Subsurface Species in Heterogeneous Catalytic Reactions: Insights by in situ Photoelectron Spectroscopy

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Outline

- Technical aspects
- Methanol oxidation over Cu
- Ethylene Epoxidation over Ag

Collaborators

LBNL & ALS: D.F. Ogletree, G. Lebedev, H. Bluhm
Z. Hussain, C.S. Fadley, M. Salmeron

FHI: M. Hävecker, K. Ihmann, E. Kleimenov,
D. Teschner, S. Zafeiratos, E. Vass,
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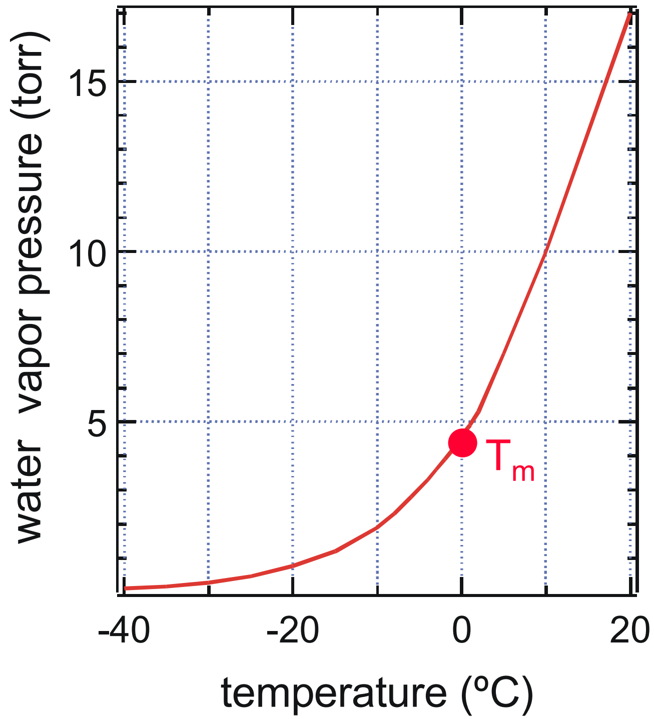
Boreskov Inst. of Catalysis: V.I. Bukhtiyarov

Why in situ XPS ?

- Many processes cannot be investigated in UHV: "Pressure Gap"
  - **environmental chemistry**
  - **catalysis**
  - corrosion
  - electrochemistry
  - biological samples



- Very few methods can investigate the solid-gas interface at high pressures
  - non-linerar optics (SFG, SHG)
  - scanning probe microscopies
  - X-ray diffraction

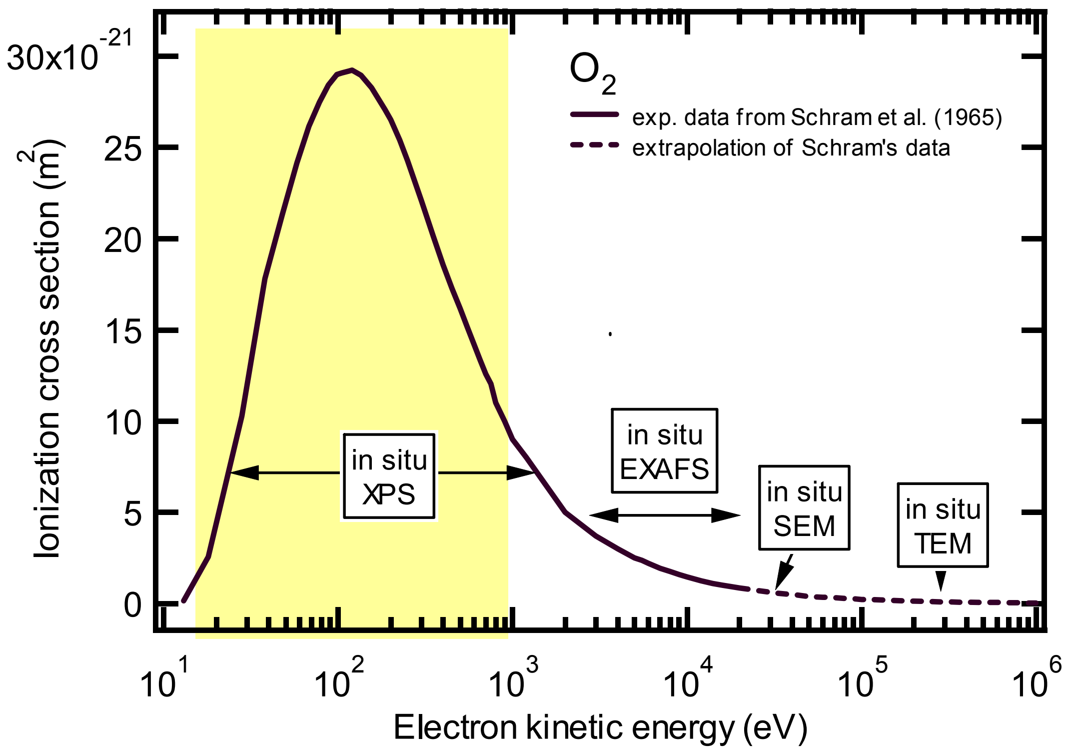
- Photoelectron spectroscopy is very powerful

