)

ratio O_2 / CO = 1

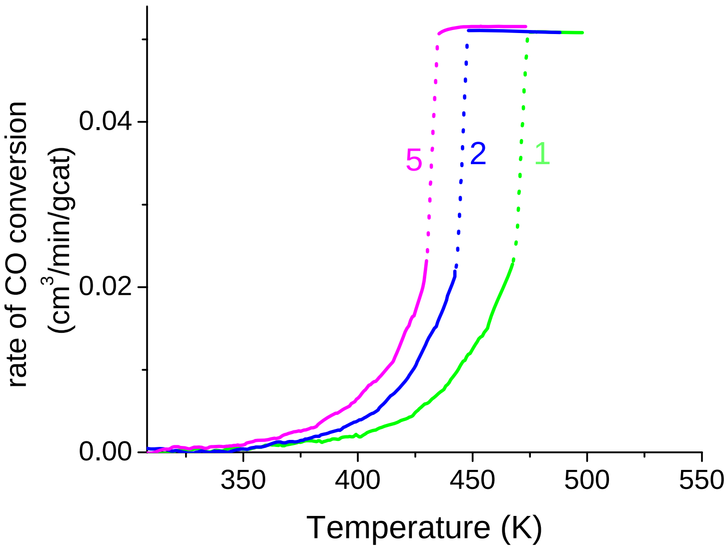


ratio O_2 / CO = 2



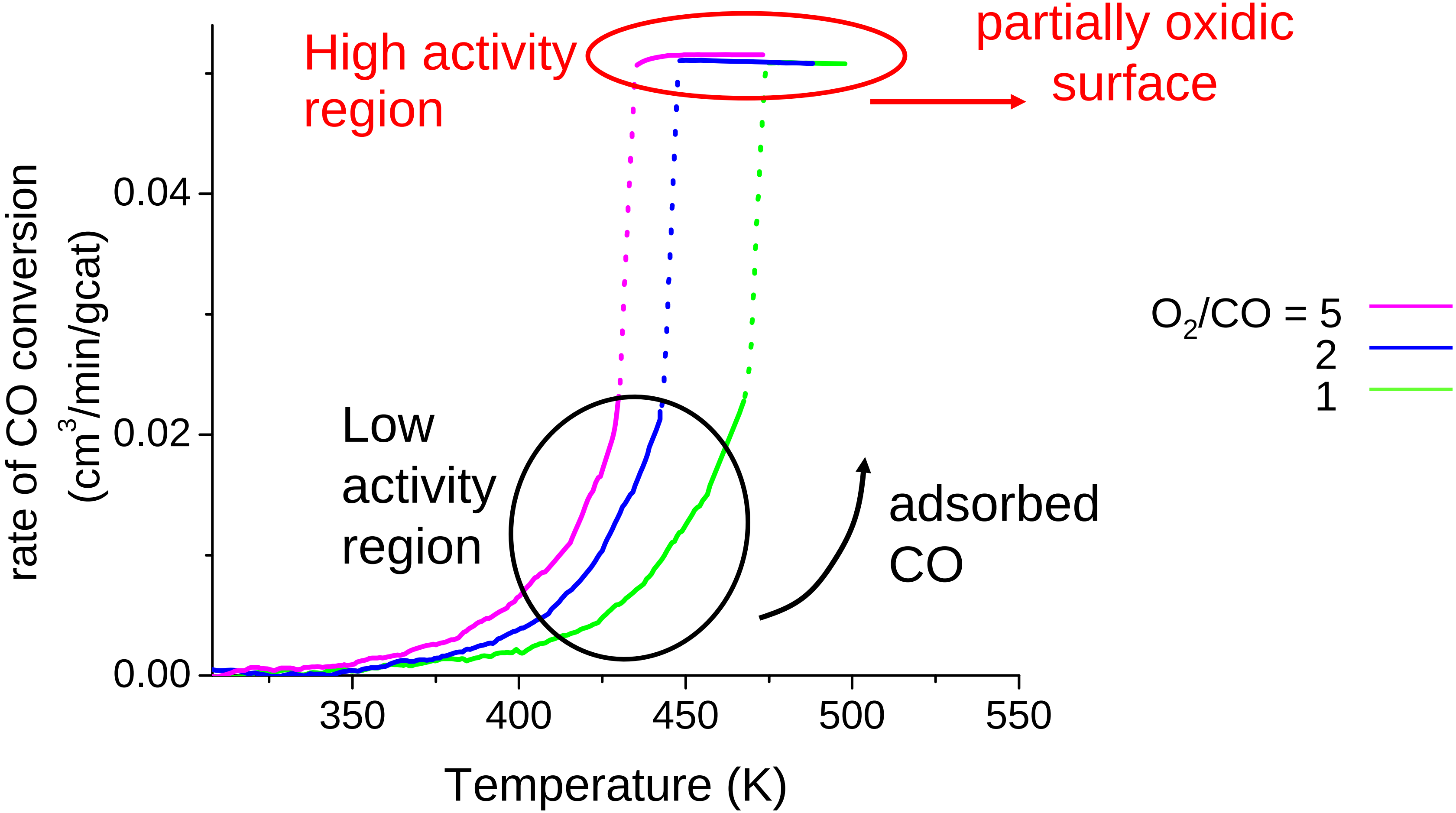


ratio O_2 / CO = 5

