Photoemission from catalytical surfaces

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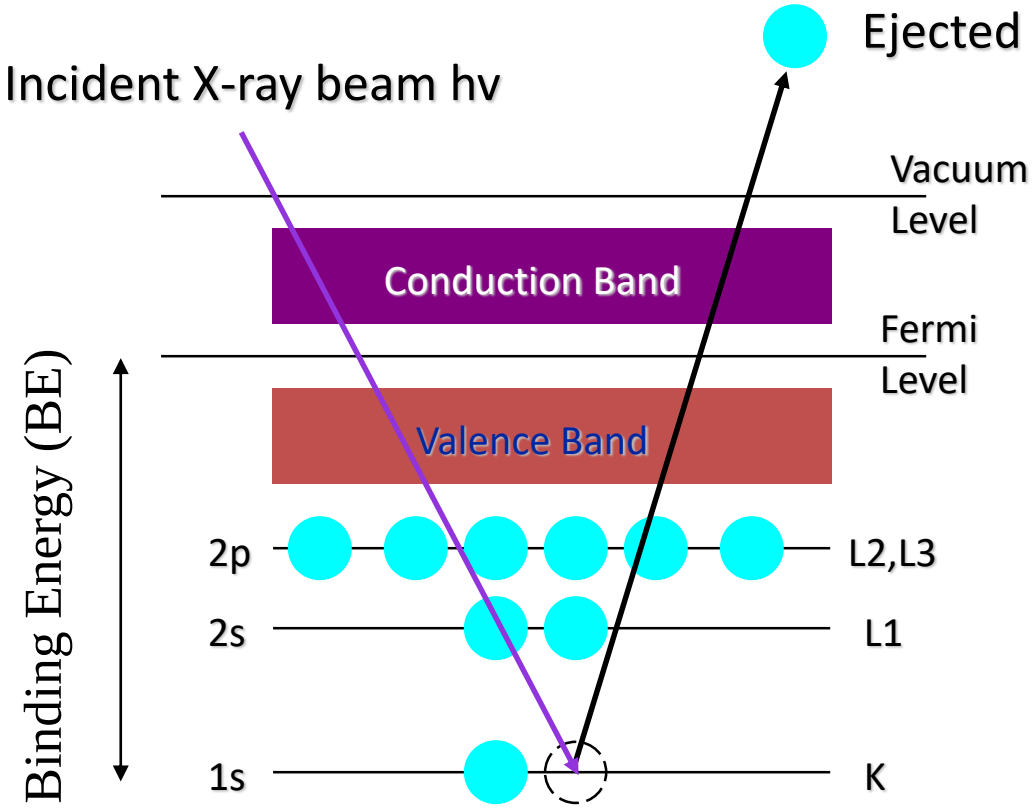
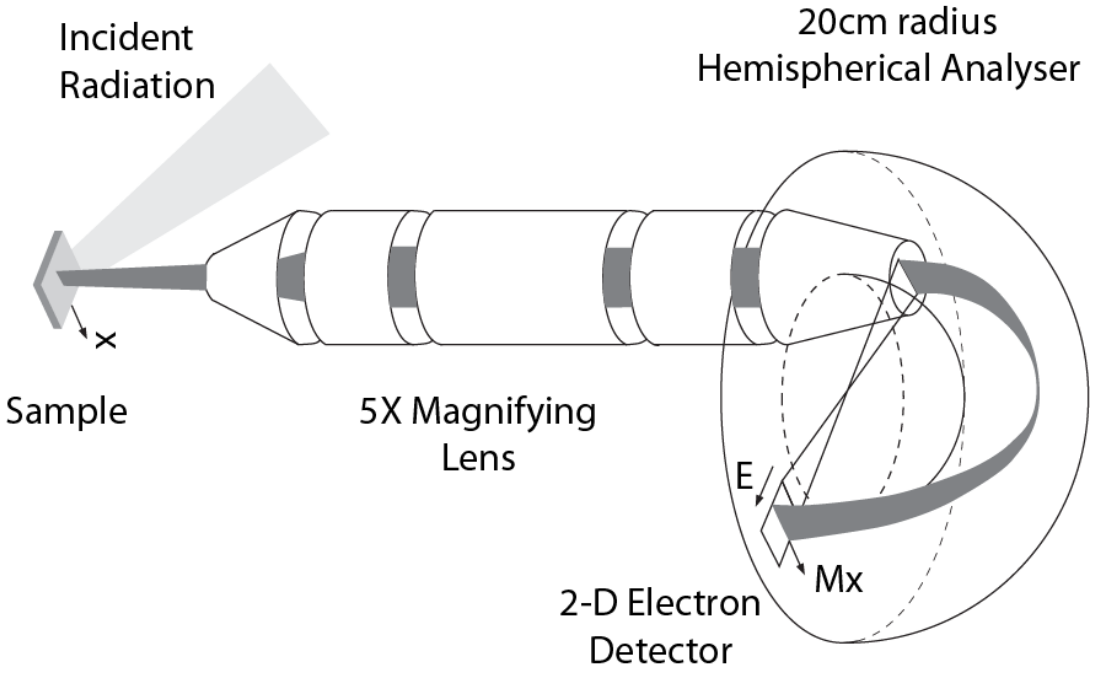


- XPS spectral lines are identified by the shell from which the electron was ejected (1s, 2s, 2p, etc.).
- The ejected photoelectron has kinetic energy:

  $KE = h\nu - BE - \Phi$

- **The binding energy (BE) is characteristic for the elements so from the measured kinetic energy we can identify the elements present.**

Φ = work function = energy to remove electron from Fermi level to vacuum

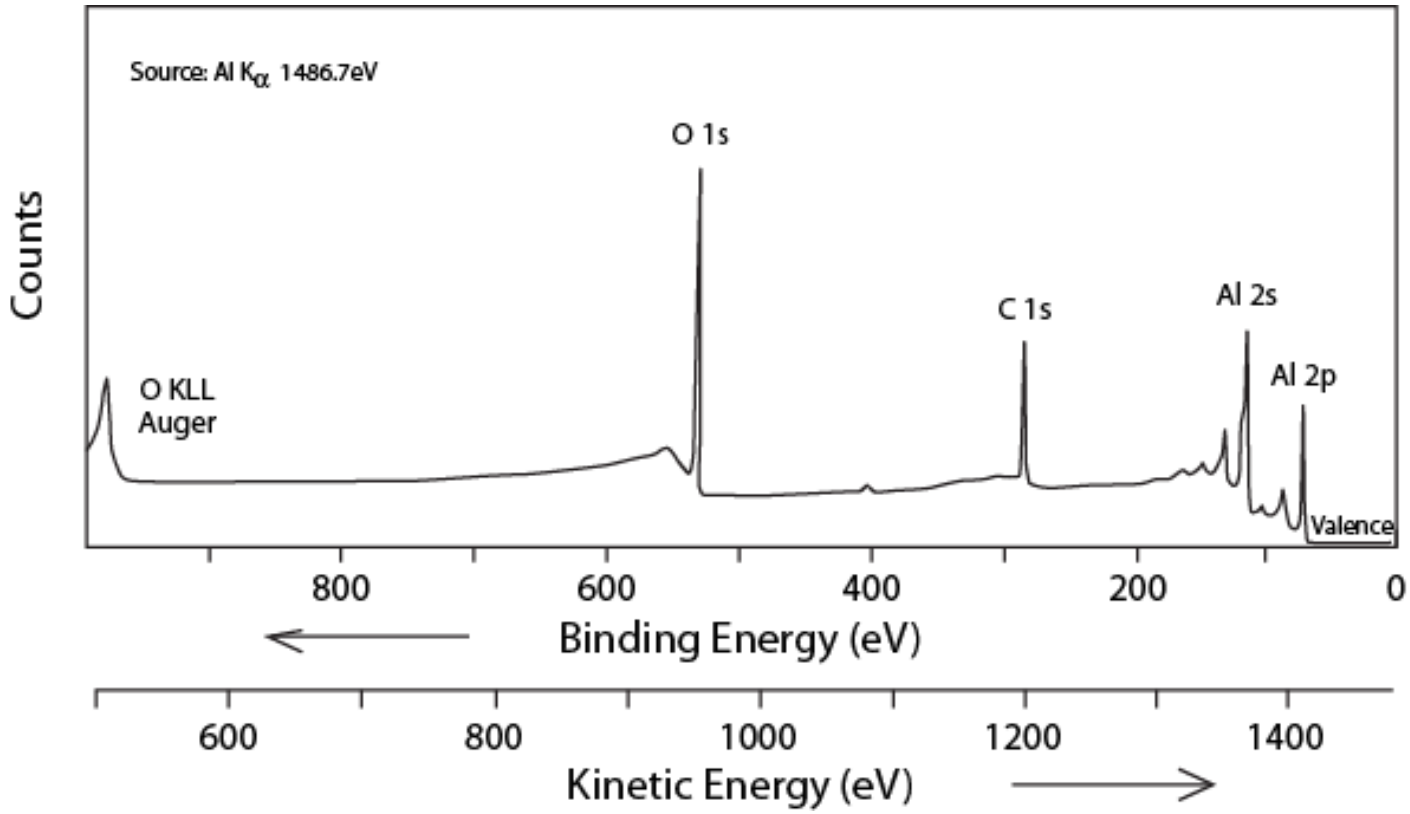


Pass Energy: 2 - 500eV

Resolution: $E/\Delta E \sim 1500$

$\Delta E_{min} = 5meV$

High energy resolution



Al, O, C can be identified

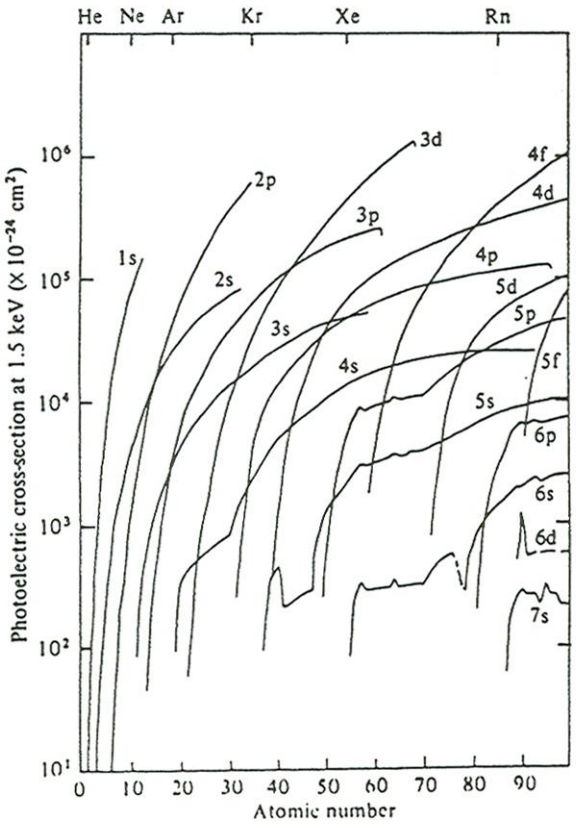
But what about the amounts?

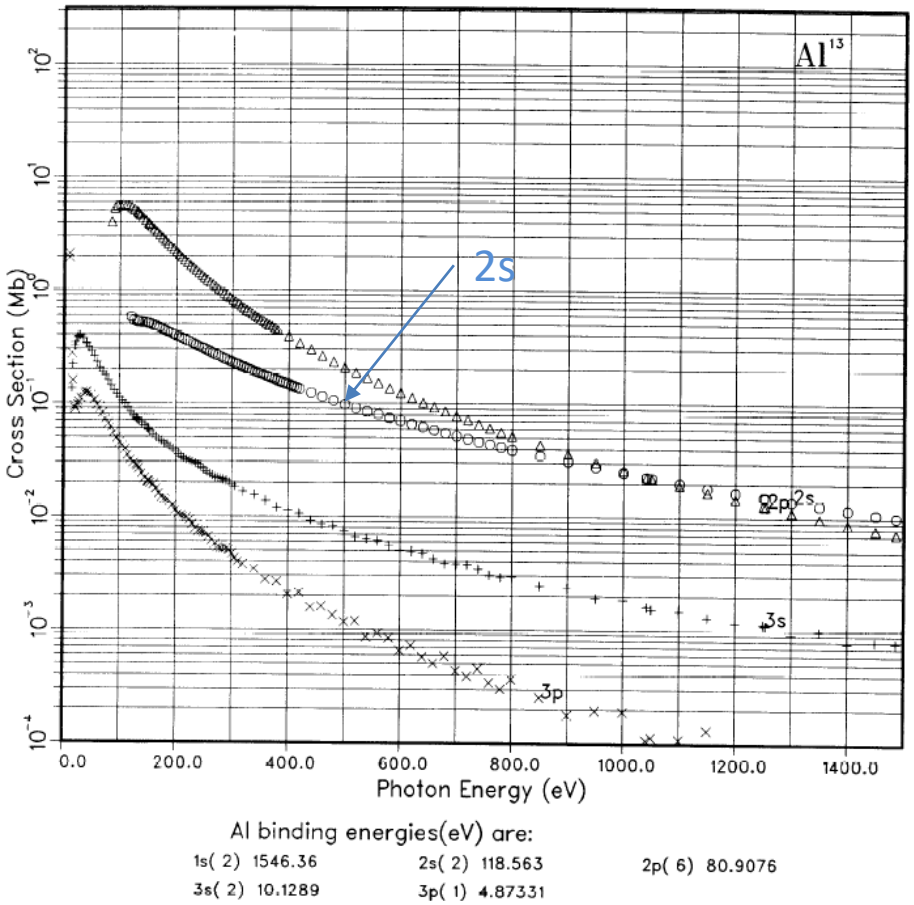
Does the Al 2s vs Al 2p intensity make sense?

Elemental analysis: Photoionization cross section

https://vuo.elettra.eu/services/elements/WebElements.html

Yeh, J. J.; Lindau, I., Atomic subshell photoionization cross sections and asymmetry parameters:
$1 \leqslant Z \leqslant 103$. At. Data Nucl. Data Tables 1985, 32 (1), 1-155.