  ⇒ Goal: XPS at pressures of at least 5 torr

In situ XPS: obstacles

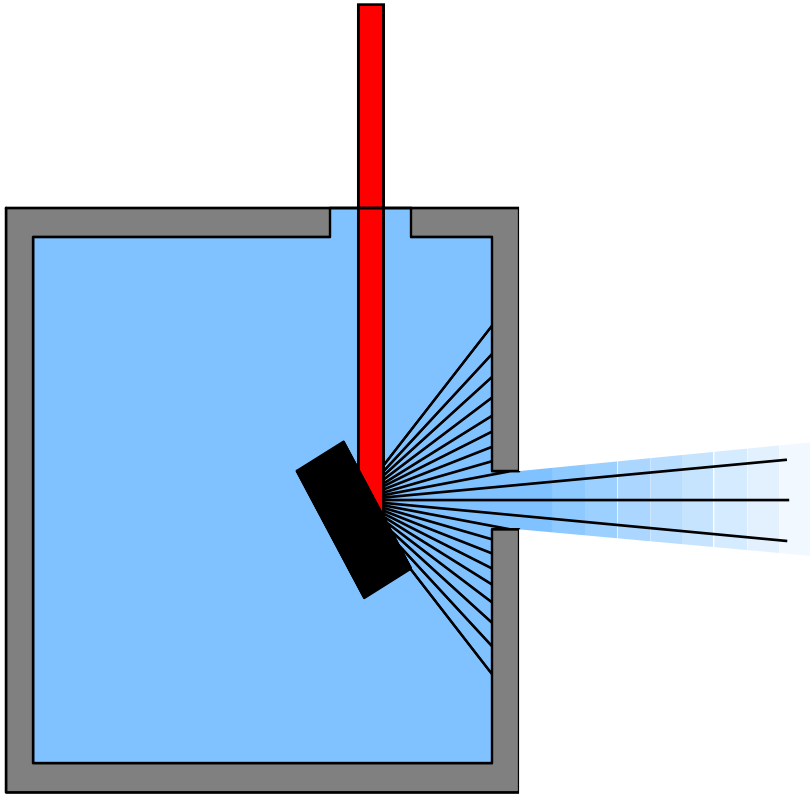
Fundamental limit:

elastic and inelastic scattering of electrons in the gas phase



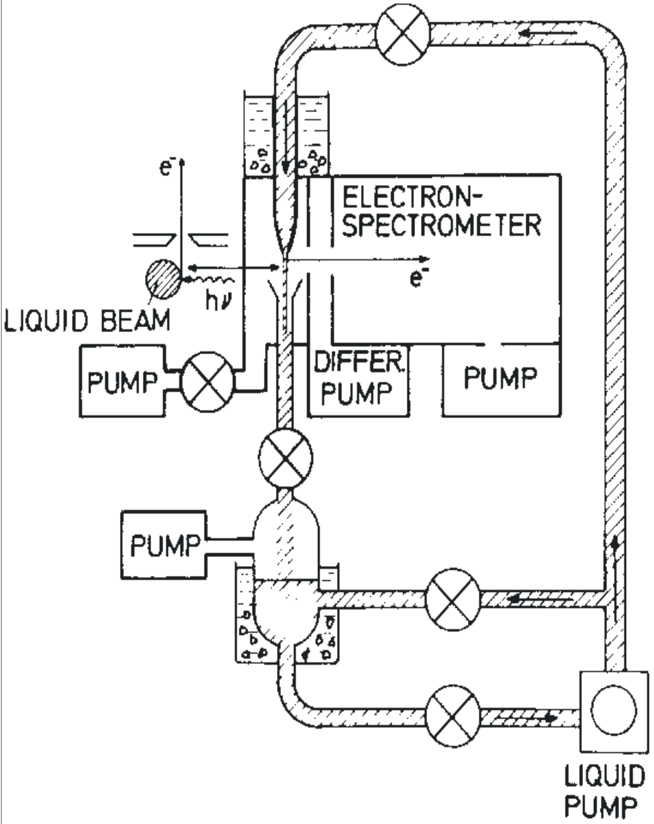
Technical issues:
- Differential pumping to keep analyzer in high vacuum
- Sample preparation and control in a flow reactor