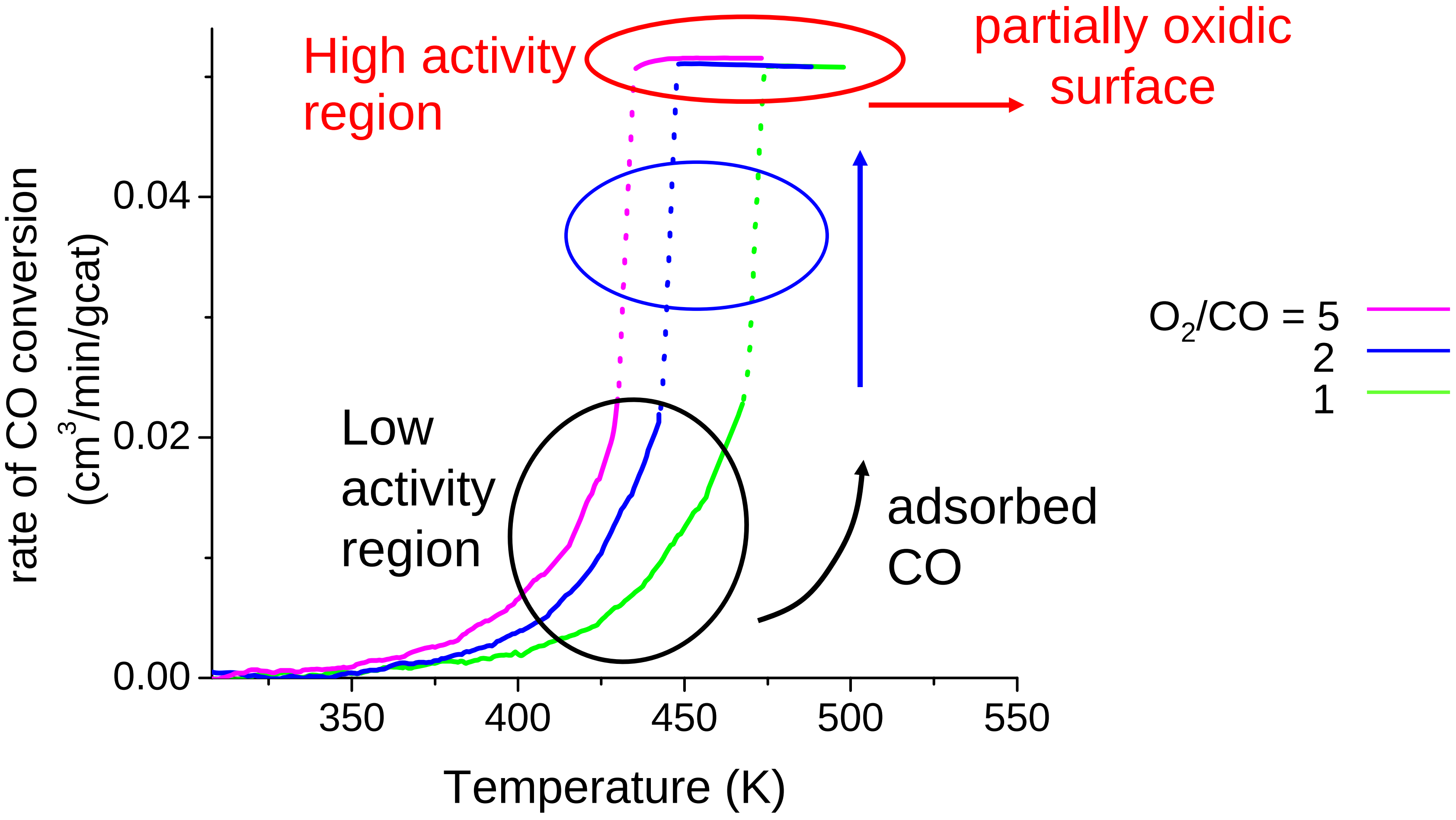


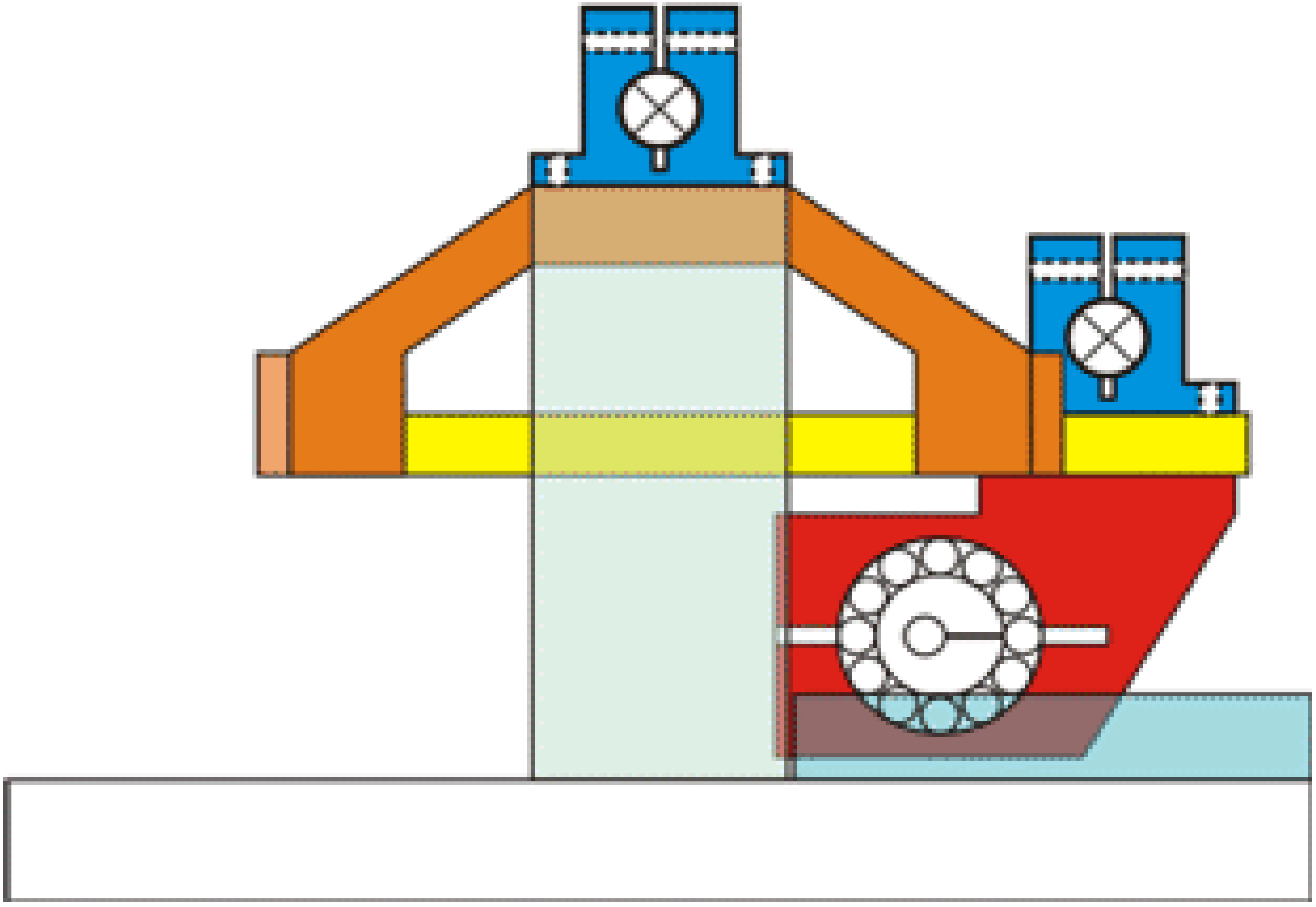
oxidation parallels ignition

Kinetics and XAS