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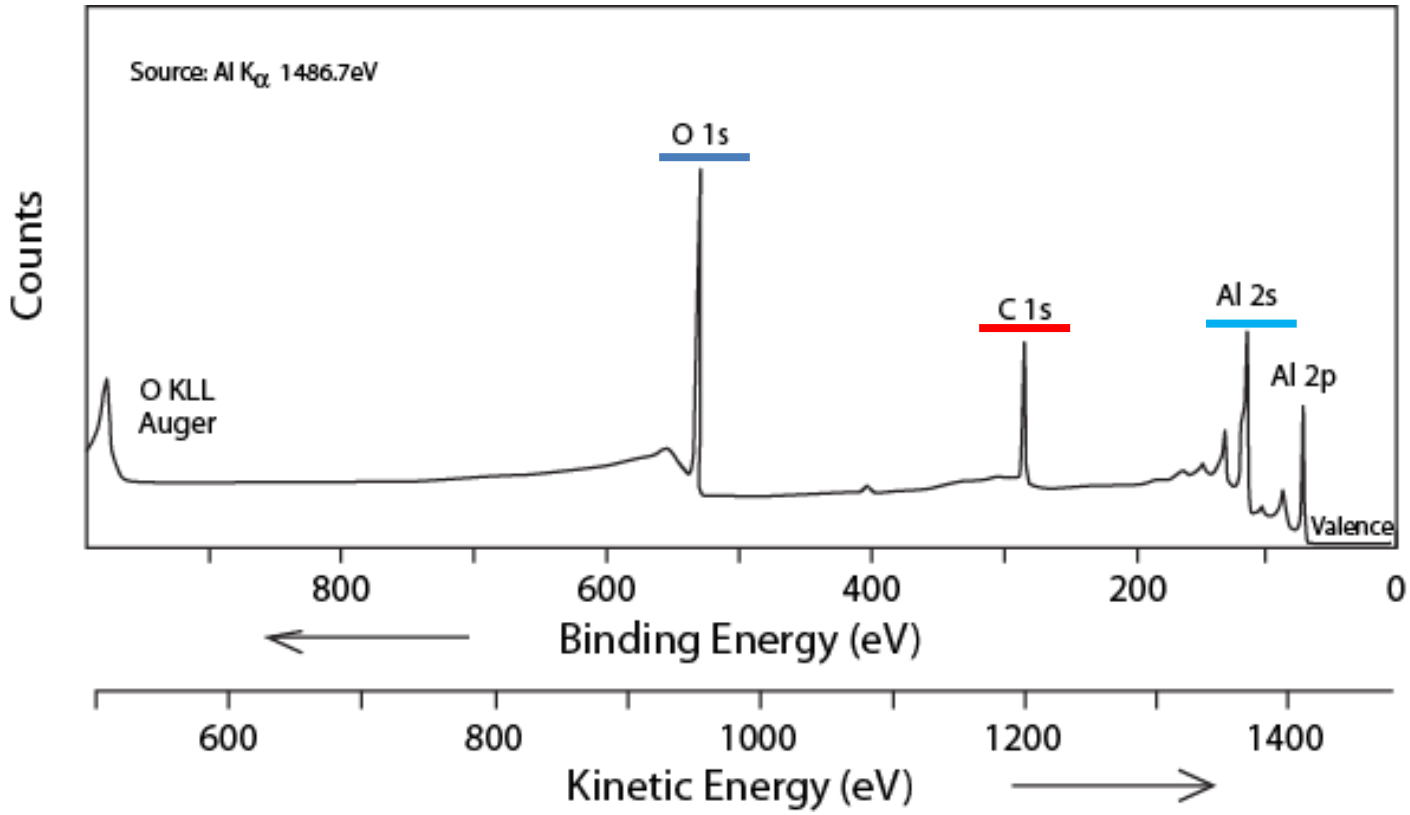
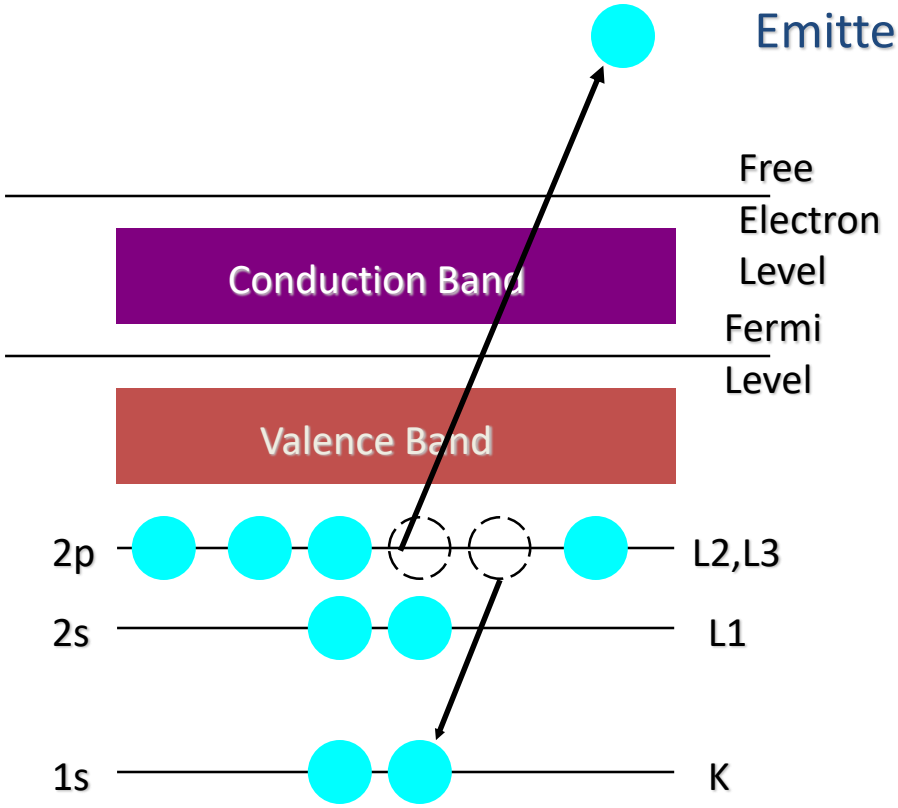
XPS on oxidized aluminum



Quantification?



Emitted Auger Electron

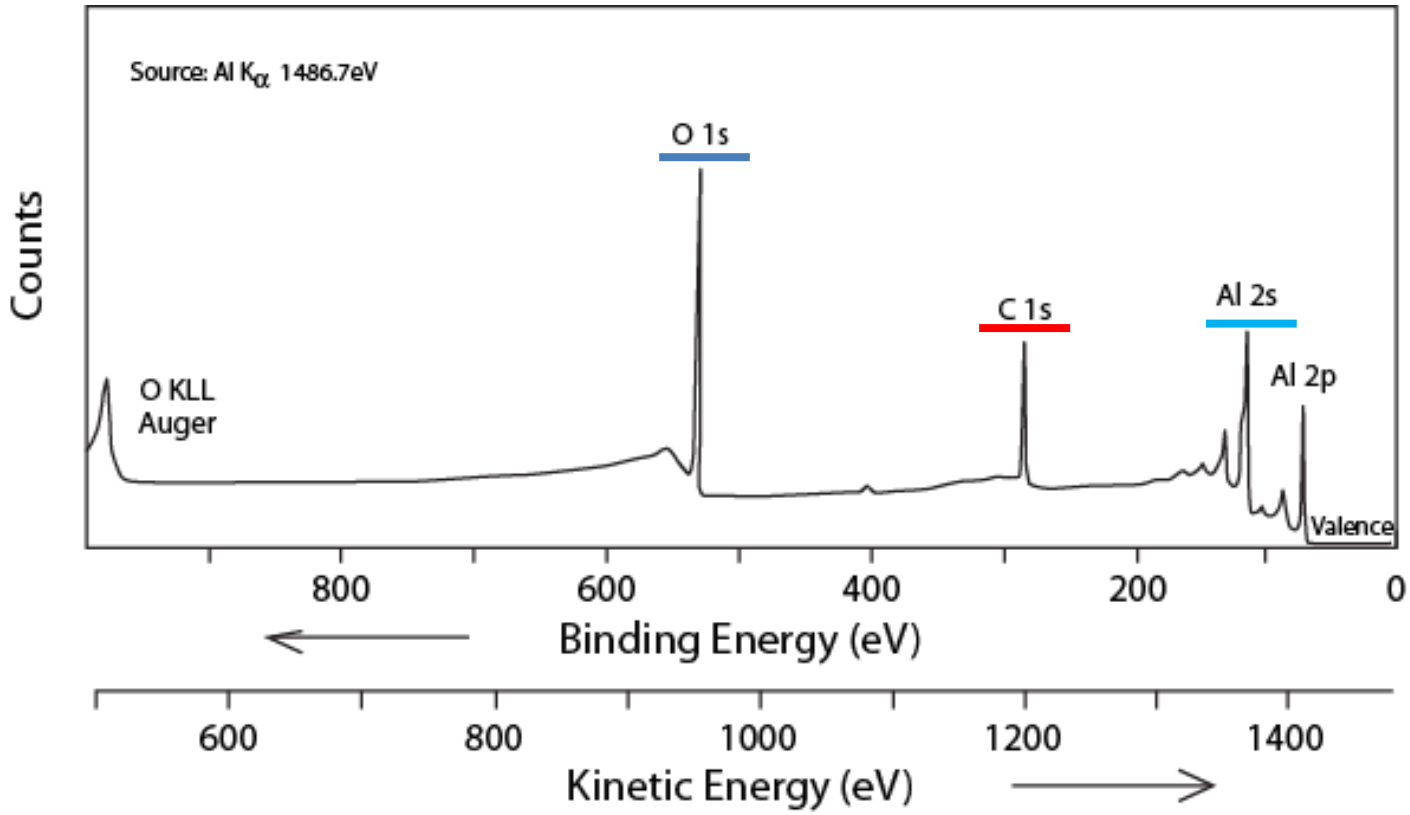
- L electron fills core level vacancy in K shell (step 1).
- Another L Auger electron emitted to conserve energy released in step 1.
- The kinetic energy of the emitted Auger electron is:

  KE=E(K)-E(L2)-E(L3).

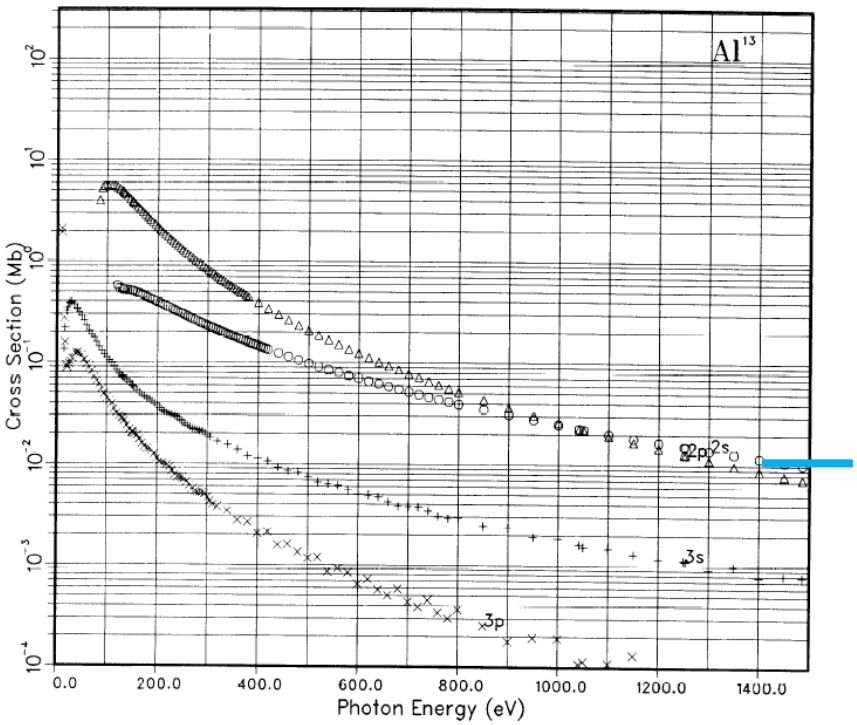
How do we distinguish photo and Auger electron emission?

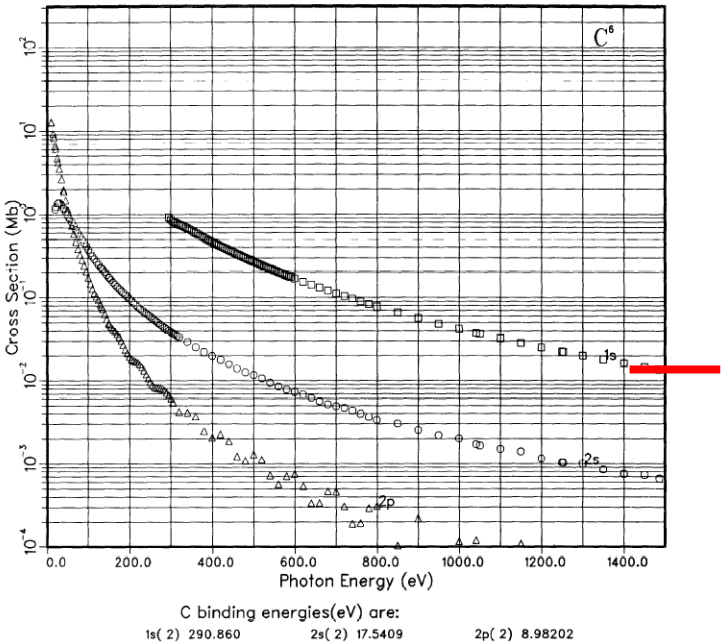
Chemical shifts?

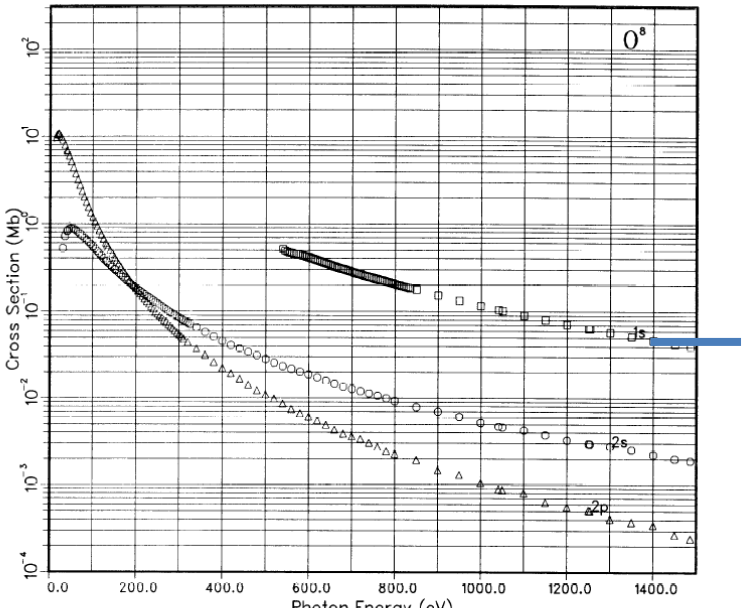
XPS on oxidized aluminum



Quantification?







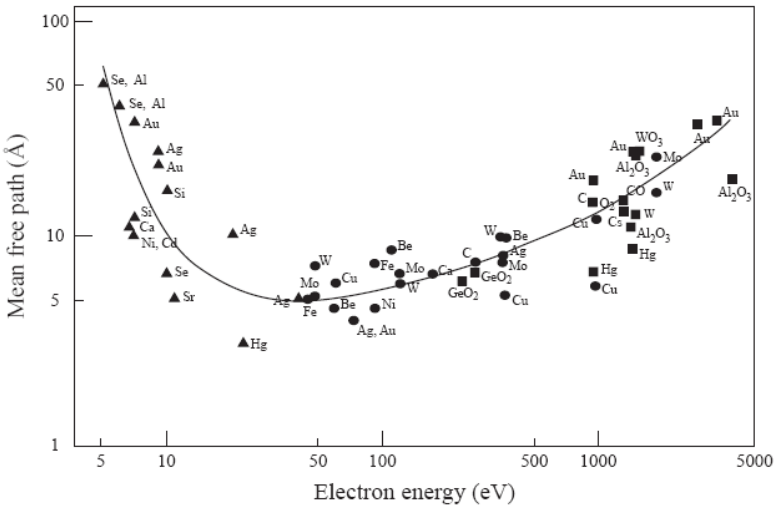
Back of the envelope for 1500 eV photons

Al (2p or 2s)	1×10^{-2} Mb
C (1s)	1×10^{-2} Mb
O (1s)	4×10^{-2} Mb

So we have about the same amount of Al and C, and the O amount is about 0.5 x the Al amount

Does that make sense?

XPS and AES rely on the **short mean free path** of **low energy electrons** in solids for achieving **surface sensitivity.**



The intensity removed (-dI) per length travelled (dx)

$-dI = \sigma N' I\, dx$ (σ: cross section for inelastic processes)

(N': Scattering centers per cm^3)

$I(x) = I_0\, e^{-\sigma N' x} = I_0\, e^{-x/\lambda}$

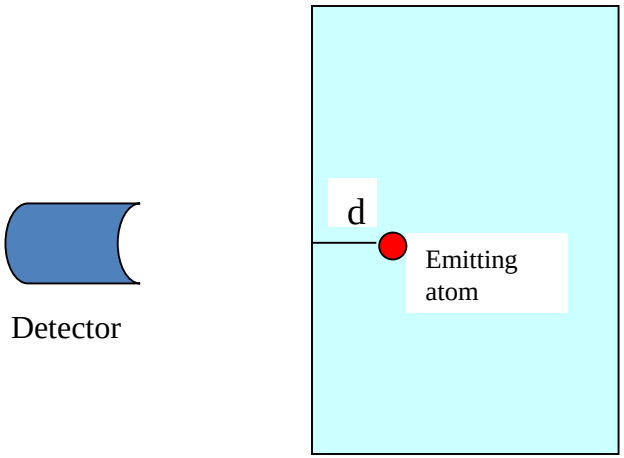
where $\lambda = (\sigma N')^{-1}$ is the mean free path

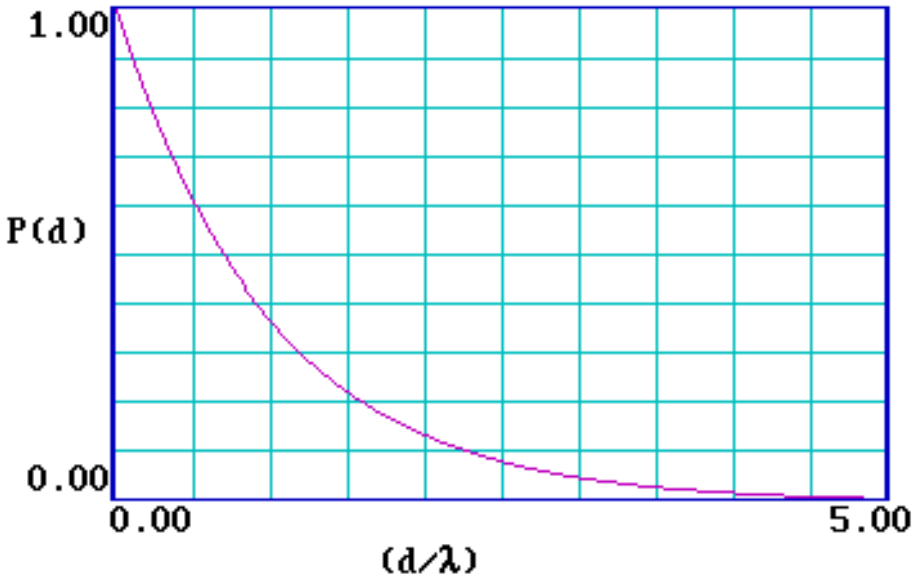
I(x) is the intensity of electrons that have not lost any energy after they have travelled the distance x in the solid.

So, if you made all atoms in a solid emit electrons at a given energy of around say 70 eV and detected all electrons coming out of the sample with that energy, the majority of the electrons would come from the first few atomic layers.