In situ XPS: basic concept



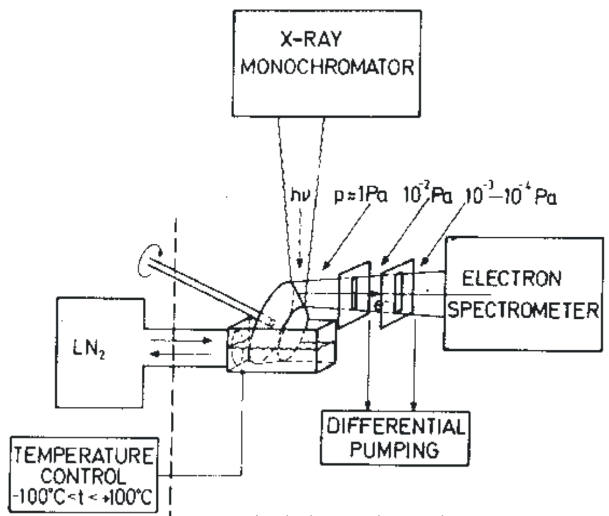
- Photons enter through a window
- Electrons and a gas jet escape through an aperture to vacuum

In situ XPS instruments: previous designs



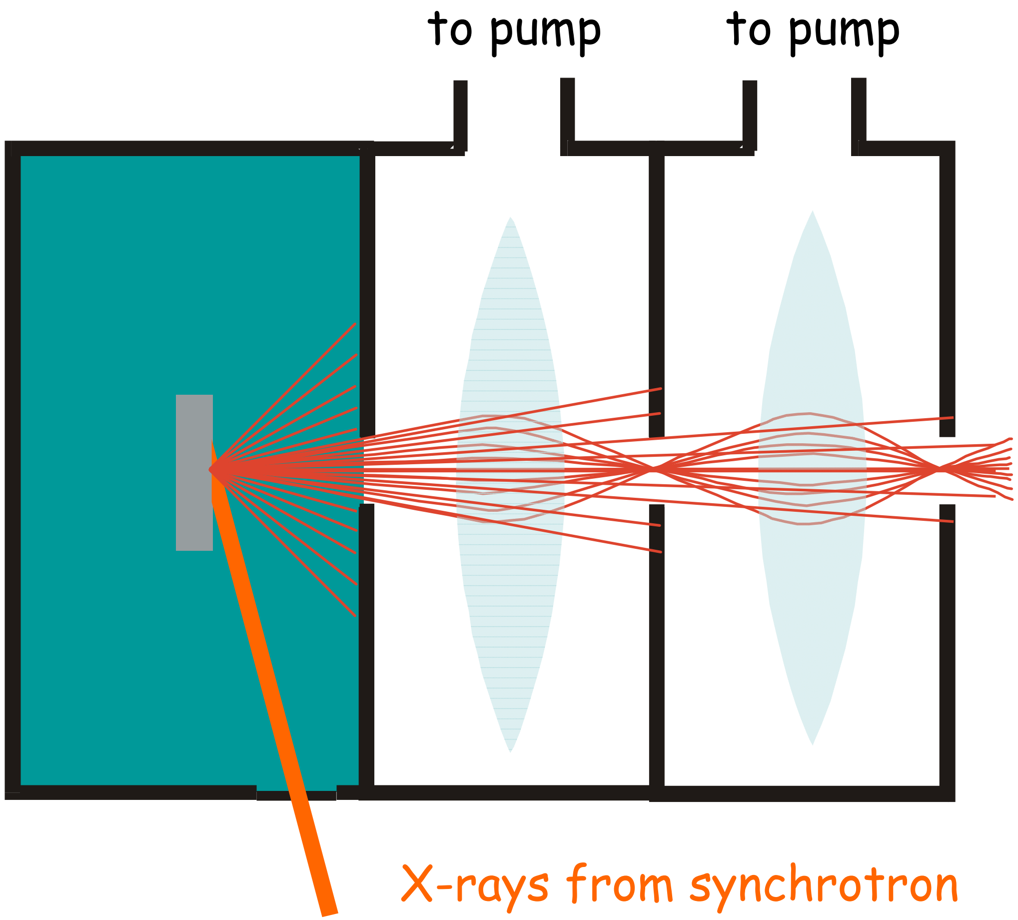
H. Siegbahn et al., J. Electron Spectrosc. Relat. Phenom. **2**, 319 (1973)