Kinetics and XAS

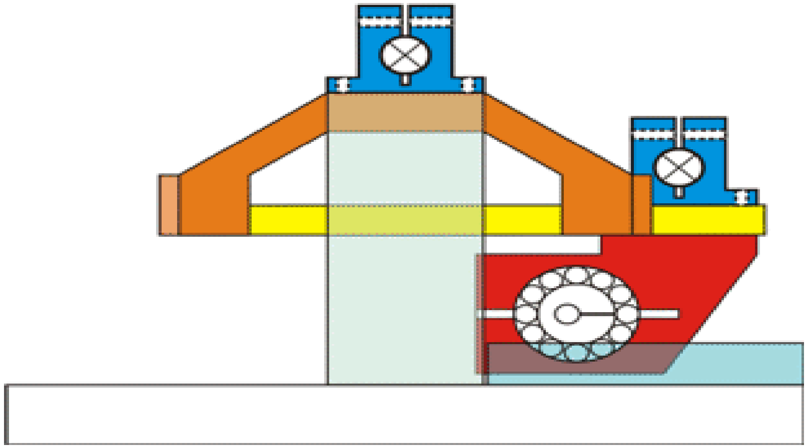


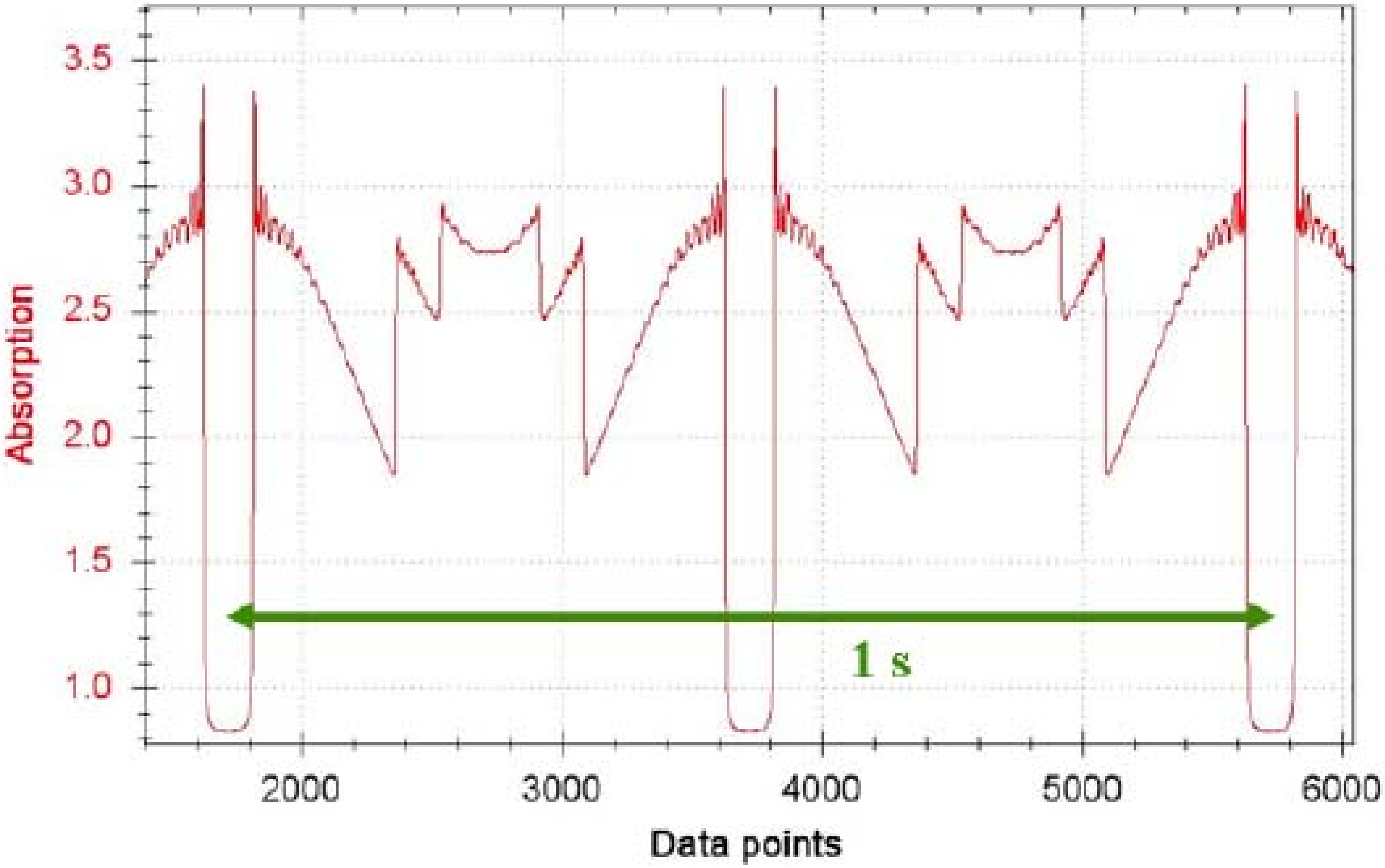


Qexafs signals

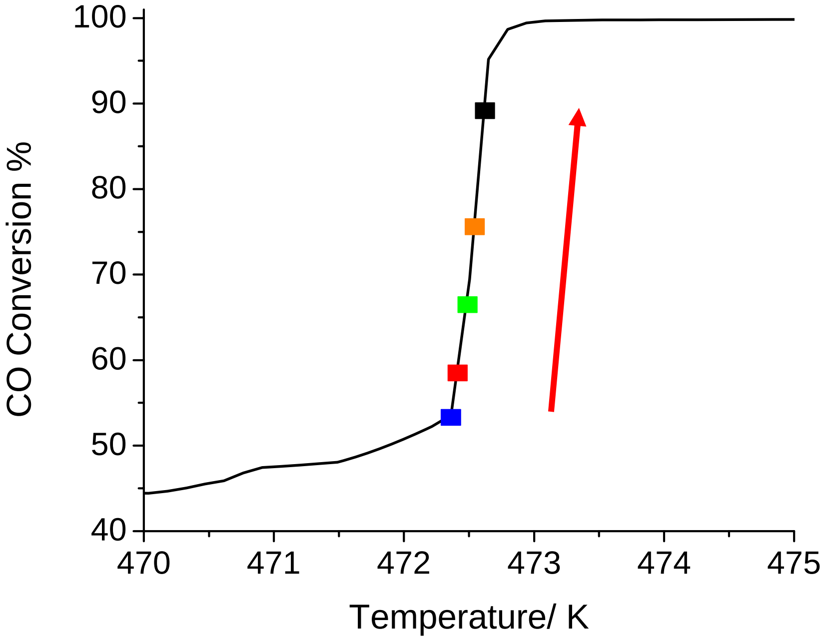