Probability of an electron travelling the distance d through a material <u>without</u> losing energy (λ : mean free path)

$P(d) = e^{-d/\lambda}$ (remember $\lambda=\lambda(E)$)





Only top most surface layers probed

Mean free path in Å as a function of energy (in eV)

$$\lambda = \frac{E}{E_p^2[\beta \ln(\gamma E) - (C/E) + (D/E^2)]}$$

$$\beta = -0.10 + 0.944(E_p^2 + E_g^2)^{-1/2} + 0.069\rho^{0.1}$$

$$\gamma = 0.191\rho^{-1/2}$$

$$C = 1.97 - 0.91U$$

$$D = 53.4 - 20.8U$$

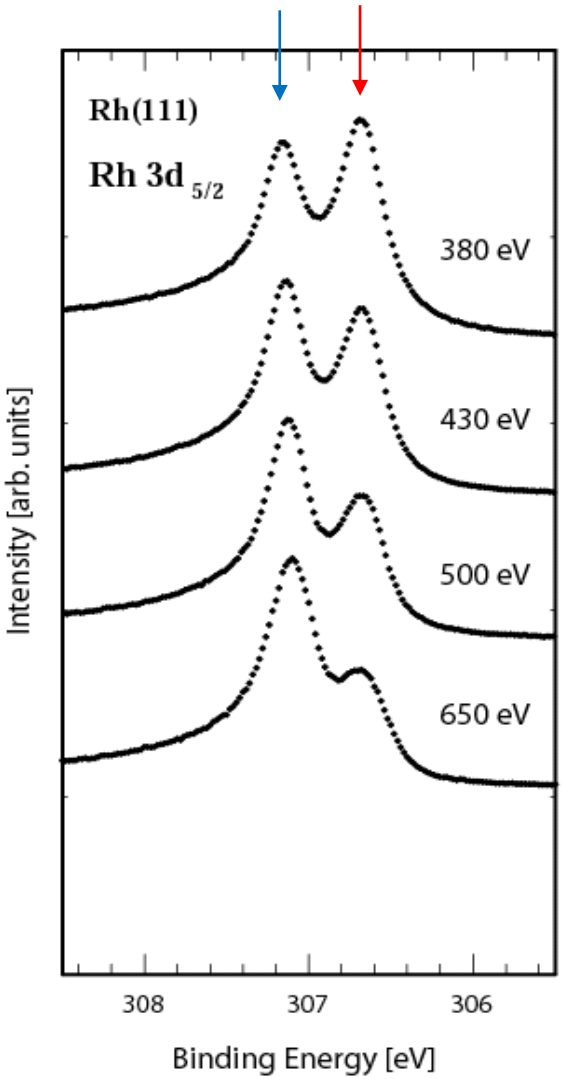
$$U = N_v\rho/M = E_p^2/829.4$$

E_p = free-electron plasmon energy (eV)
E_g = band gap (eV)
ρ = density (g/cm^3)
M = atomic weight
N_v = number of valance electrons per atom

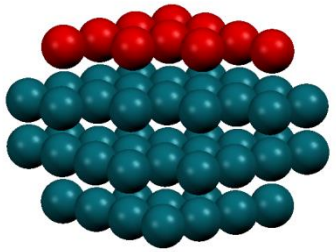
Tanuma, S.; Powell, C. J.; Penn, D. R., Calculation of electron inelastic mean free paths (IMFPs) VII. Reliability of the TPP-2M IMFP predictive equation. Surface and Interface Analysis 2003, 35 (3), 268-275.

Tanuma, S.; Powell, C. J.; Penn, D. R., Calculations of electron inelastic mean free paths. V. Data for 14 organic compounds over the 50–2000 eV range. *Surface and Interface Analysis* **1994,** *21* (3), 165-176.

Surface core level shifts

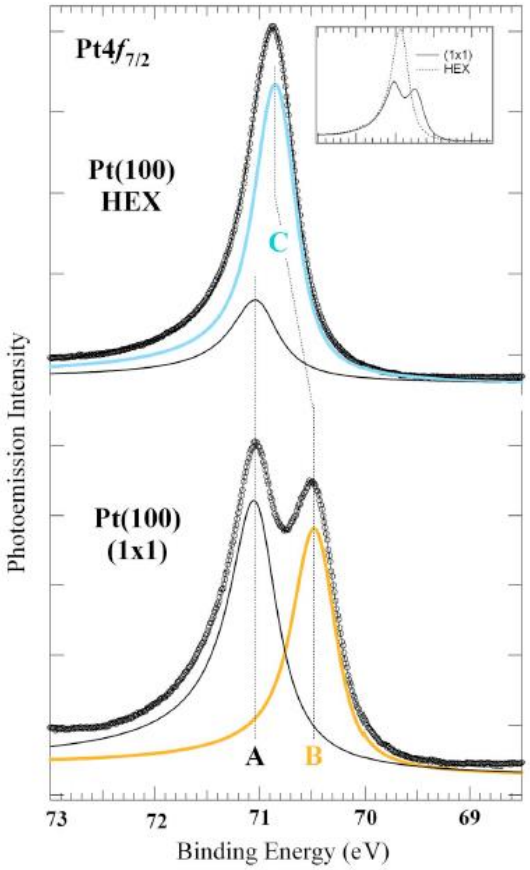


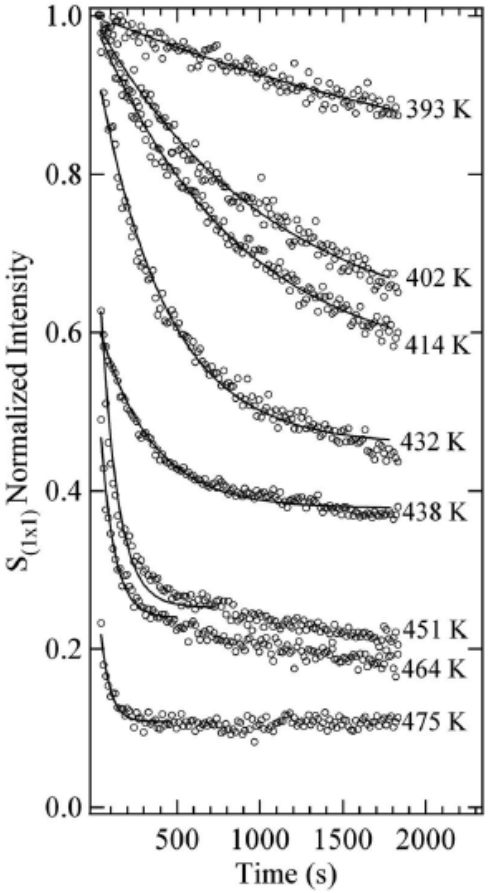
Rh(111) surface (FCC)

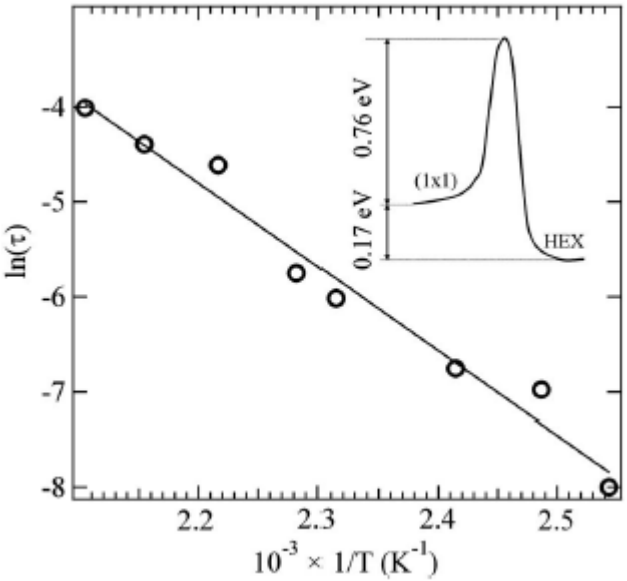


Tune surface sensitivity by photon energy

Surface core level shifts: Pt(100)

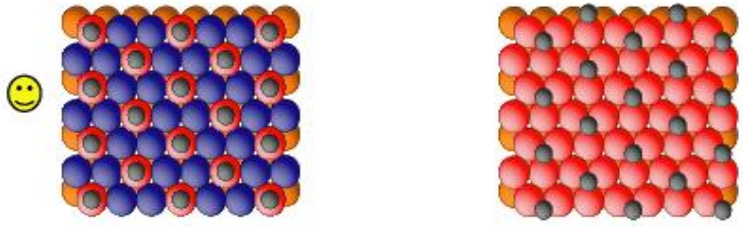


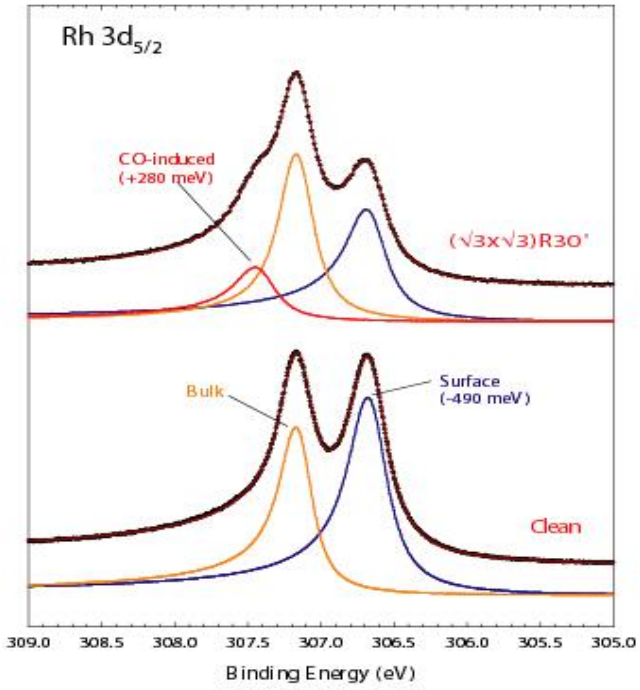




Baraldi, A.; Vesselli, E.; Bianchettin, L.; Comelli, G.; Lizzit, S.; Petaccia, L.; de Gironcoli, S.; Locatelli, A.; Mentes, T. O.; Aballe, L.; Weissenrieder, J.; Andersen, J. N., The (1x1)-> hexagonal structural transition on Pt(100) studied by high-energy resolution core level photoemission. *J. Chem. Phys.* **2007,** *127* (16), 164702.

Extract activation energies





Theory results

Total energies: almost degenerate for CO in top and 3fold sites (which they should be!!)

Rh 3d shifts:

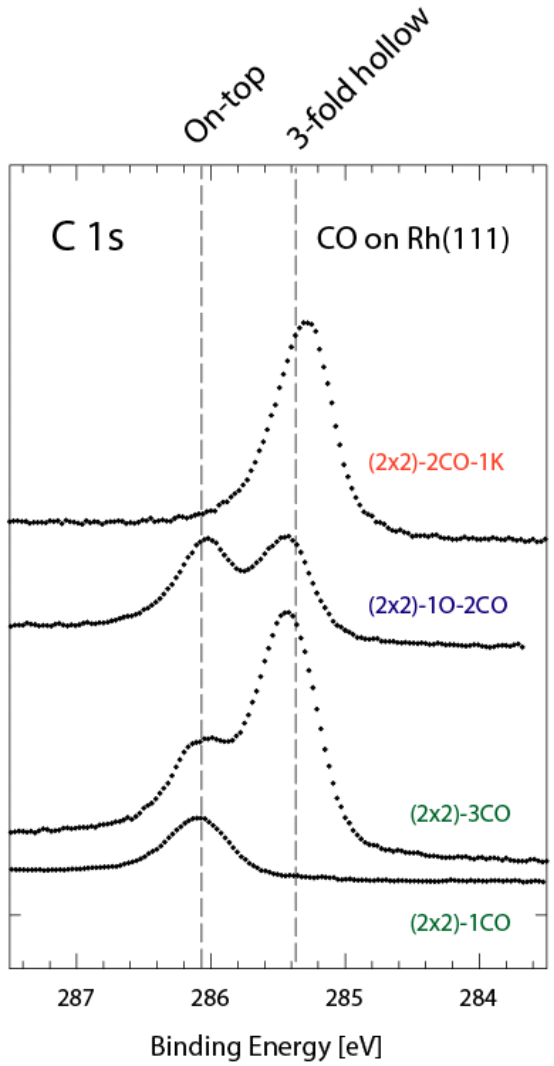
Clean: –500 meV

CO ind. (top): +450 meV (no buckling)
+240 meV (+0.2Å buckling)

CO ind. (3-fold): –220 meV

Surface peak decrease in intensity with 1/3

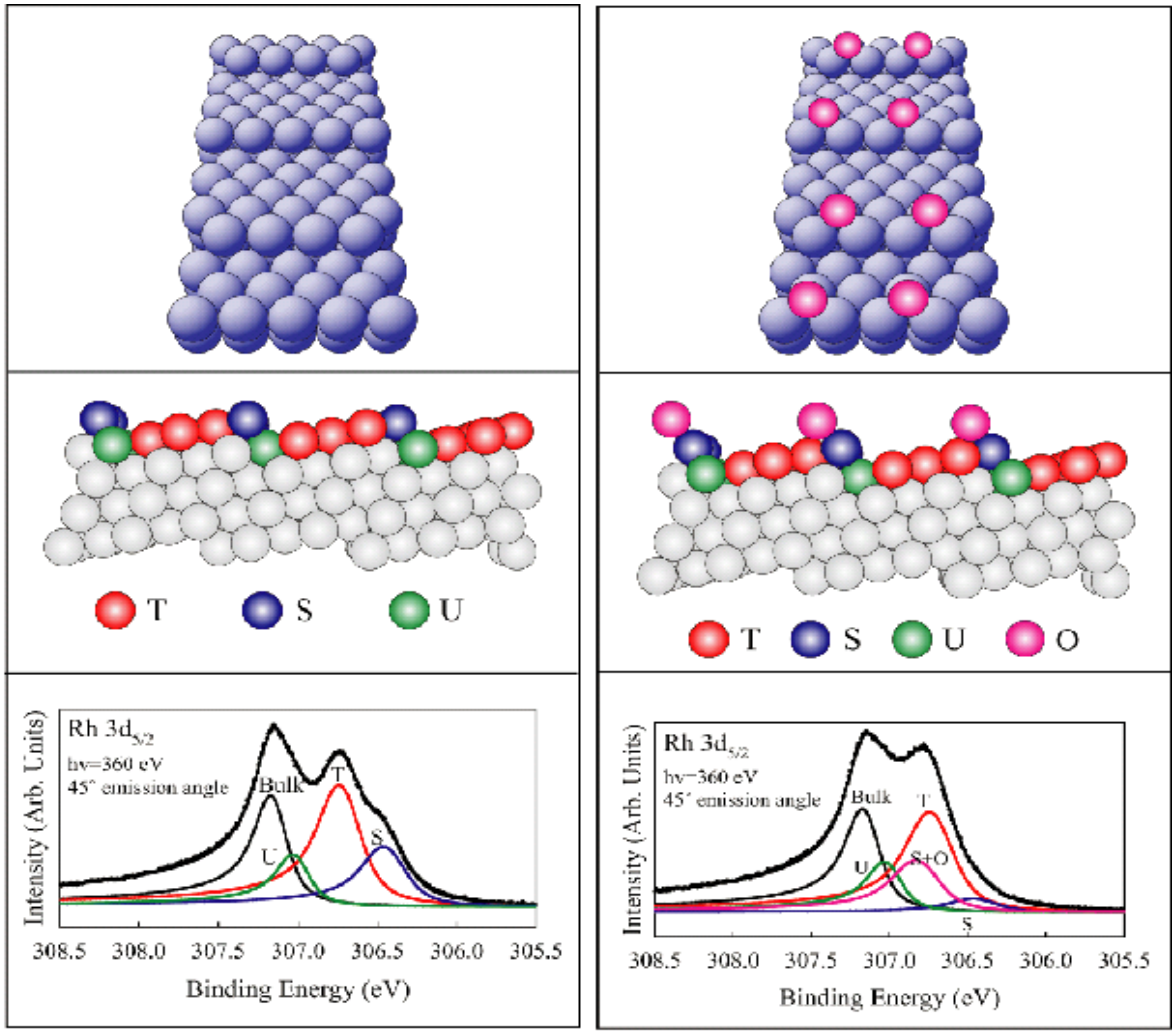
Conclusion: CO in the on-top site on a buckled surface