- H. Siegbahn et al. (1973-)
- M.W. Roberts et al. (1979)
- M. Faubel et al. (1987)
- M. Grunze et al. (1988)
- P. Oelhafen (1995)



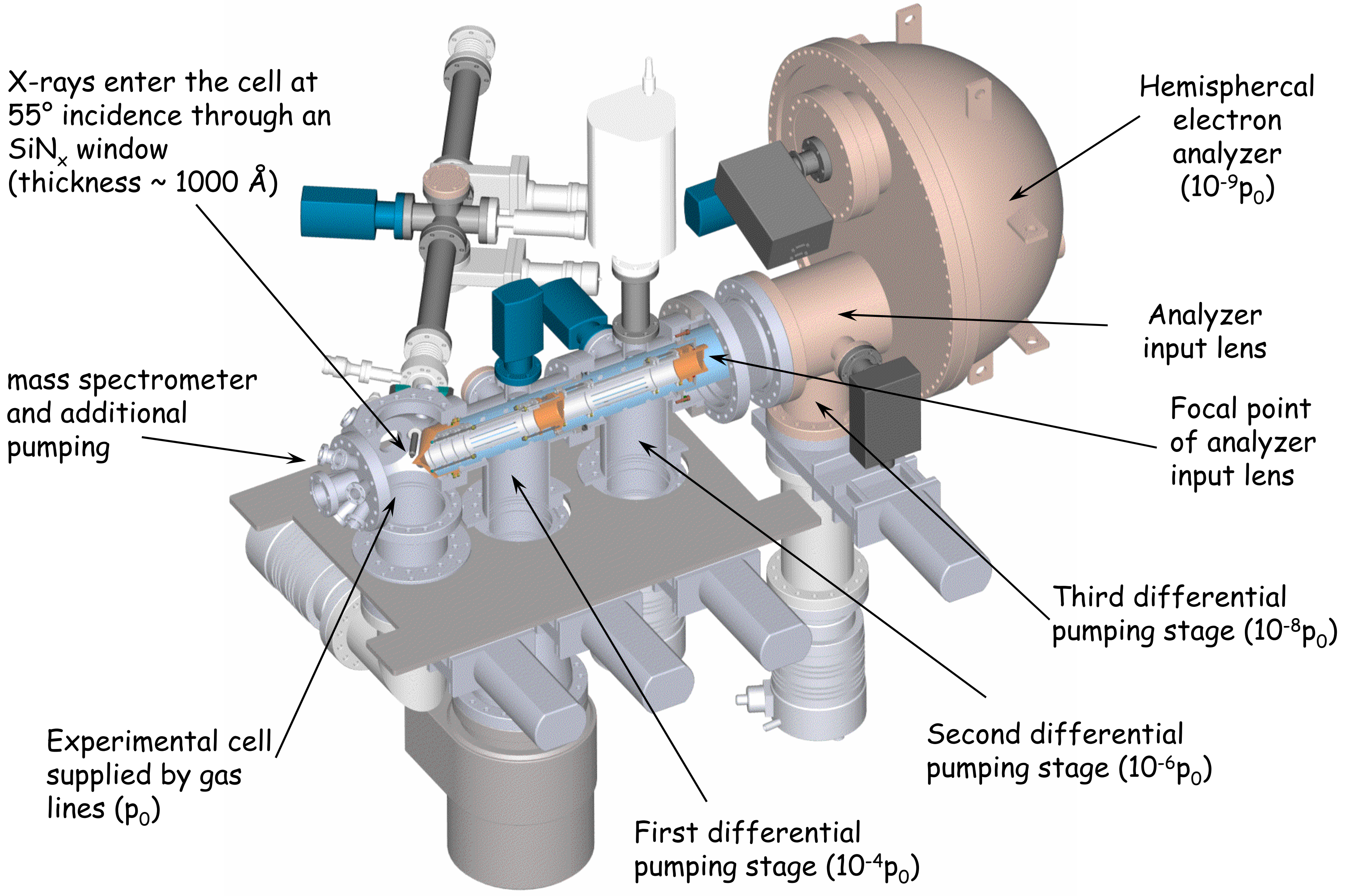
H. Siegbahn et al., J. Electron Spectrosc. Relat. Phenom. **24**, 205 (1981)