Pt foil

L_3, L_2, L_1 edges

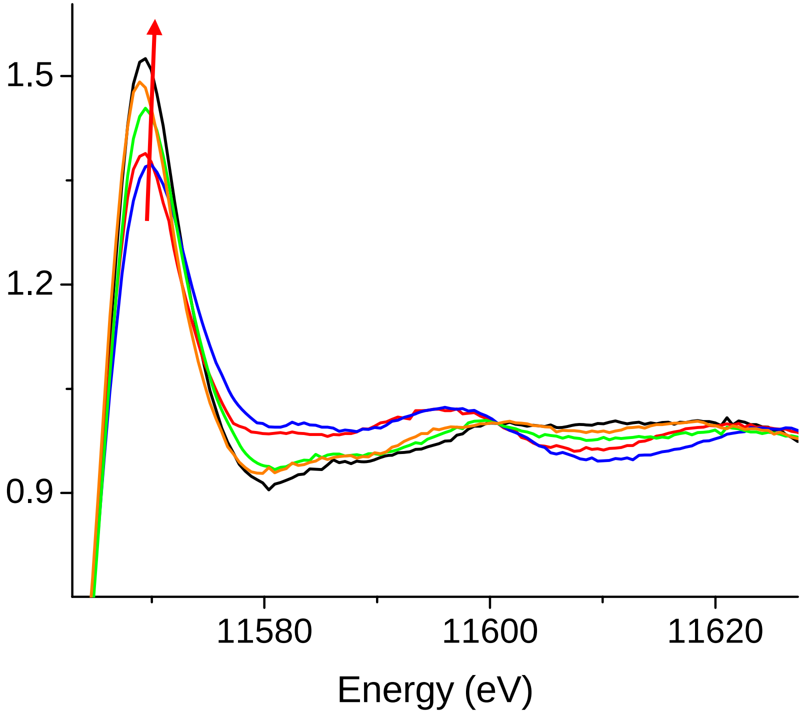




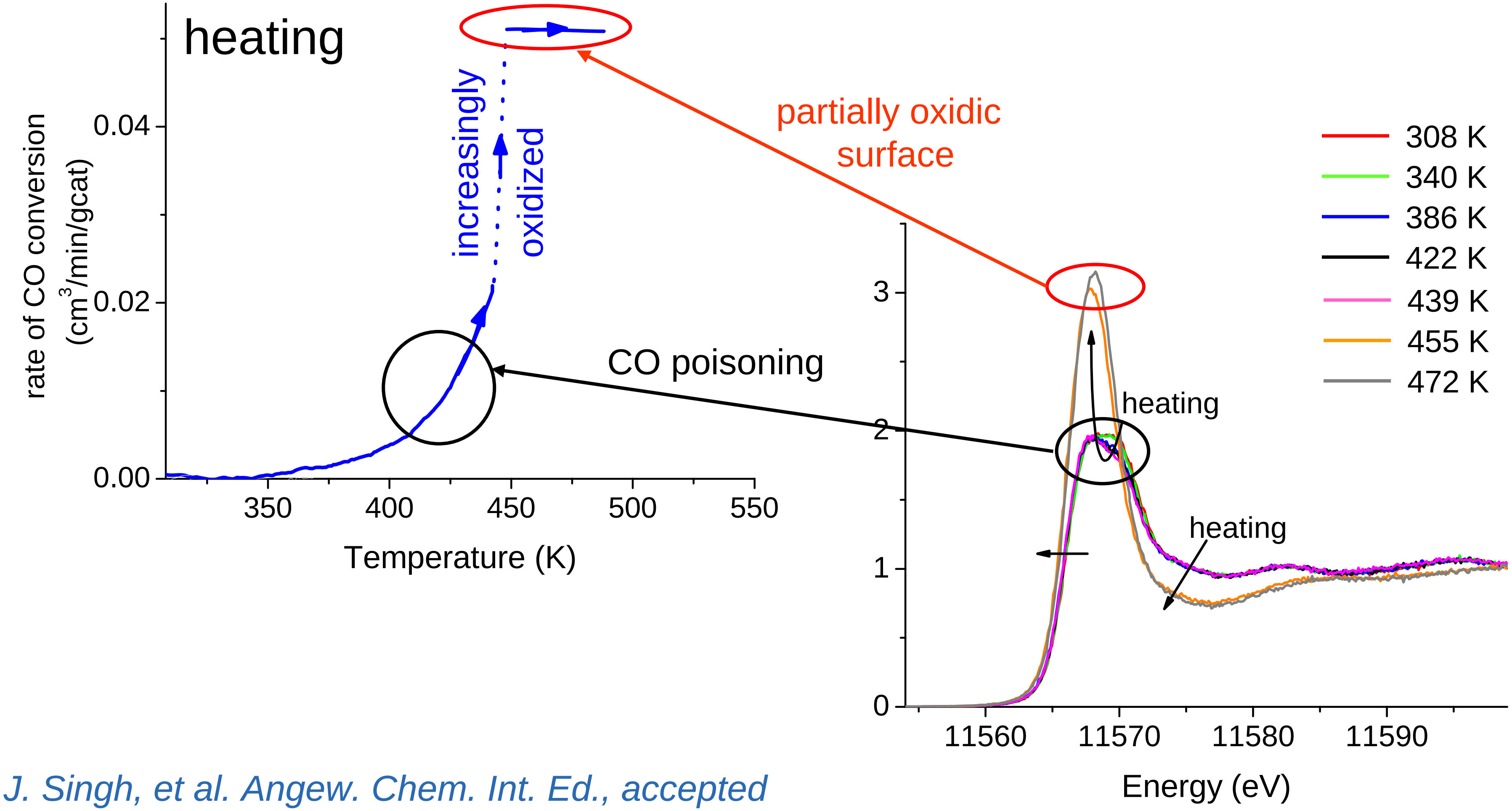
XAS (QEXAFS)