Blocking sites with K and O

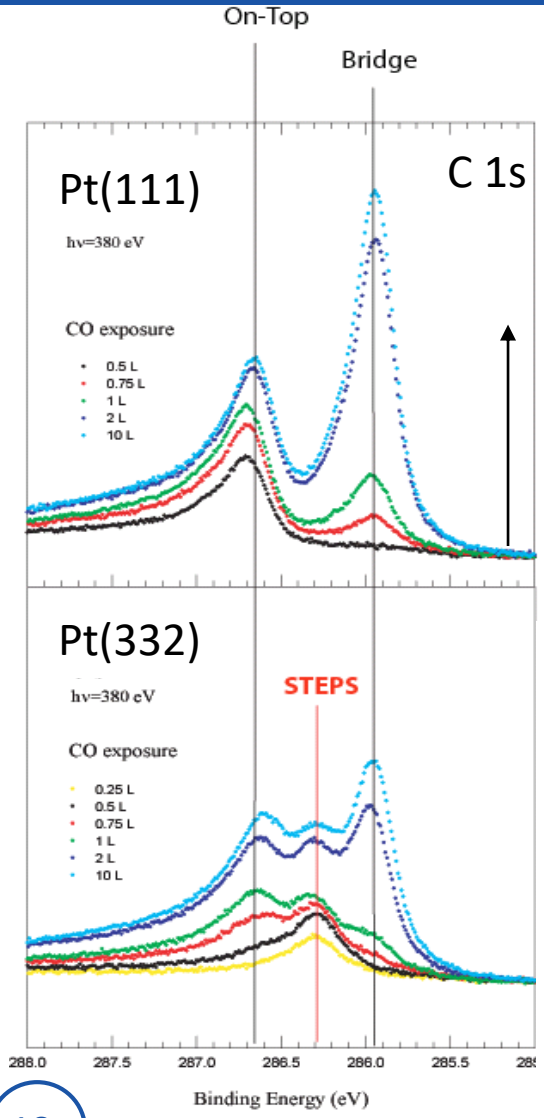
- For adsorbed CO the C1s binding energy provides a good fingerprint of the adsorption site. Nearest neighbors.
- Ex. CO on Rh(111), pure CO, and co-adsorbed with O and K
- Large shifts even when ground-state total energies are almost degenerate
- General rule: The C 1s binding energy for CO decreases as the coordination to the substrate increases

Rh(553) – observing steps and following oxygen adsorption



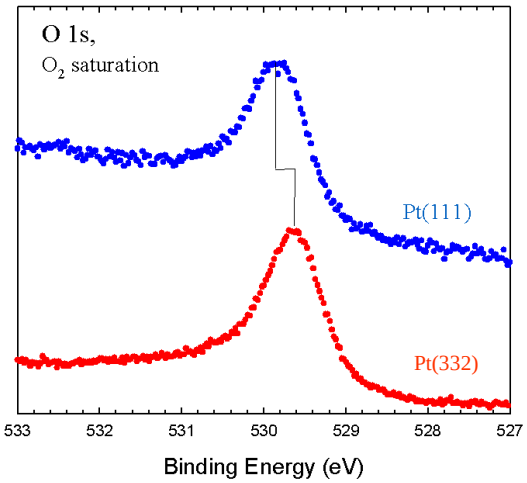
J. Gustafsson et al. PRL 91 (2003) 056102

Finger prints also on a more mesoscopic length scale



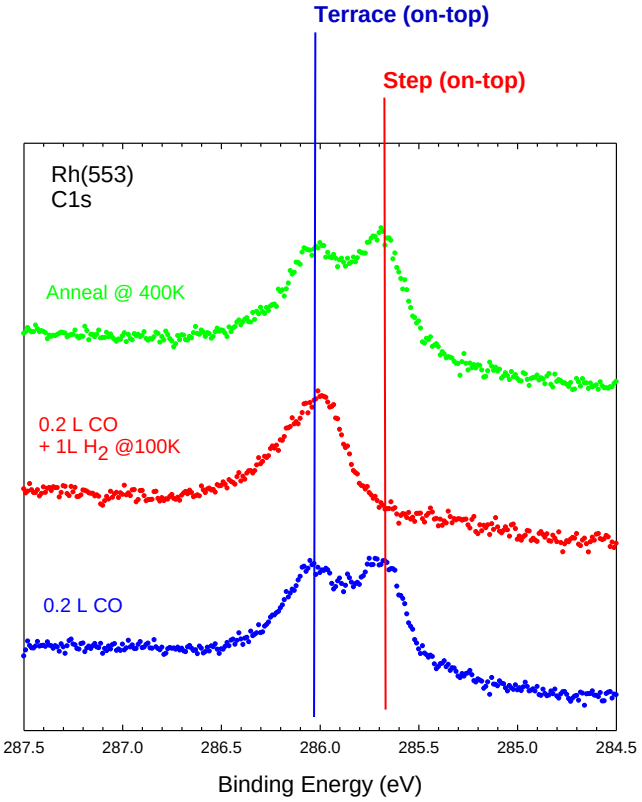
Dose CO

Pt(332) - O



Lowest energy site

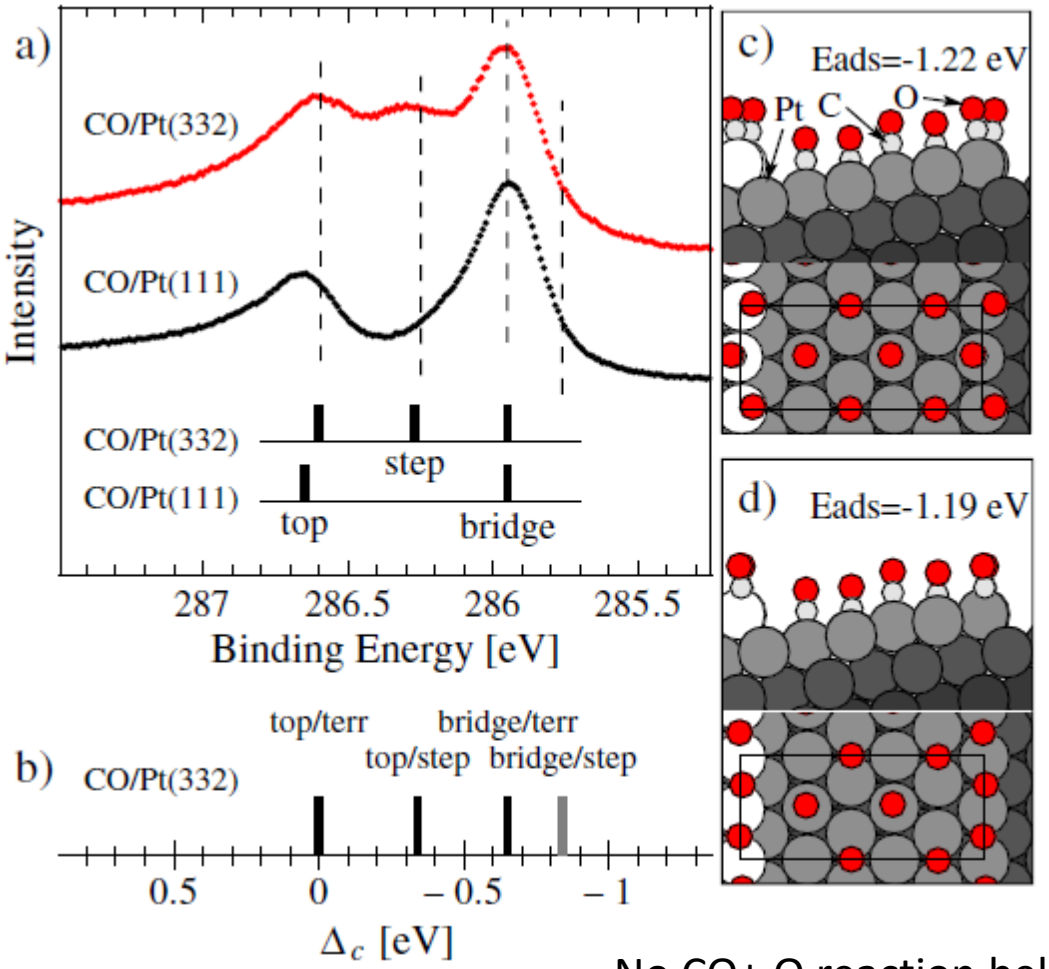
Rh(553) - CO - H

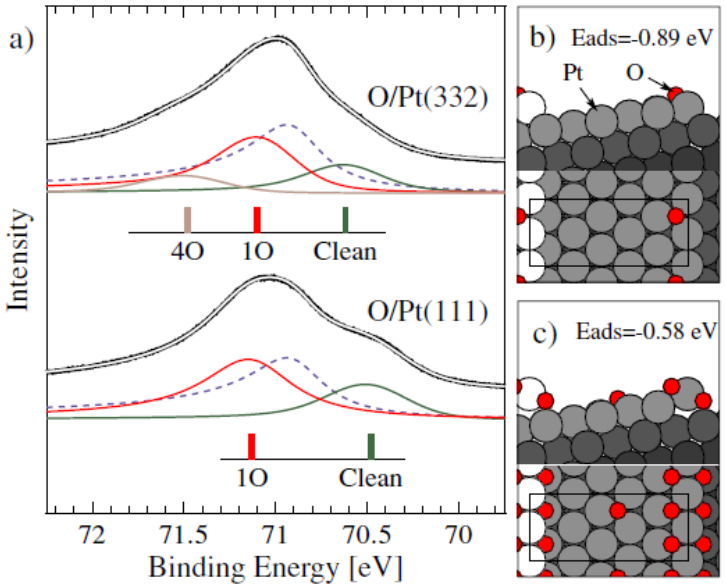


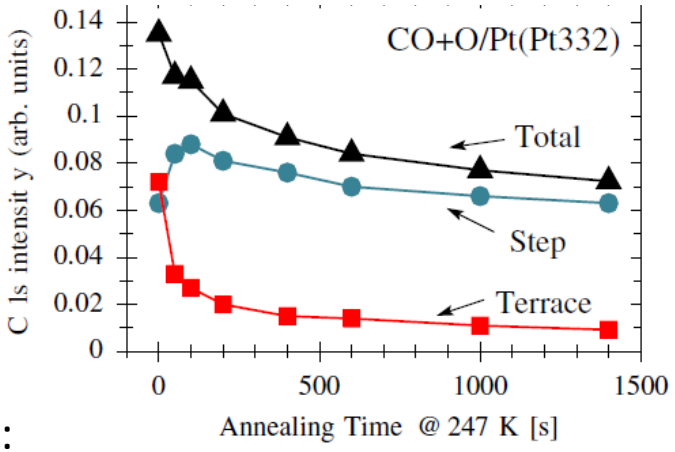
Active Site

...

Pt(332) – Probing site specific CO oxidation



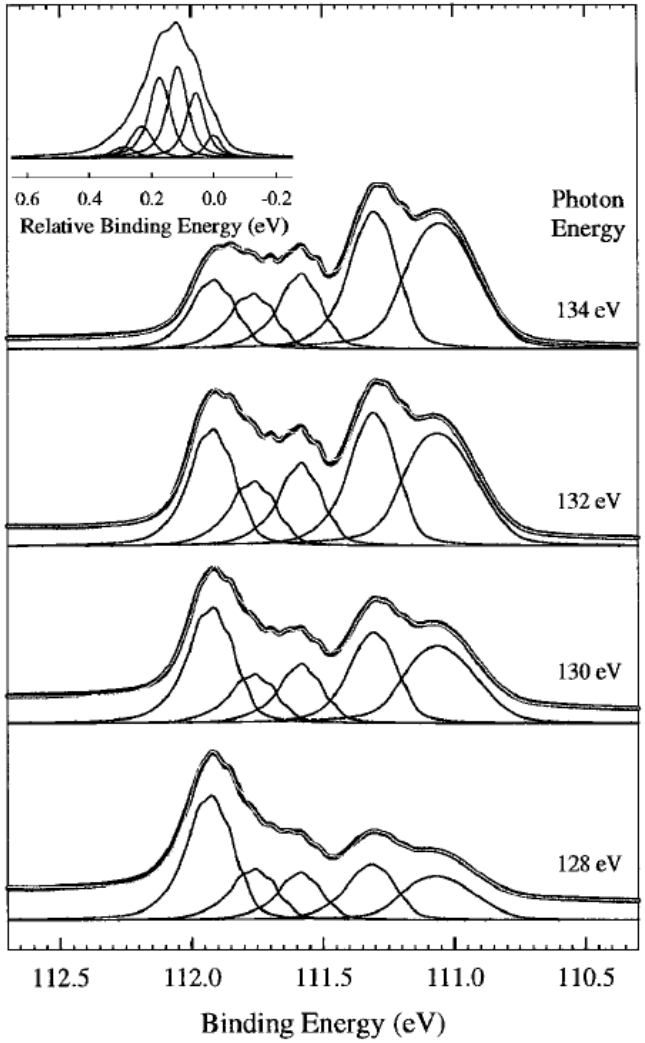




No CO+ O reaction below:
Pt(111) 270 K
Pt(332) 220 K

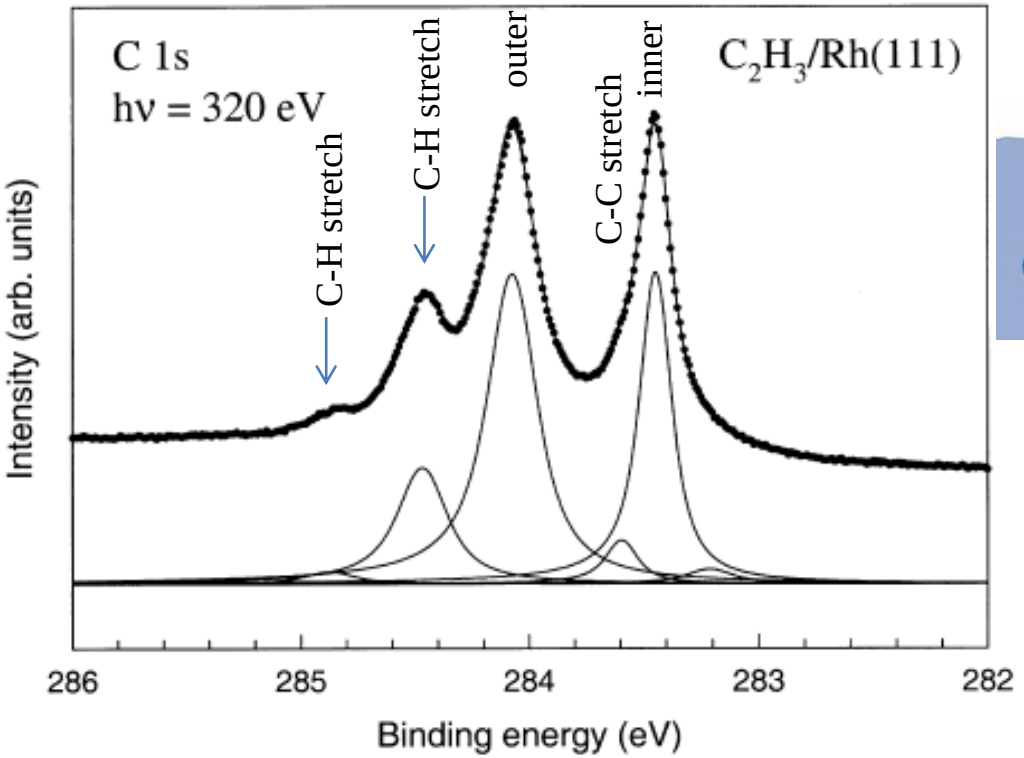
PRL 95 (2005) 256102

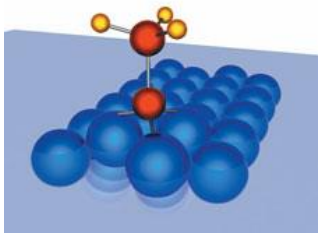
Phonon replicas and in Be 1s

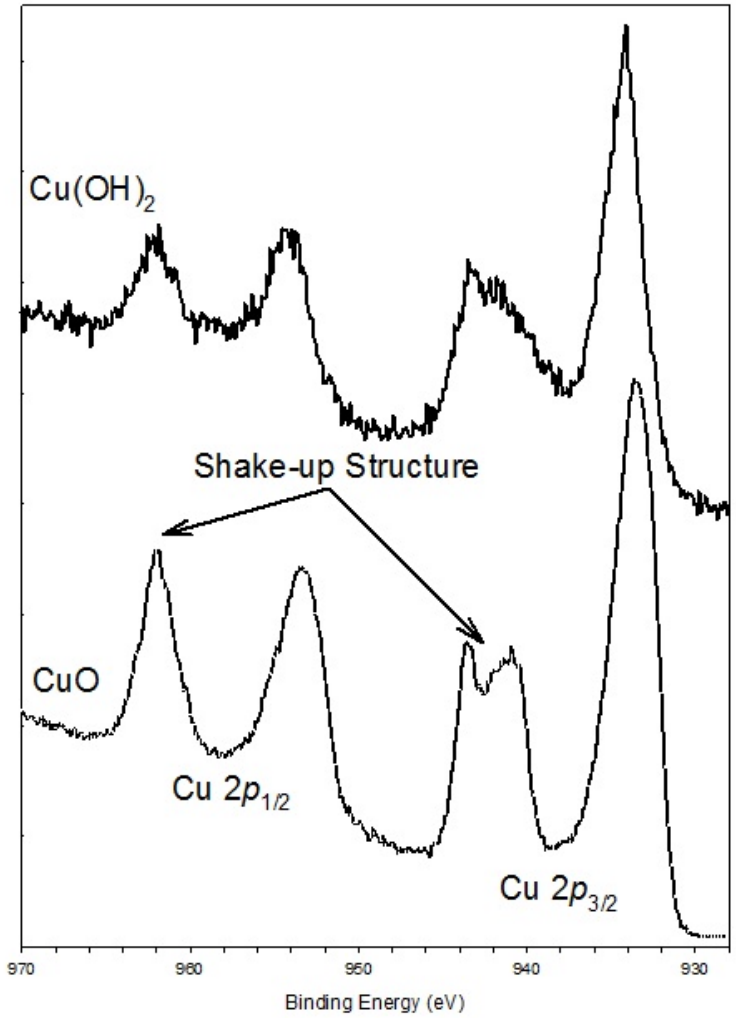


Andersen et al. PRL 86 (2001) 4398.