In situ XPS using differentially pumped electrostatic lenses

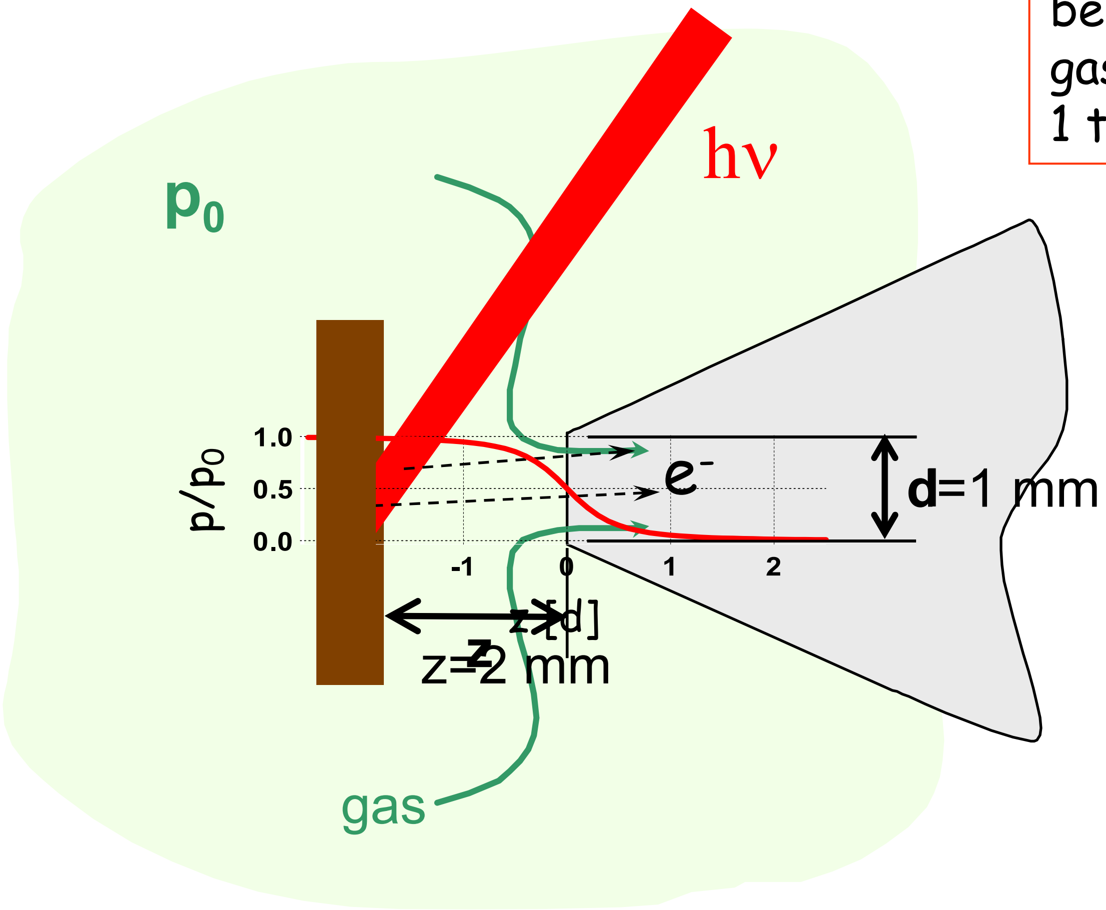


D.F. Ogletree, H. Bluhm, G. Lebedev, C.S. Fadley, Z. Hussain, M. Salmeron, Rev. Sci. Instrum. 73 (2002) 3872.