$O_2/CO = 1$



Kinetics and XAS

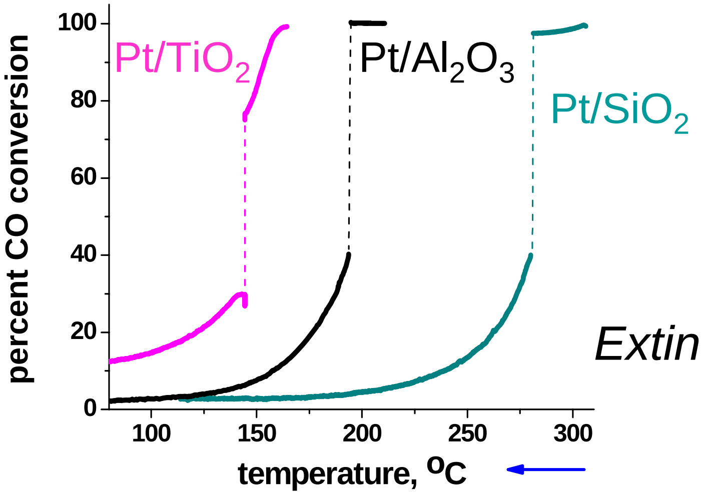


J. Singh, et al. Angew. Chem. Int. Ed., accepted

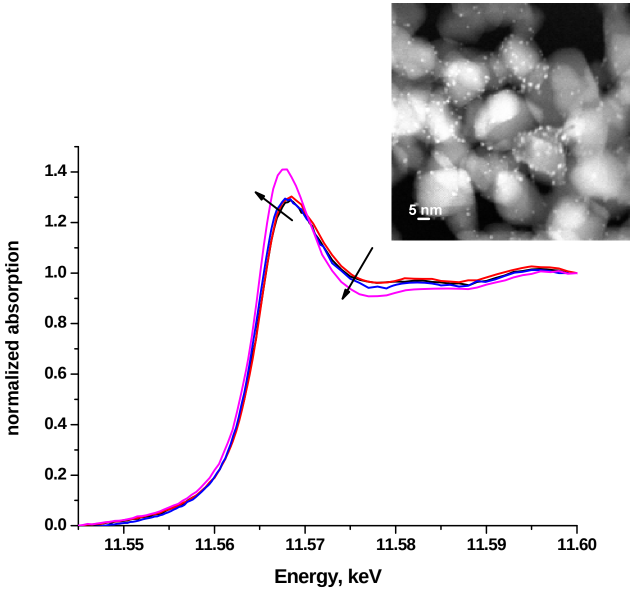
Conclusions

- 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.

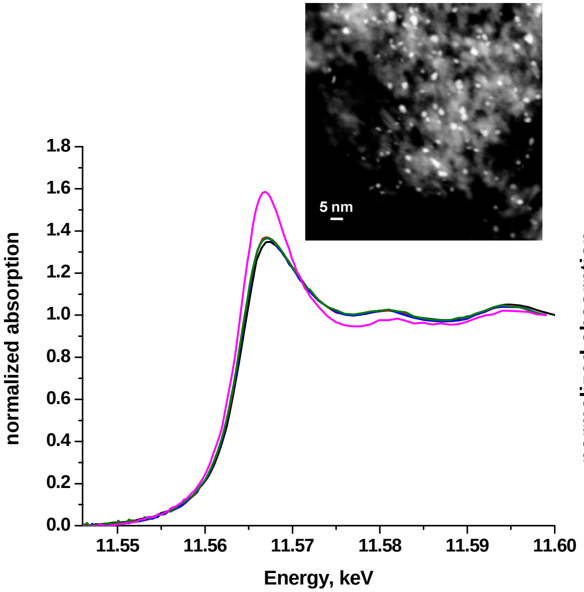
Other supports
(normal XAS)