Bulk and first 4 layers resolved on Be(0001) – 1s

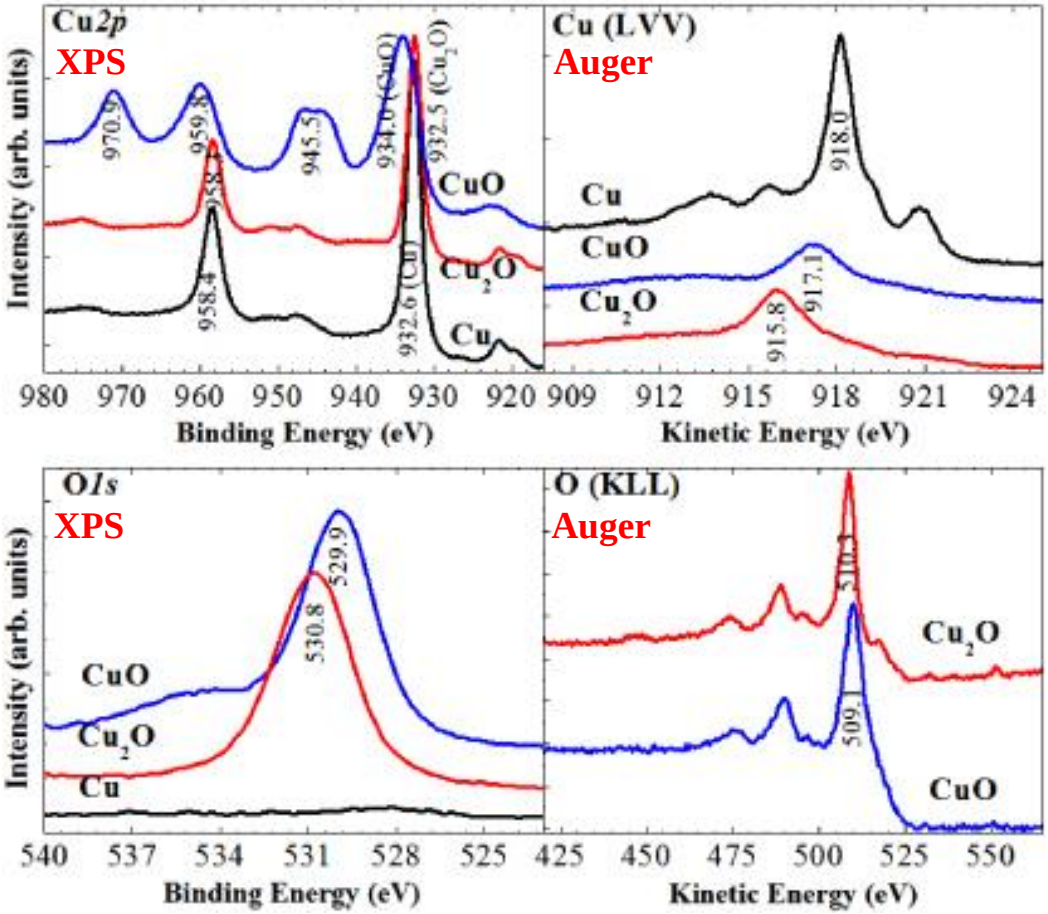

C 1s
hν = 320 eV
C-H stretch
C-H stretch
outer
C-C stretch
inner
C_2H_3/Rh(111)
Intensity (arb. units)
286
285
284
283
282
Binding energy (eV)



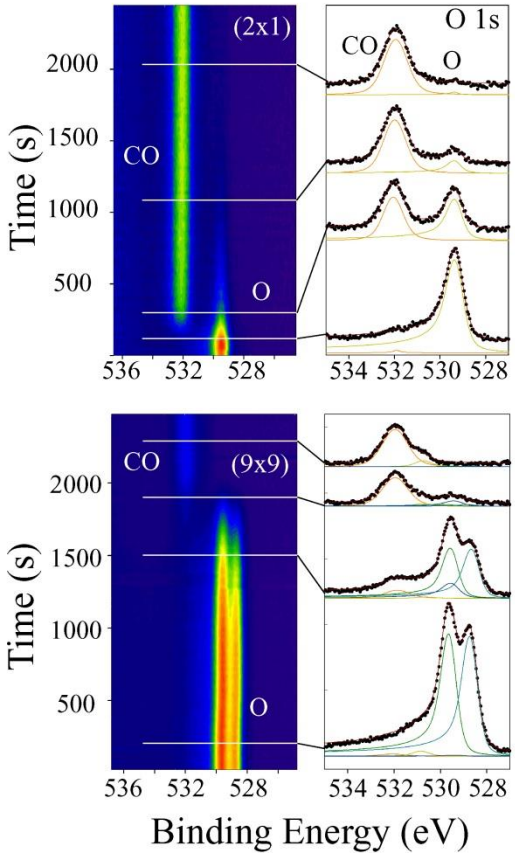


Excited final states

Figure 2 from Dahlang Tahir and Sven Tougaard
2012 J. Phys.: Condens. Matter 24 175002



Excited final states

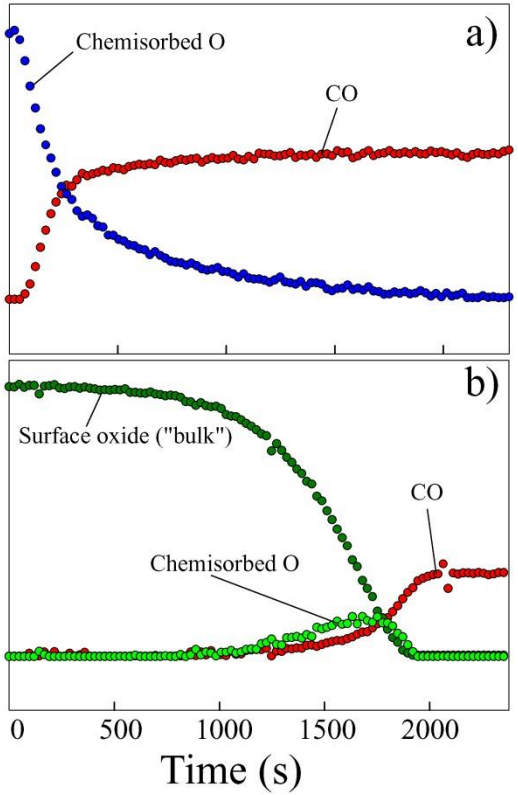


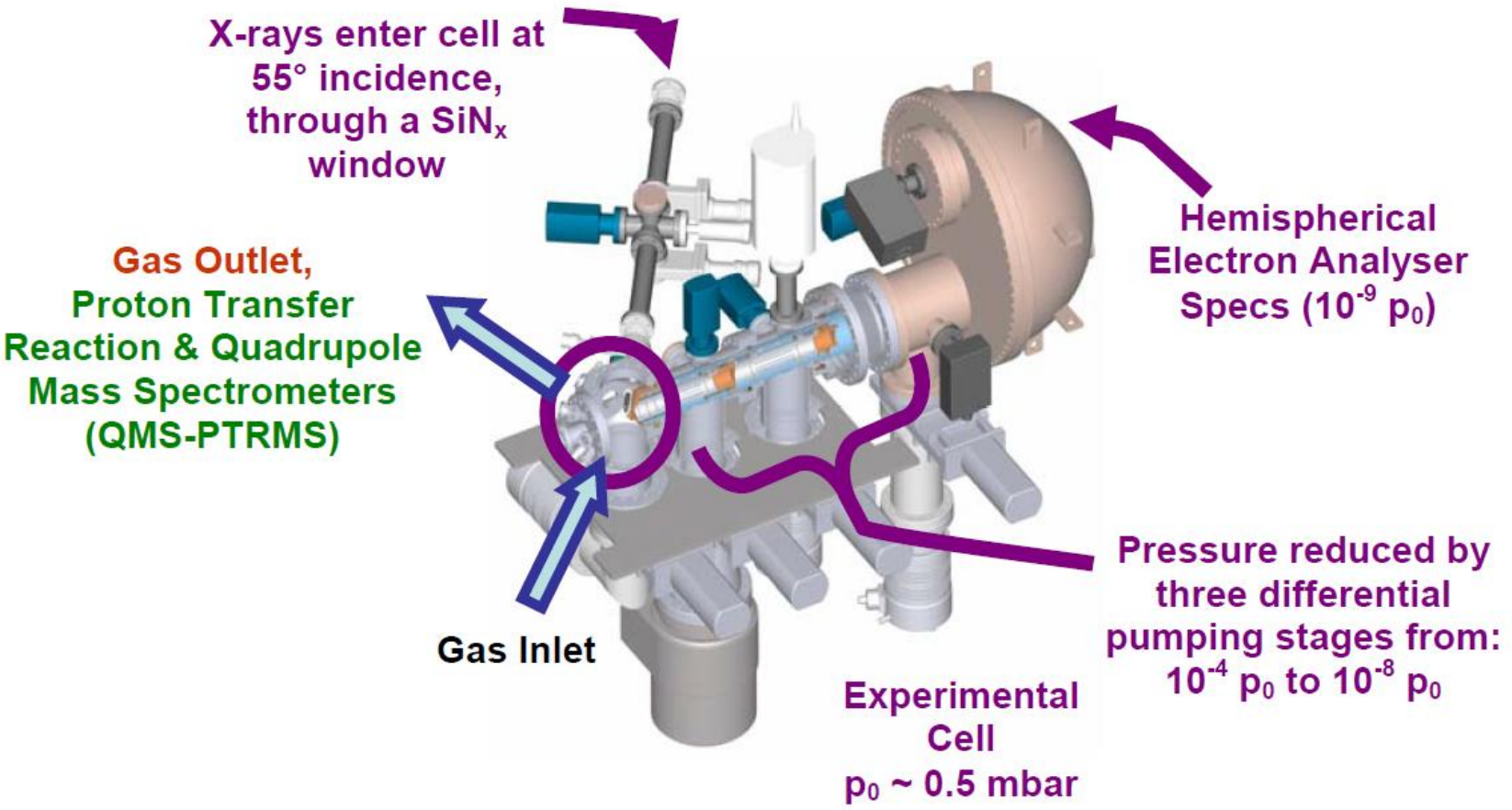
2x1

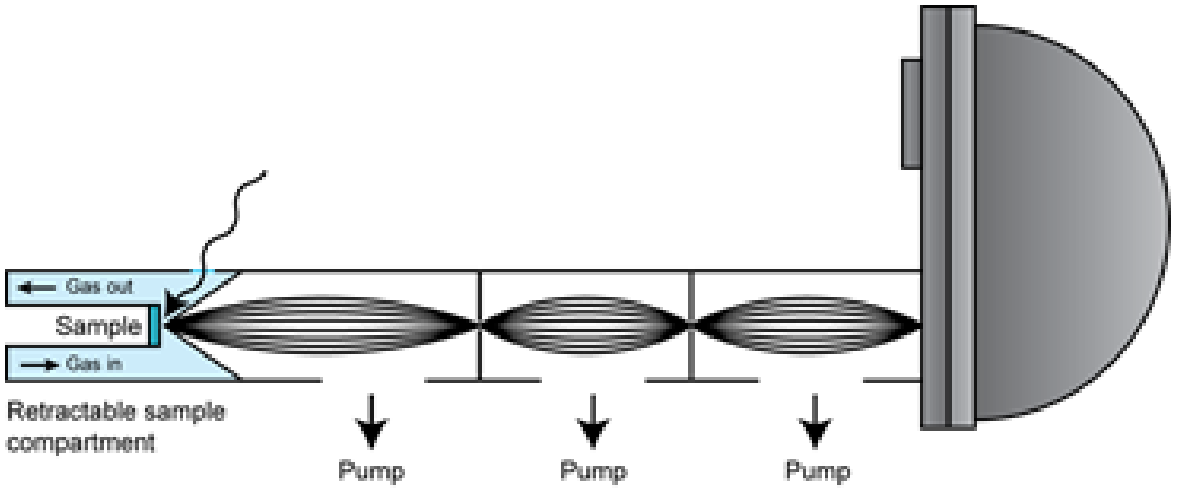
Chemisorbed O

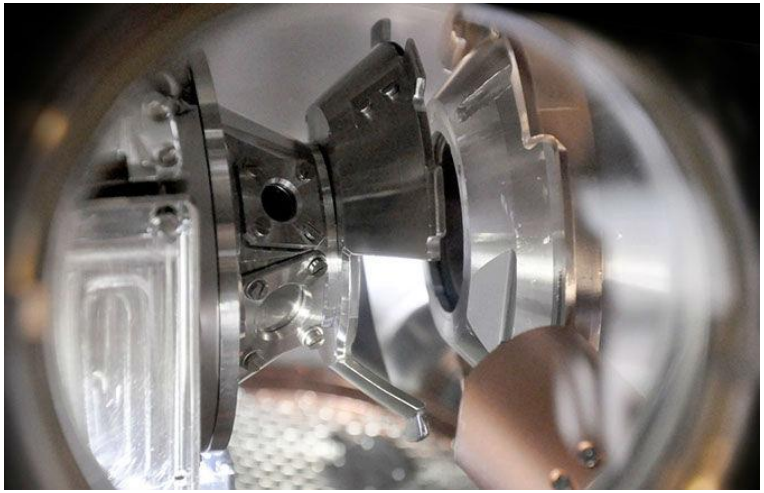
9x9

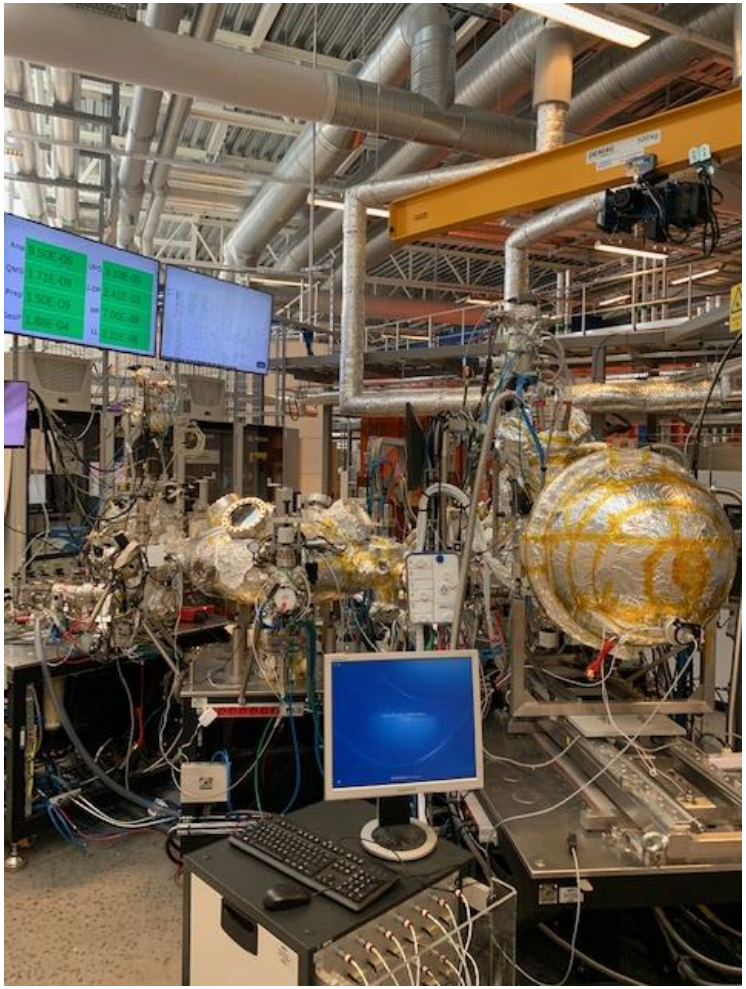
Oxide




X-rays enter cell at 55° incidence, through a SiN_x window
Gas Outlet, Proton Transfer Reaction & Quadrupole Mass Spectrometers (QMS-PTRMS)
Hemispherical Electron Analyser Specs (10^{-9} p_0)
Gas Inlet
Pressure reduced by three differential pumping stages from: 10^{-4} p_0 to 10^{-8} p_0
Experimental Cell
p_0 ~ 0.5 mbar