In situ XPS system

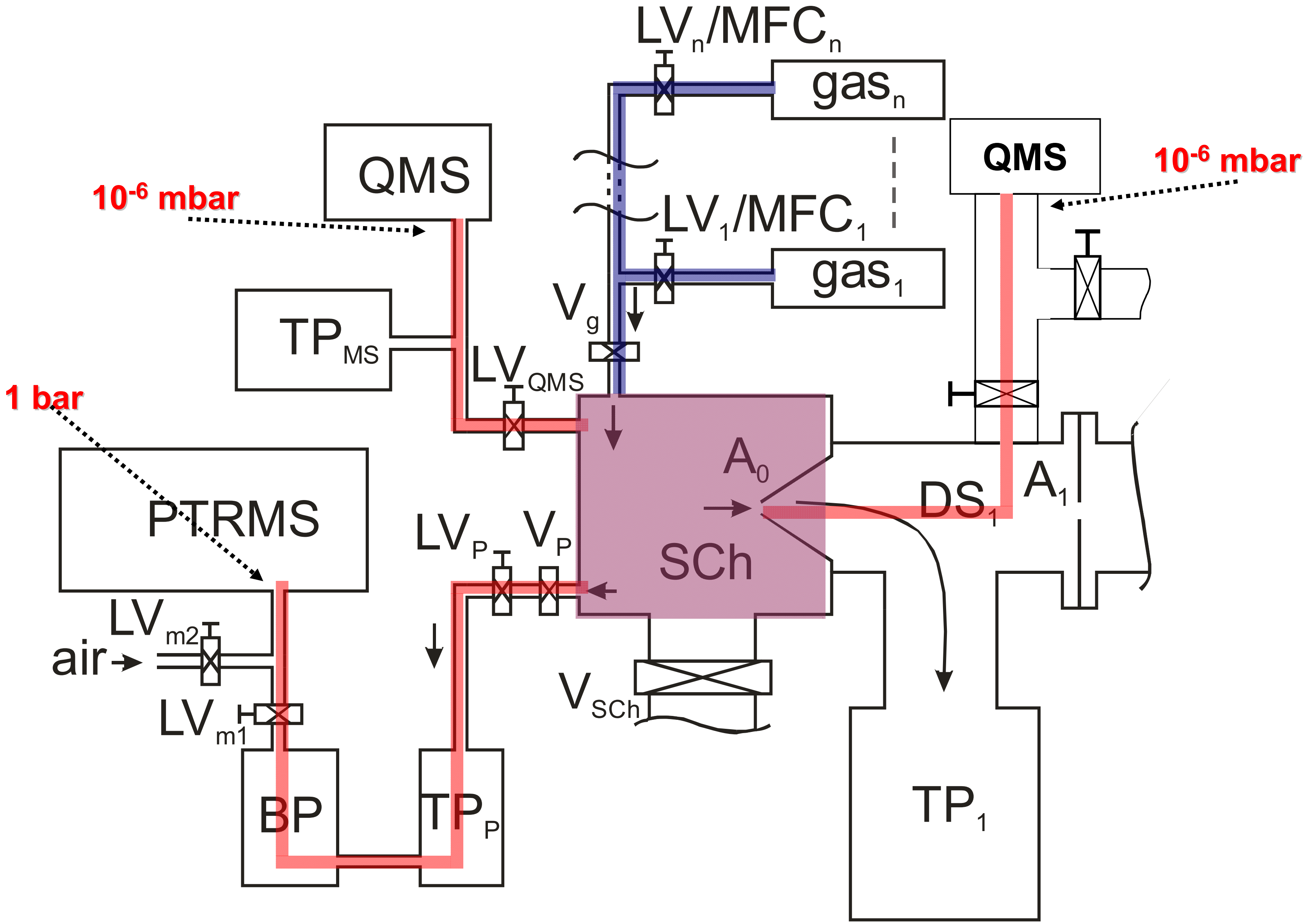


Close-up of sample-first aperture region



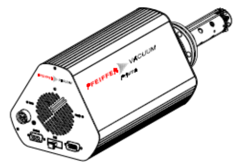
Gas phase composition can be measured by XPS.
gas phase signal:
1 torr·mm ~ a few monolayers