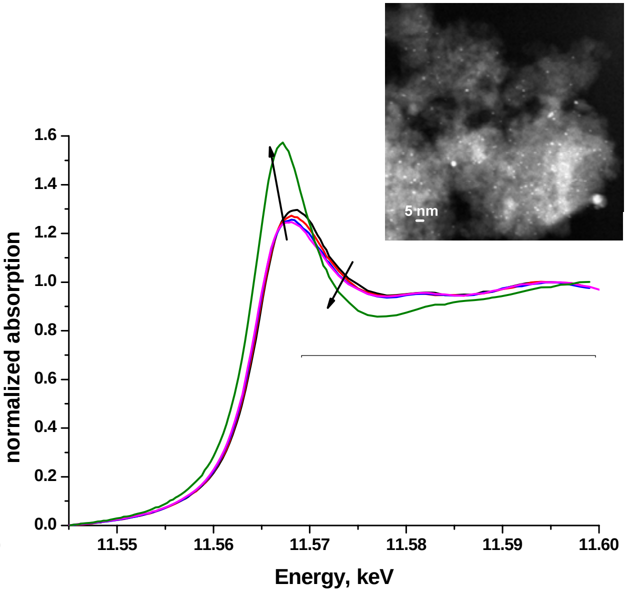
Extinction plots



TiO_2, 1.3 nm

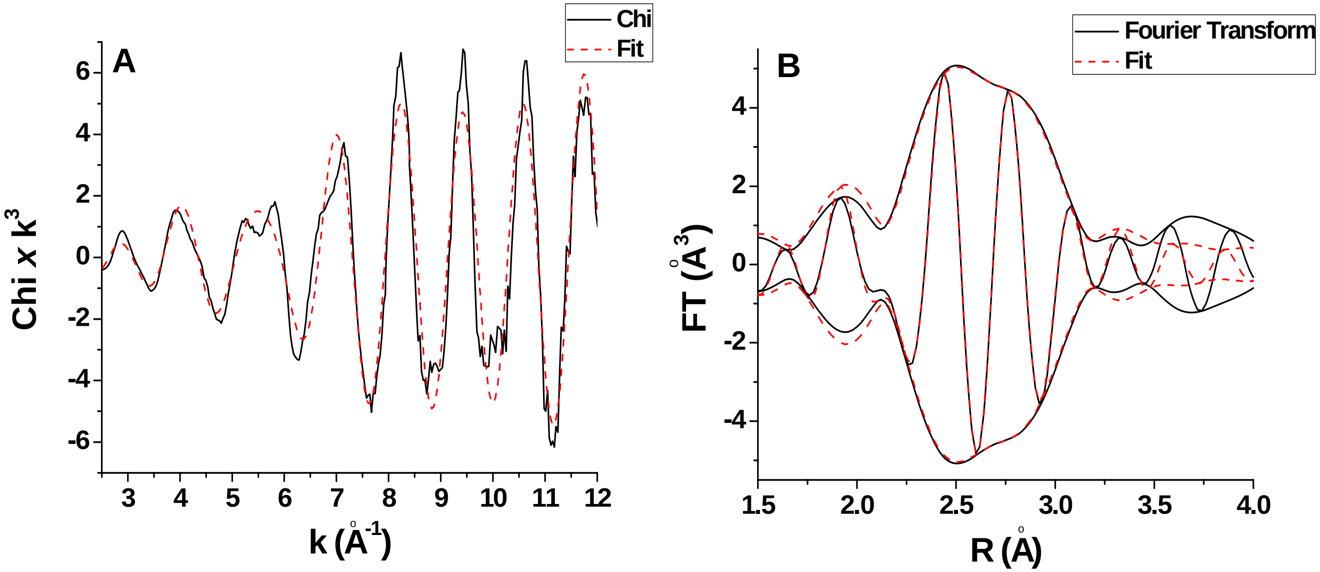


Pt/Al_2O_3L, 2 nm



SiO_2, 1.5-3 nm

EXAFS analysis
Below and above temperature of ignition

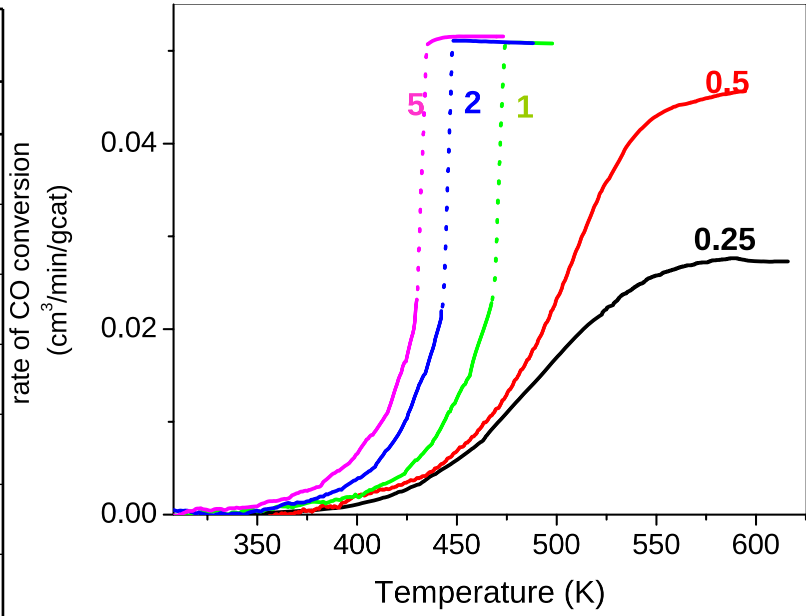


K^3 weighted CHI and Fourier transform
$2.5 < k < 12$ Å^{-1}
Pt/Al_2O_3L reduced, hydrogen removed; He (RT)