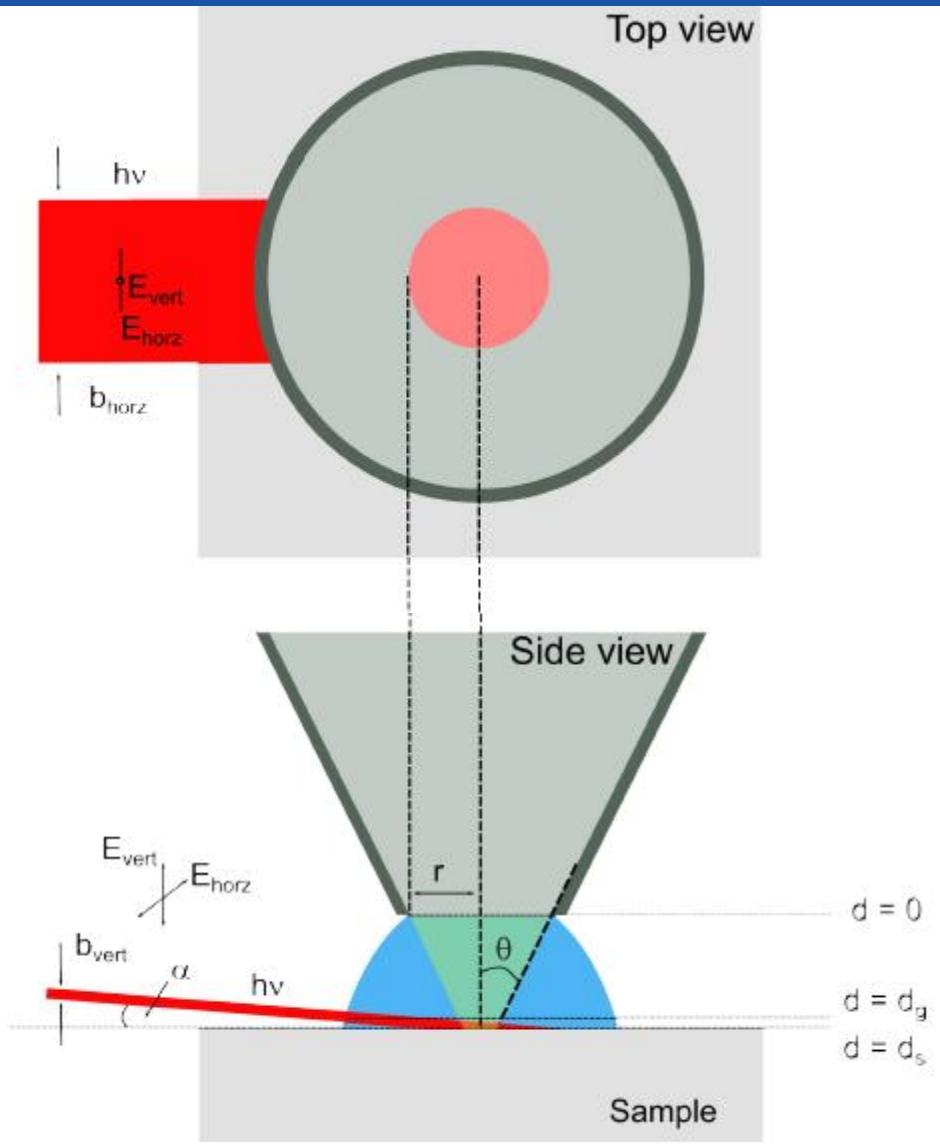

Gas out
Sample
Gas in
Retractable sample compartment
Pump
Pump
Pump





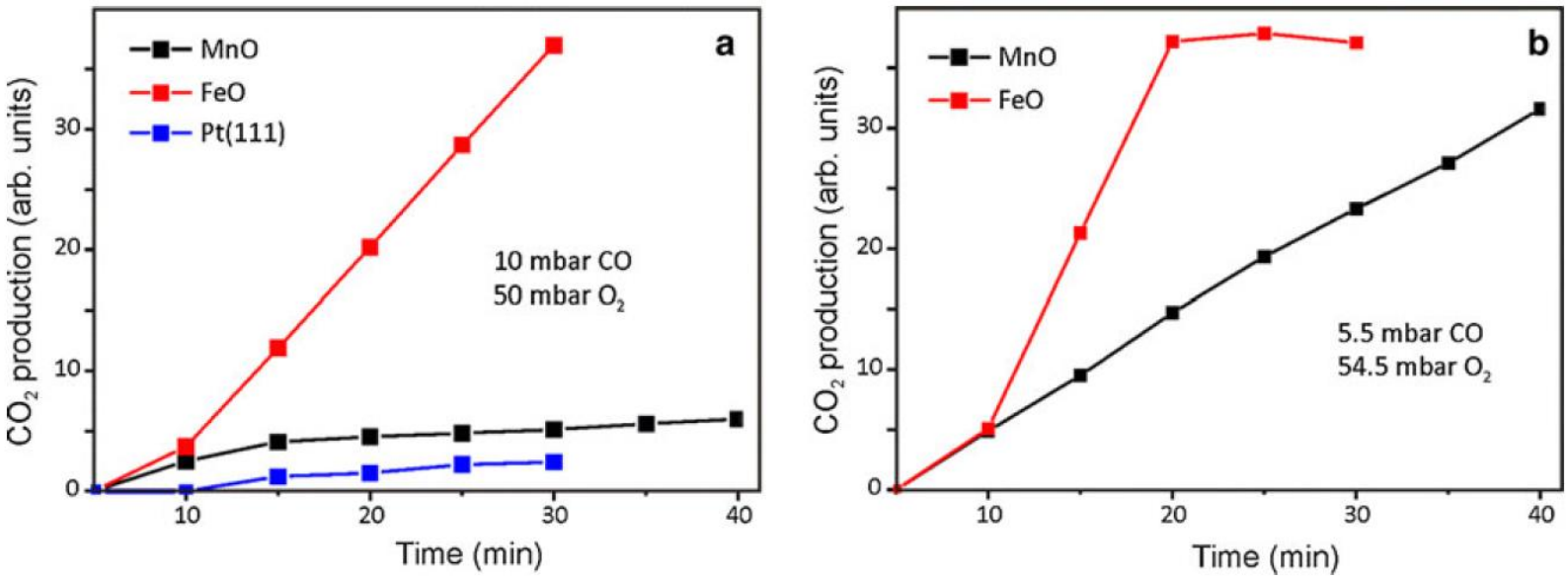
Docking of gas cell

Light on sample in front of analyzer nozzle



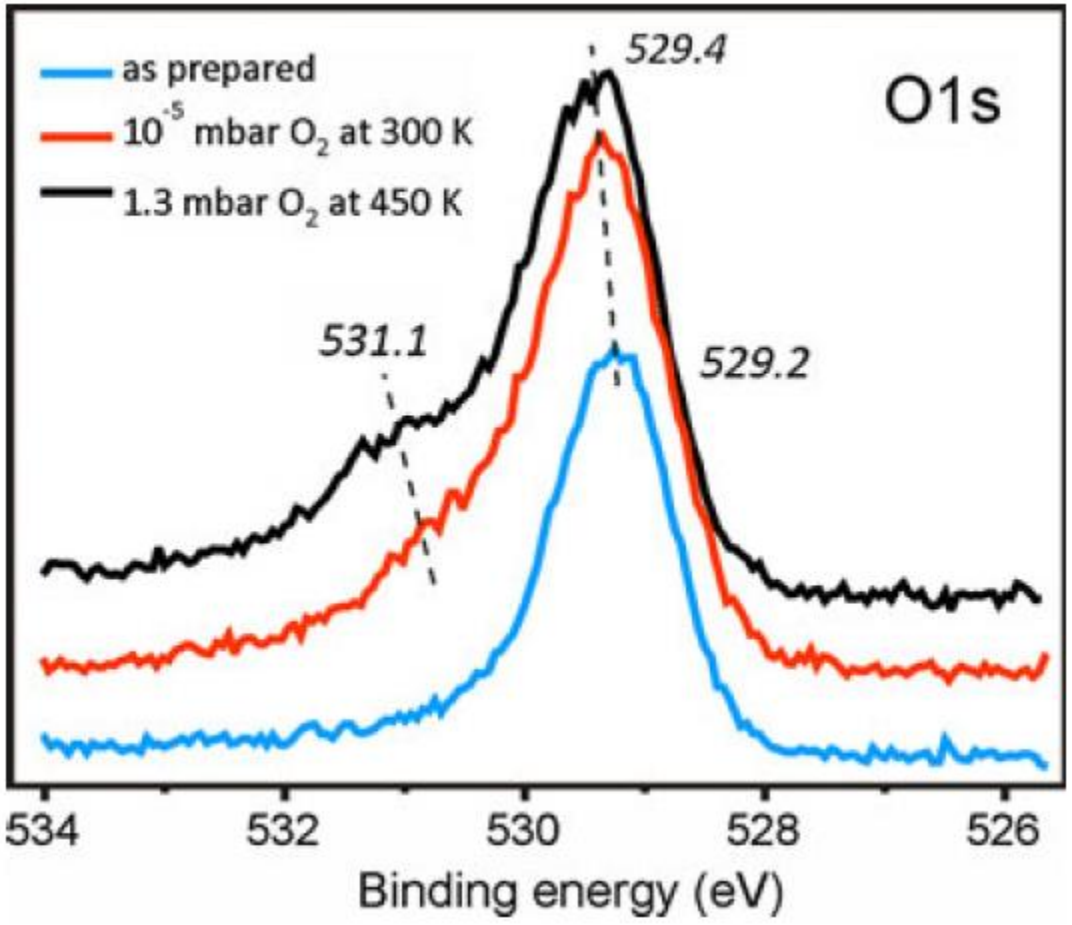
Small spot to increase count rate

Example of catalysis: CO oxidation at ambient conditions

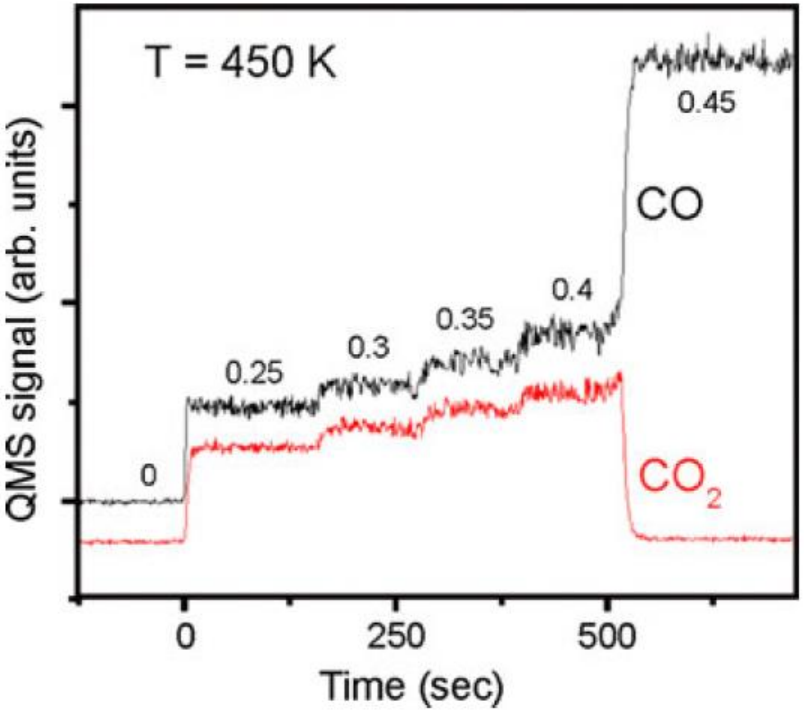


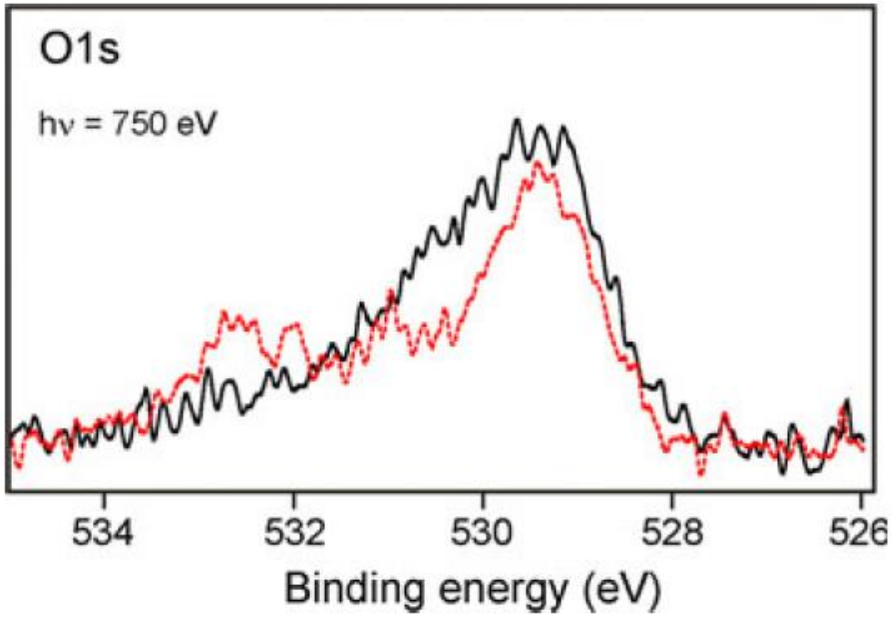
Reactivity: FeOx > Mn-ox > ZnO (unreactive)

More reactive than Pt(111) under O-rich conditions



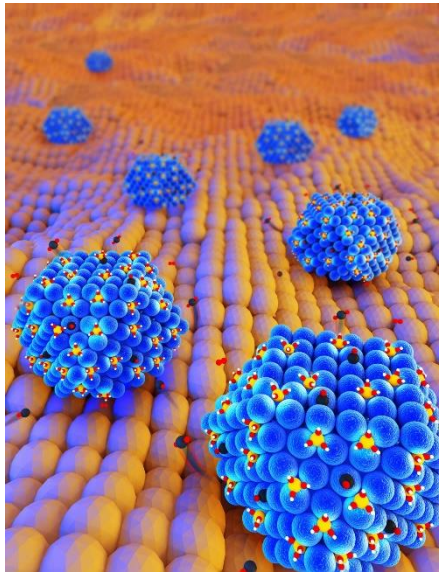
Additional components after formation of O-rich film



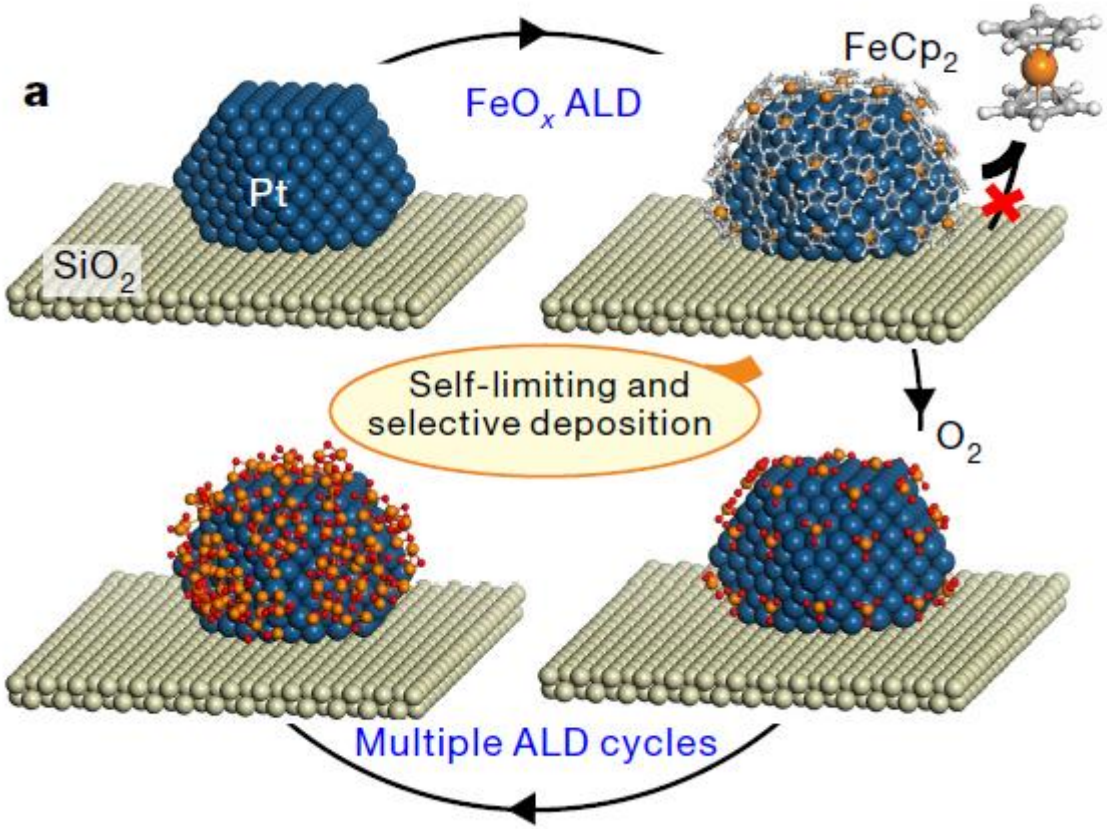


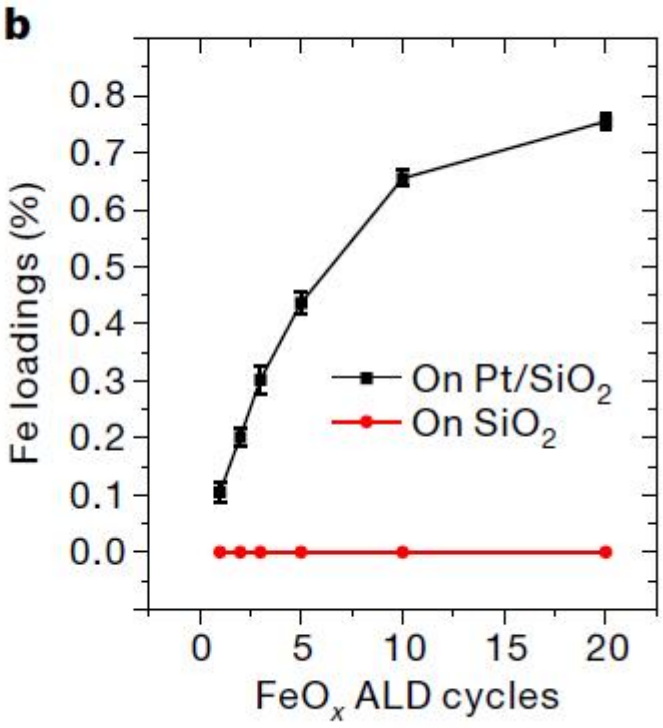
High energy shoulder correlate to high reaction rate

Atomically dispersed iron hydroxide anchored on Pt for preferential oxidation of CO in H_2



Preparation including Atomic Layer Deposition



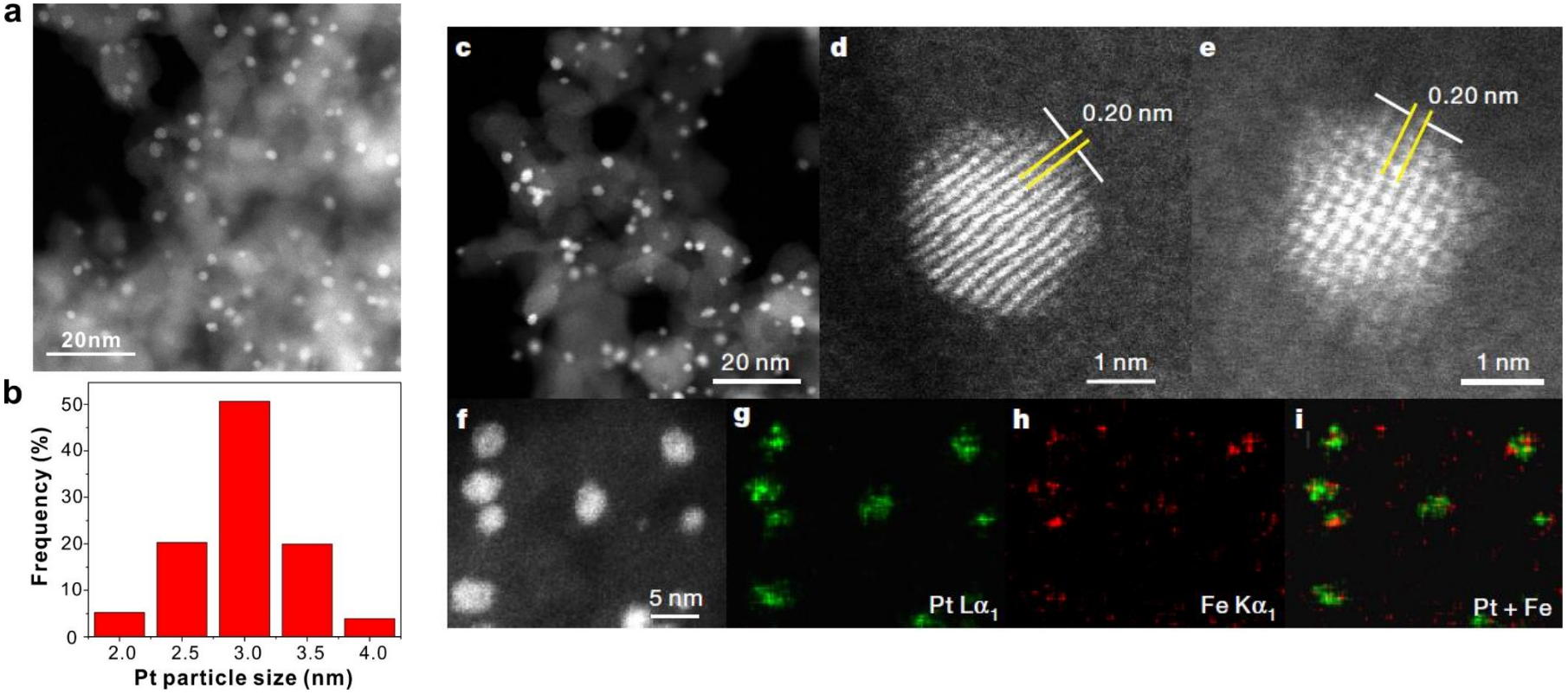


Cycles of $FeCp_2$ + O_2 at 393 K

Cao et al. Nature 565 (2019) 631.

Ferrocene ($FeCp_2$), steric hindrance, isolated sites

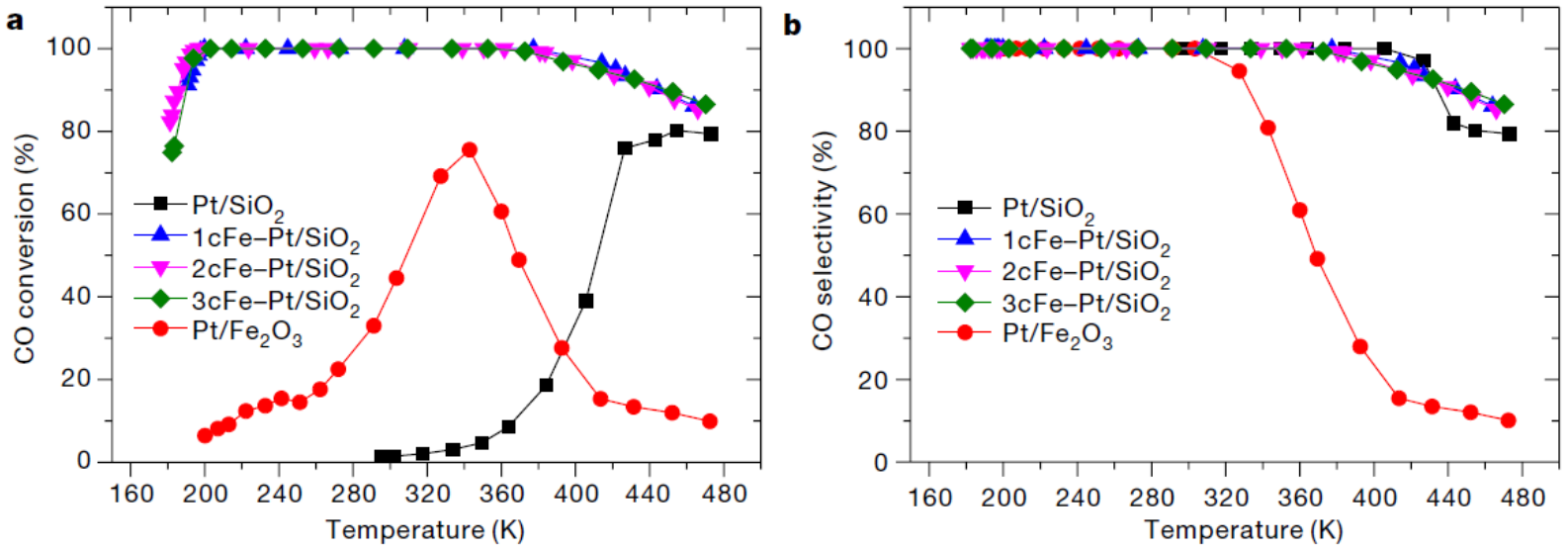
STEM of ALD grown Pt/SiO_2 and of 10 ALD cycle catalysts



Pt particle size a few nm, Selective Fe deposition on Pt

Catalytic Performance (flow reactor)

PROX reaction: 1% CO + 0.5% O_2 + 48% H_2 + He (balance)



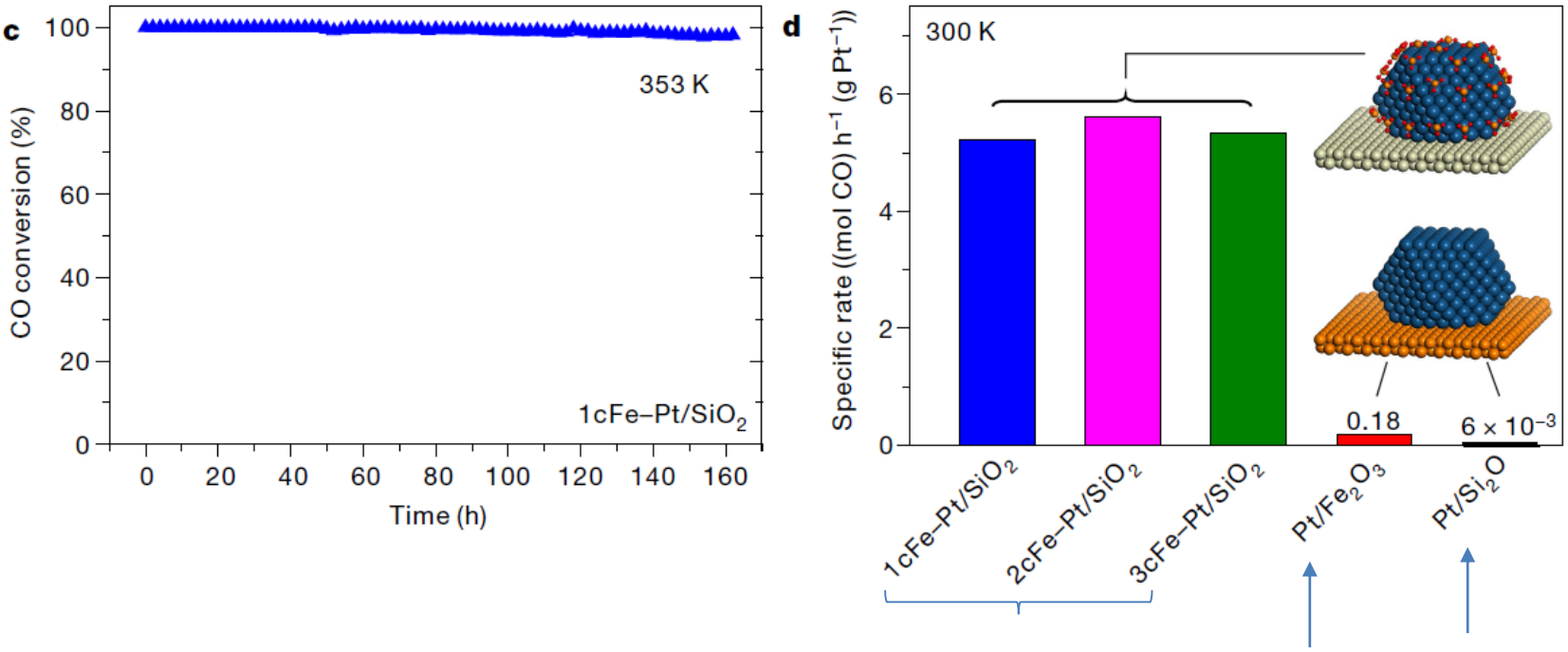
$$\text{CO conversion (\%)} = \frac{[\text{CO}]_{in} - [\text{CO}]_{out}}{[\text{CO}]_{in}} \times 100$$

$$\text{CO selectivity (\%)} = \left\{0.5 \times \frac{[\text{CO}]_{in} - [\text{CO}]_{out}}{[\text{O}_2]_{in} - [\text{O}_2]_{out}}\right\} \times 100$$

Cao et al. Nature 565 (2019) 631.

Wide temperature range: 198 – 380 K

Stability and mass specific rates

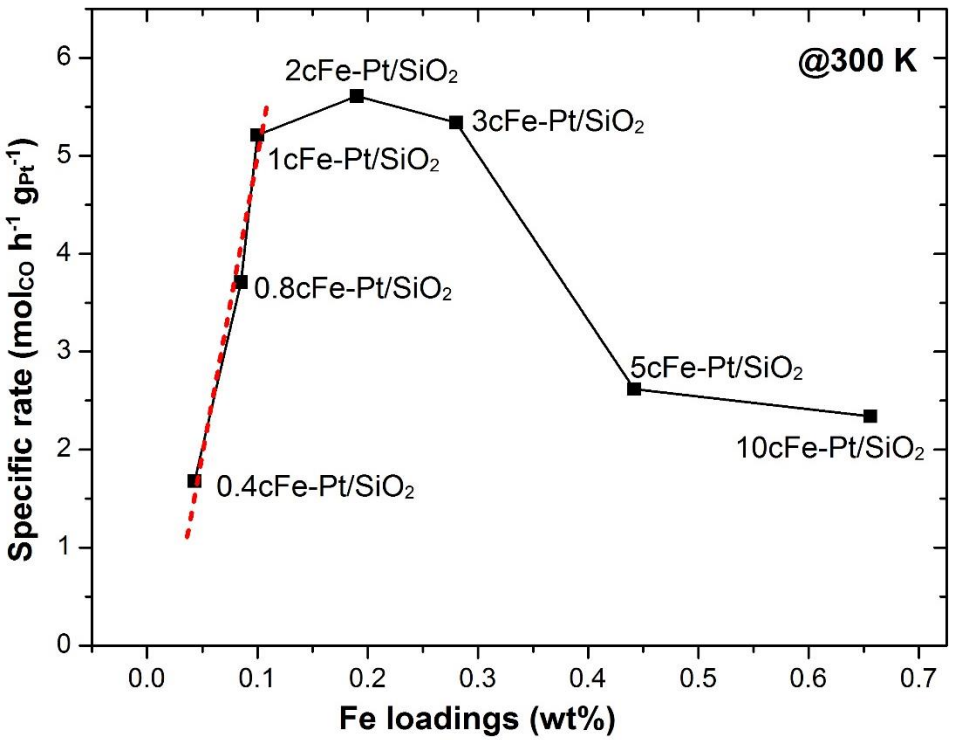


Apparent activation barriers: 0.10–0.11 eV 0.11 eV 0.71 eV

Cao et al. Nature 565 (2019) 631.

Stable under PEMFC operating conditions

Mass specific rates as a function of Fe loading



0.4cFe-Pt/SiO_2 and 0.8cFe-Pt/SiO_2 were prepared using shorter $FeCp_2$ exposure time during FeO_x ALD.

Linear dependence on Fe loading. Vulcano -> reaction at interface

Performance relative to some other catalysts

Catalysts	Pt loadings (wt%)	Transition metal loadings (wt%)	Composition of feed gas (%)			Space velocity (mL $h^{-1}g_{cat}^{-1}$)	Maximal CO conversion (%)	Temperature window for the maximal CO conversion (K)		Notes
			CO	O_2	H_2			Temperature window	ΔT	
1cFe-Pt/SiO_2	3.6	0.10	1	0.5	48	36000	100	~198-380	182	This work
Pt-Fe/SiO_2	4	0.5	1	0.5	98.5	36000	100	~300-320	20	Ref [17]
Pt-Fe/SiO_2	1	0.11	0.5	0.5	45	120000	~98	~423	0	Ref [29]
Pt-Fe/Al_2O_3	0.71	0.23	1	1	50	20000	100	~298-353	55	Ref [30]
Pt-Fe/Al_2O_3	3	1.72	2	1	40	40000	50	~373	0	Ref [31]
Pt-Fe/γ-Al_2O_3	1	2.87	1	1	10	60000	95	~350	0	Ref [32]

17 Fu, Q. *et al.* Interface-confined ferrous centers for catalytic oxidation. *Science* **328**, 1141-1144 (2010).

29 Siani, A. *et al.* Improved CO oxidation activity in the presence and absence of hydrogen over cluster-derived $PtFe/SiO_2$ catalysts. *Langmuir* **22**, 5160-5167 (2006).