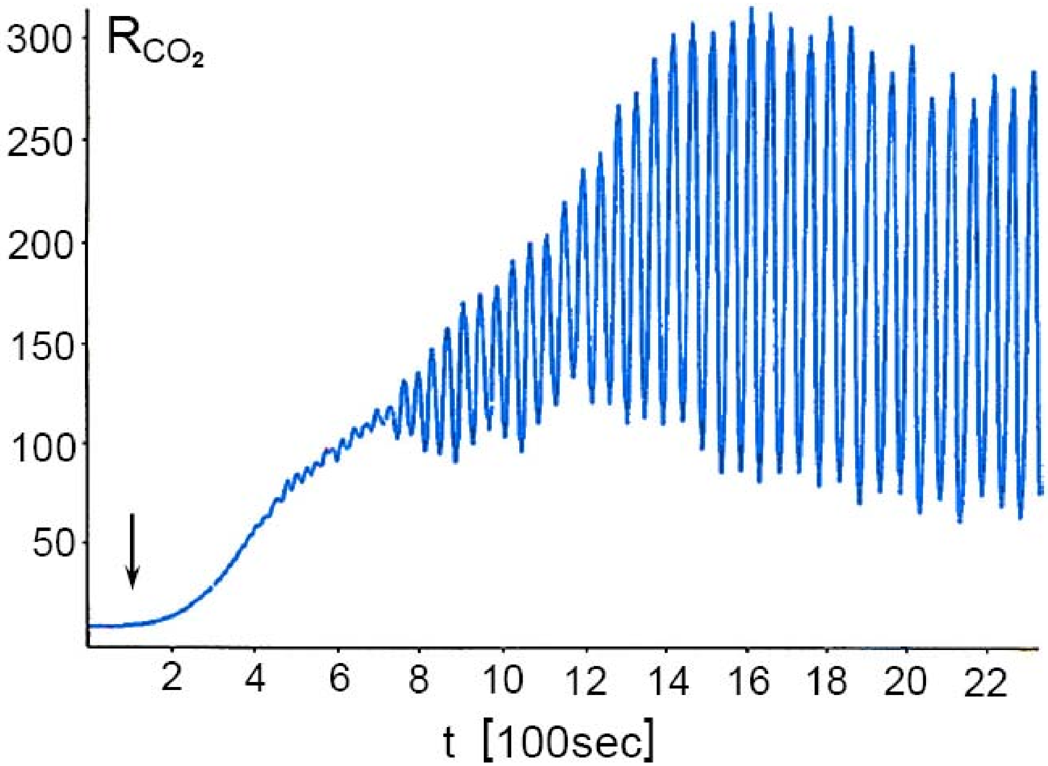
EXAFS analysis

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

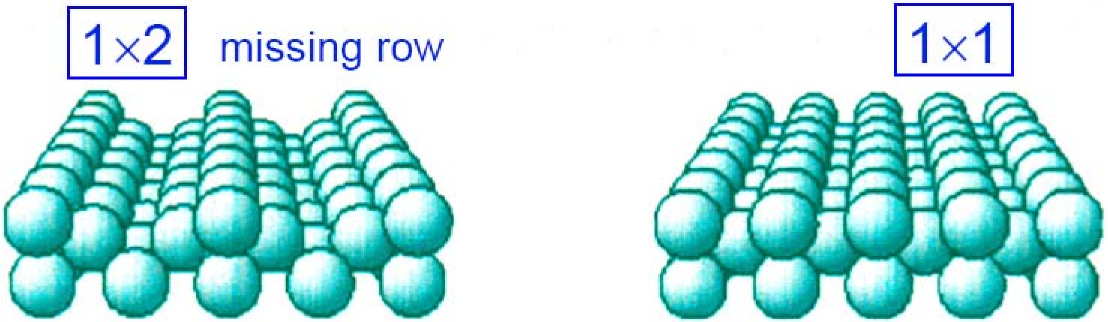


T = 470K
p_{CO}= 3×10^{-5}mbar
p_{O2}= 2.0→2.7×10^{-4}mbar

Pt (110)

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

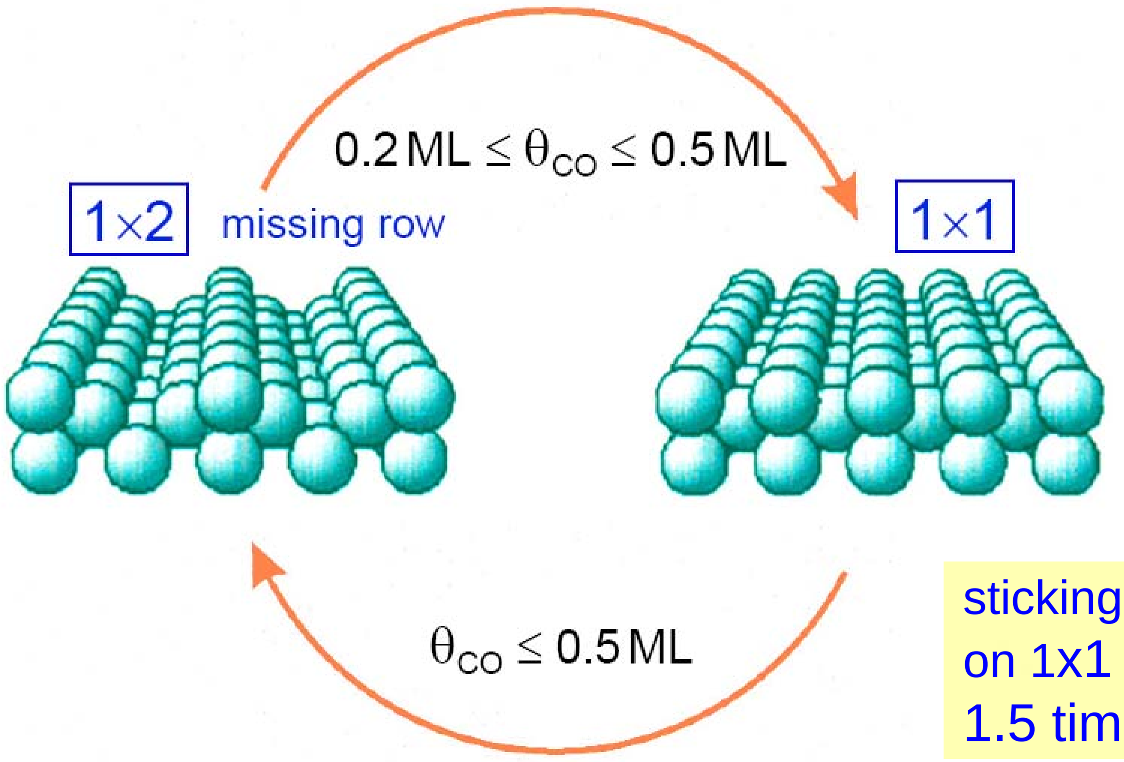
Kinetic oscillations – Single Crystals



bulk crystal plane

Pt (110)