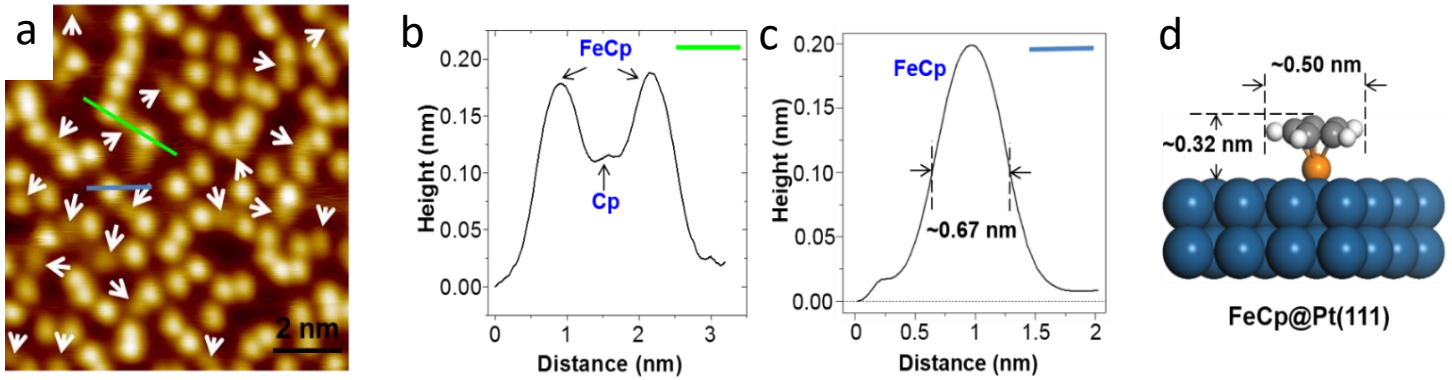
30 Zhang, H. *et al.* Construction of ultrafine and stable PtFe nano-alloy with ultra-low Pt loading for complete removal of CO in PROX at room temperature. *Appl. Catal. B-Environ.* **180**, 237-245 (2016).

31 Yin, J., Wang, J., Zhang, T. & Wang, X. Novel Alumina-Supported PtFe Alloy Nanoparticles for Preferential Oxidation of Carbon Monoxide in Hydrogen. *Catal. Lett.* **125**, 76-82 (2008).

32 Ko, E. Y. *et al.* Selective CO oxidation in the presence of hydrogen over supported Pt catalysts promoted with transition metals. *Korean J. Chem. Eng.* **23**, 182-187 (2006).

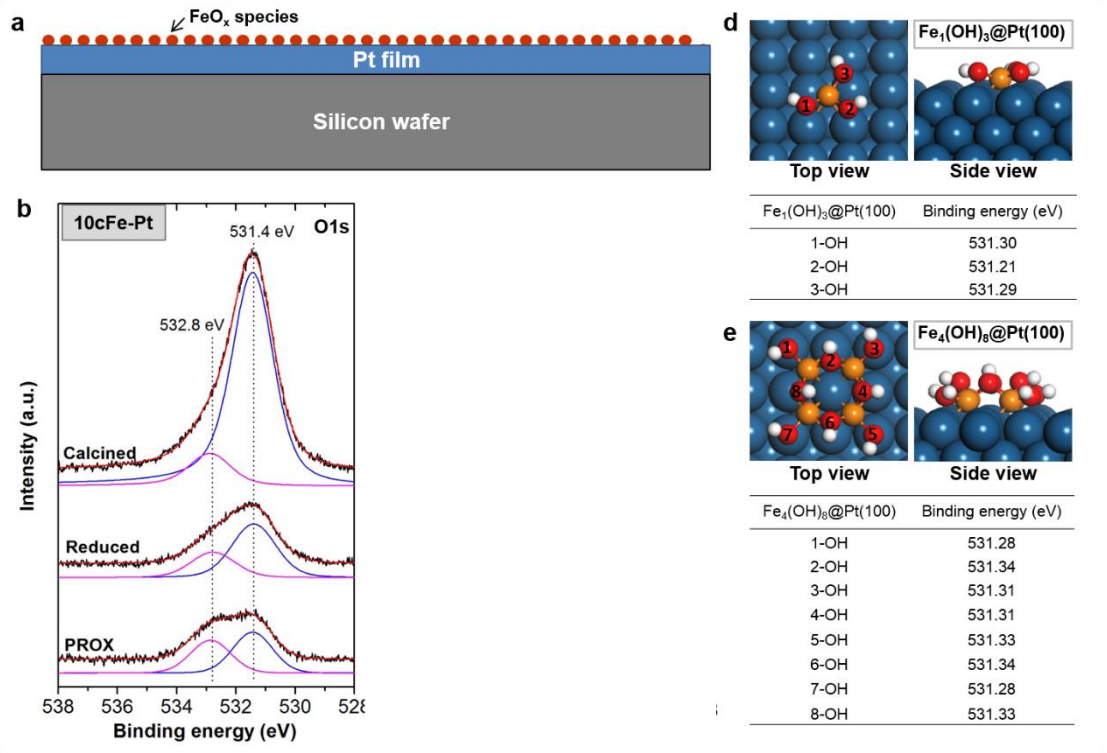
Widest reported low temperature window

STM – comparison to molecule size



Similar size as the DFT model of the adsorbate

Ex-situ results (ALD reactor grown) – prepared at beamline



Cao et al. Nature 565 (2019) 631.

Binding energy from DFT in agreement with OH position

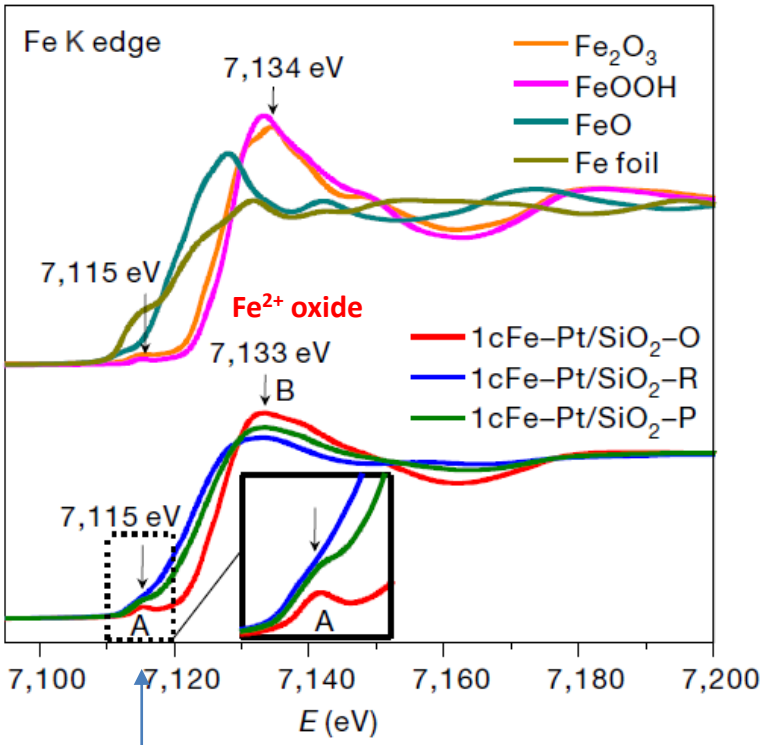
In-situ XANES and EXAFS: Fe K edge at 300 K on 1 cycle samples

XANES

R: 10% H_2 in He

P: 1:0.5:48 $CO:O_2:H_2$ He bal

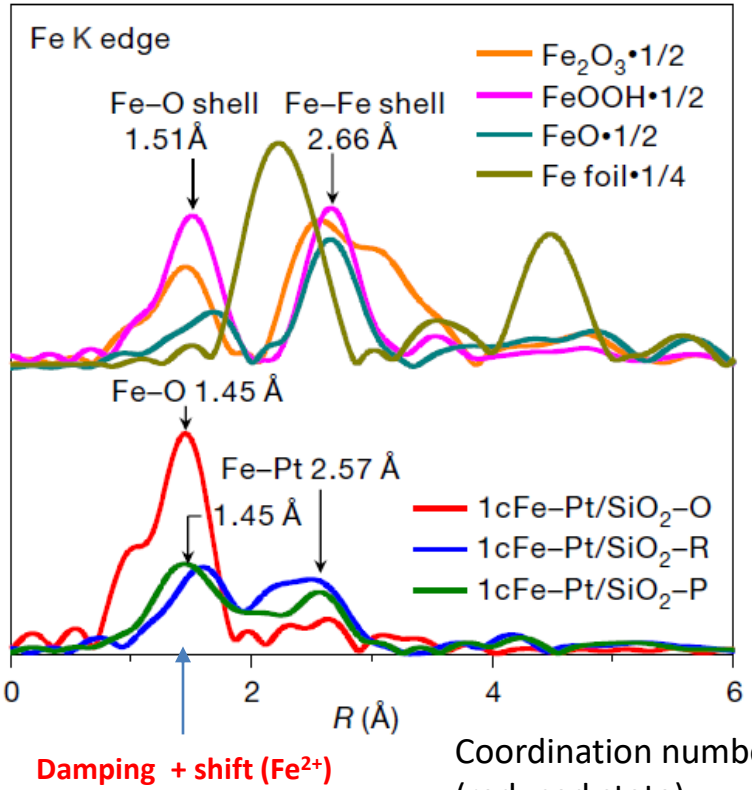
FFT EXAFS



1*s*–3*d* transition of Fe^{3+} oxide

Reduced: pre-edge down = Fe^{3+} down, Fe^{2+} up

PROX: pre-edge peak reappear



Damping + shift (Fe^{2+})

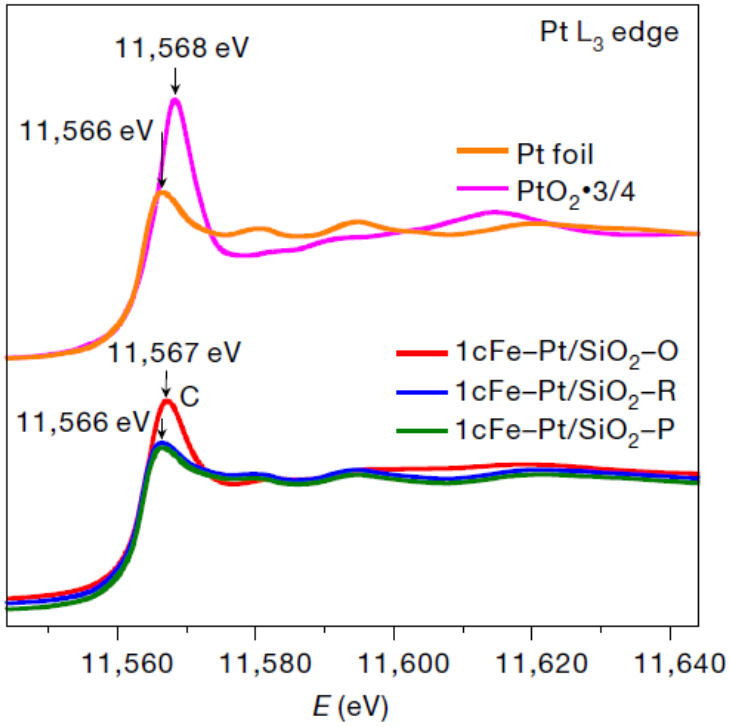
Coordination numbers (reduced state):

Fe–O	1.9
Fe–Pt	4.1
Fe–Fe	0.3

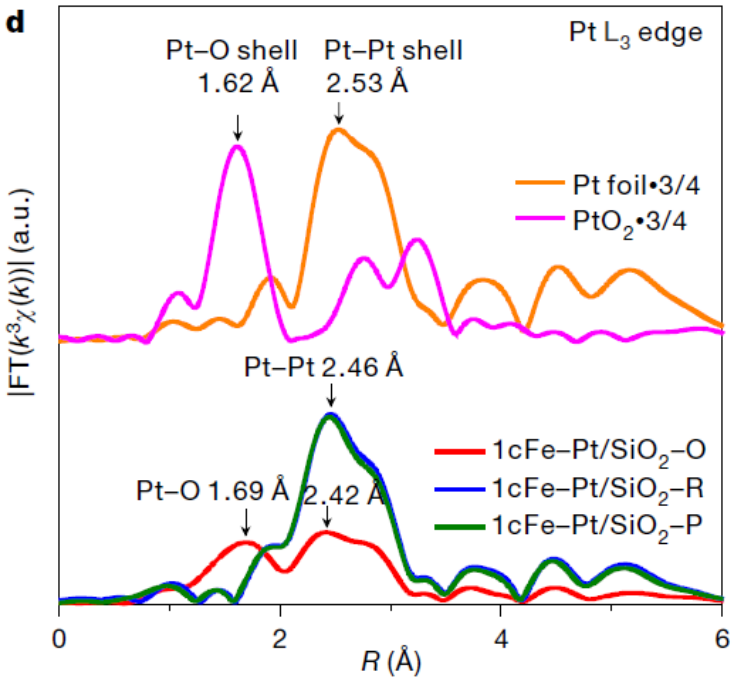
Mostly monomers. Reduction (in agreement with XPS).

In-situ XANES and EXAFS: Pt L3 edge at 300 K

XANES



FFT EXAFS



Two Fe-O distances are 1.96 Å and one at 2.01 Å

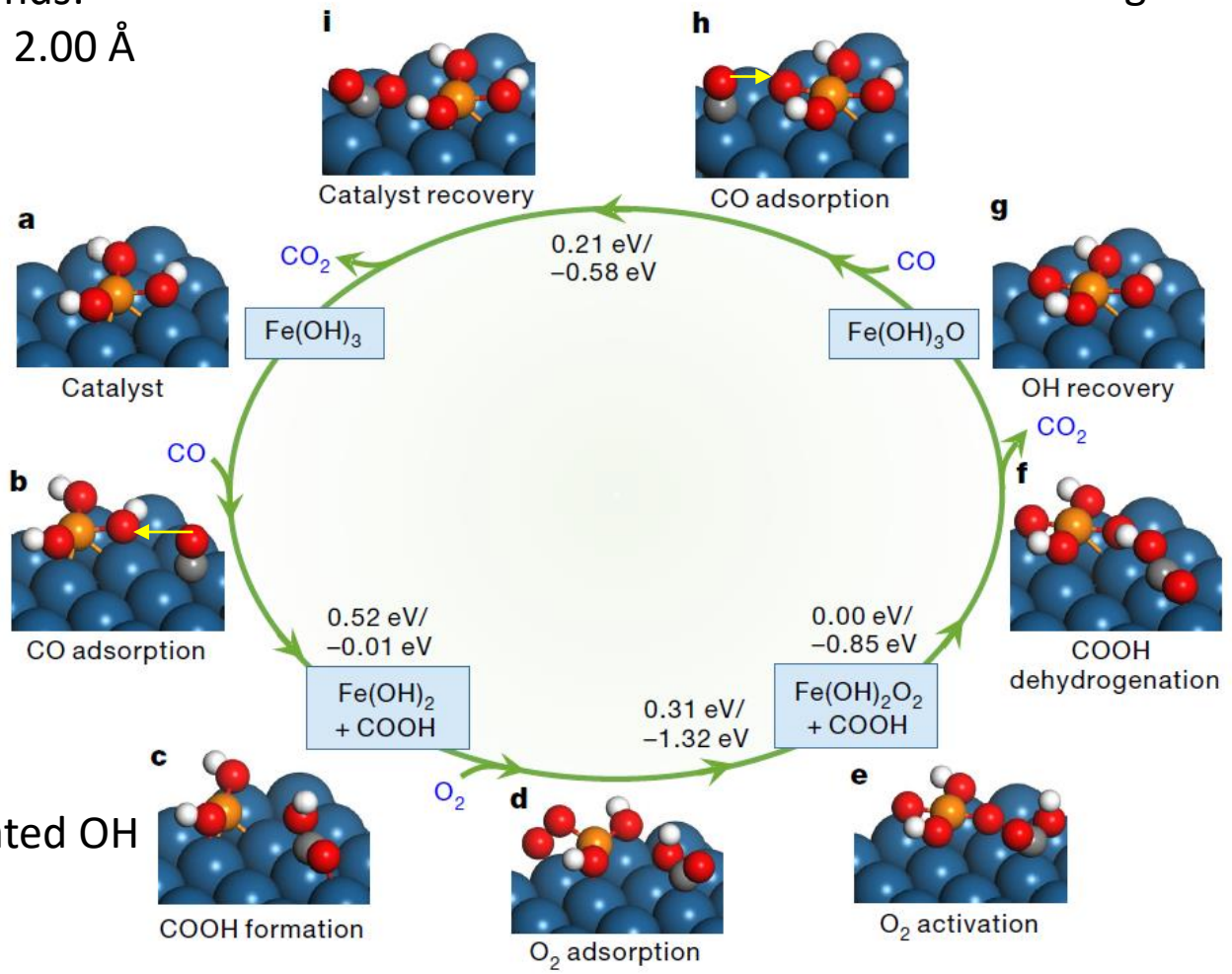
Cao et al. Nature 565 (2019) 631.

Used in calculations of coordination. Pt metallic under PROX.

Proposed reaction pathway for CO oxidation during PROX

DFT Fe–OH bonds:
1.93, 1.94 and 2.00 Å

Binds to elongated O-



Binds to elongated OH

O_2 bridge to two Pt atoms and Fe

$Fe(OH)_3$ and Pt collaborate

Intermediate summary

Selective ALD Fe deposition on Pt

Steric hindrance: Formation of monomers

FeOHx catalyst highly reducible

100% CO conversion 198 – 380 K

Reaction takes place at $Fe(OH)_3$ and Pt interface

Results from a large collaboration

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