Kinetic oscillations – Single Crystals



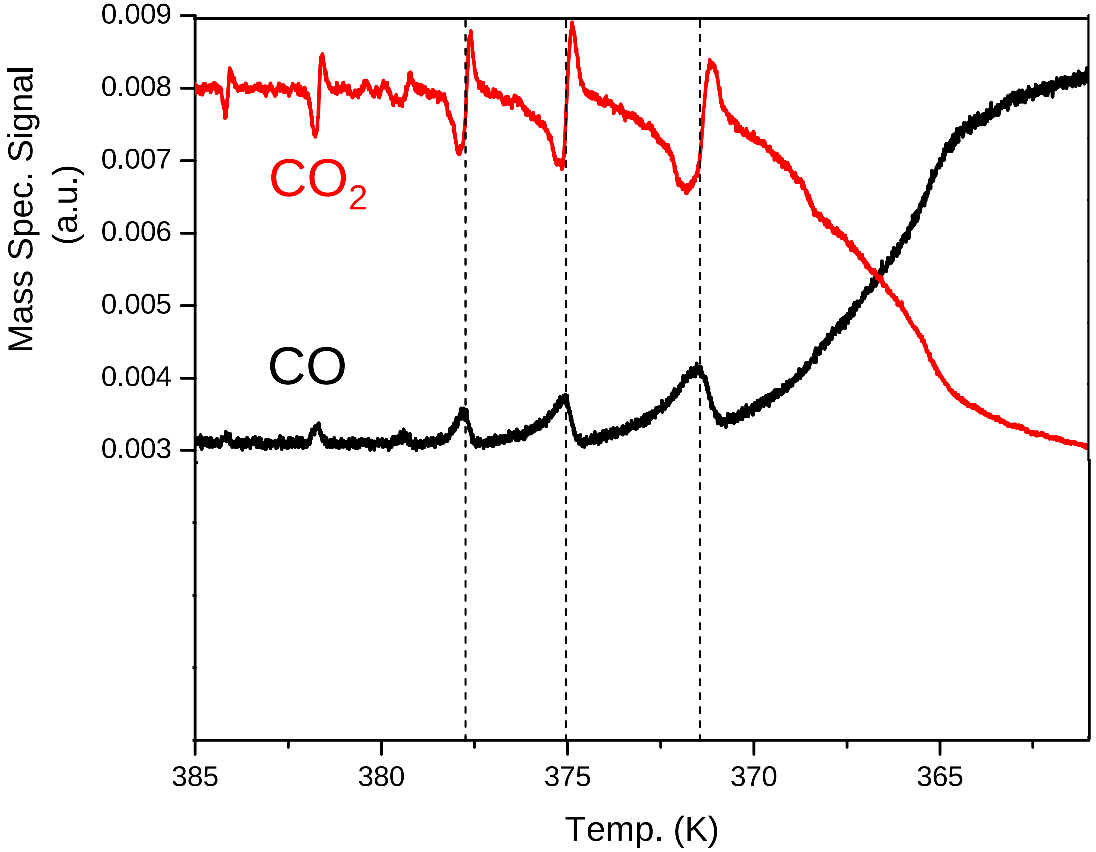
lower adsorption energy of CO

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*

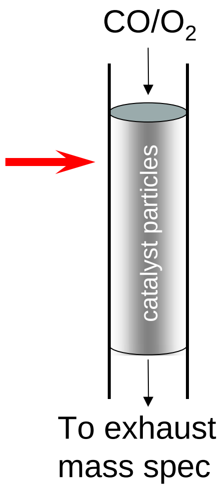
Kinetic oscillations - 2wt% Pt/Al_2O_3



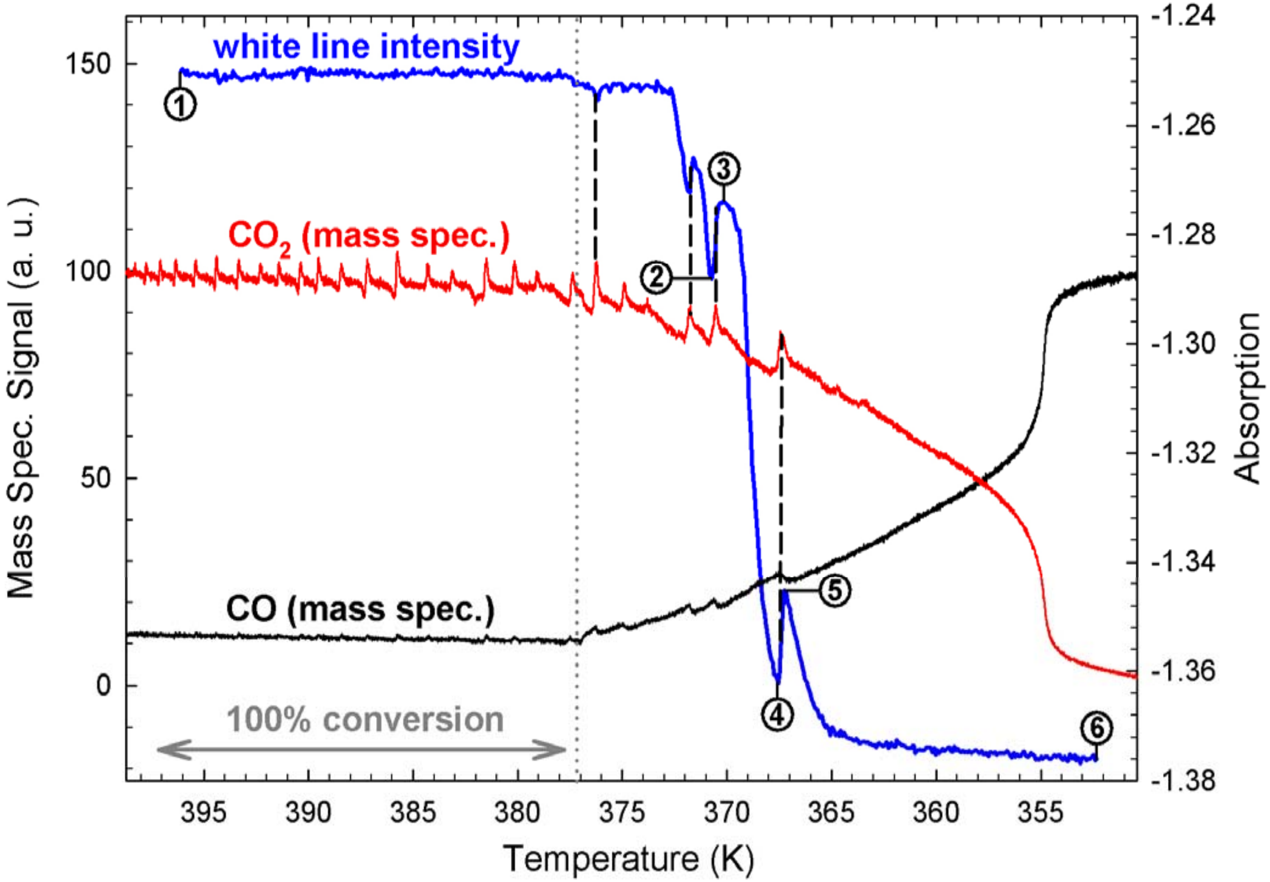
- storage of CO that is released in sudden spike of CO_2

- 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%