Gas Flow system



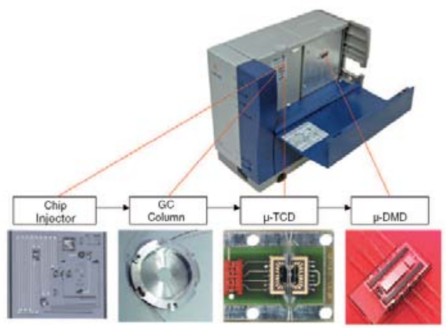
Gas Phase analysis

- **Quadrupole Mass Spectrometry (QMS)**
  - Simple in use
  - Real time investigation
  - Sensitive (10 ppb)
  - Relatively quantitative
  - High fragmentation rate at high masses



- **Proton Transfer Reaction Mass Spectrometer (PTR-MS)**
  - Very sensitive to volatile organic compounds (< 1 ppb)
  - Low fragmentation rate
  - Selective to substance with proton affinities higher than water

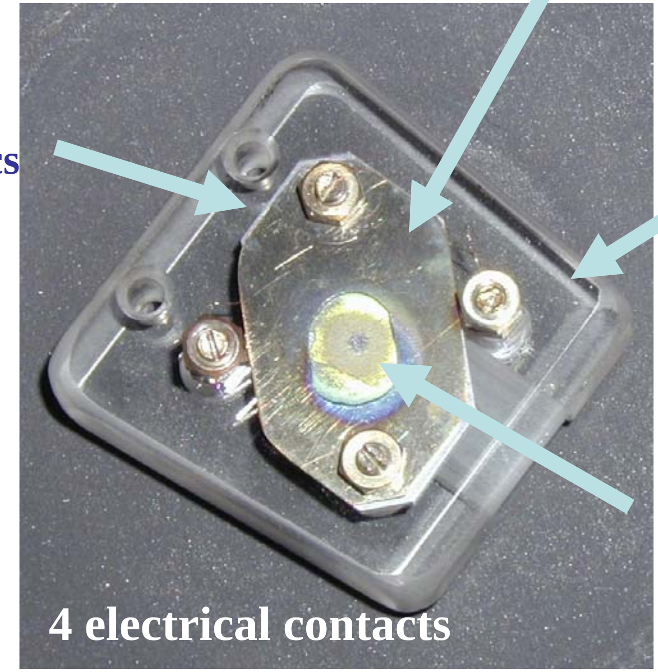
- **Micro Gas Chromatography (Micro-GC)**
  - Detection sensitivity (1 ppm)
  - Quantitative analysis
  - Not real time detection (> 30 s)



Sample holder

Stainless steel
mask

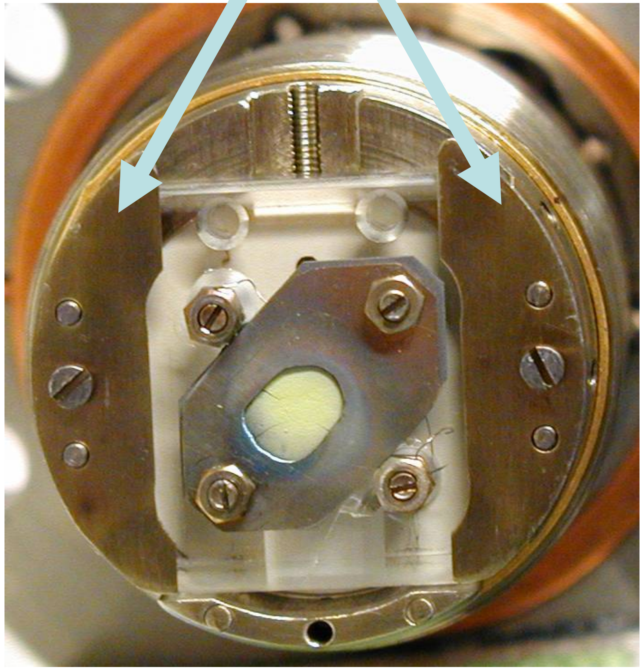
Si-SiC
ceramics



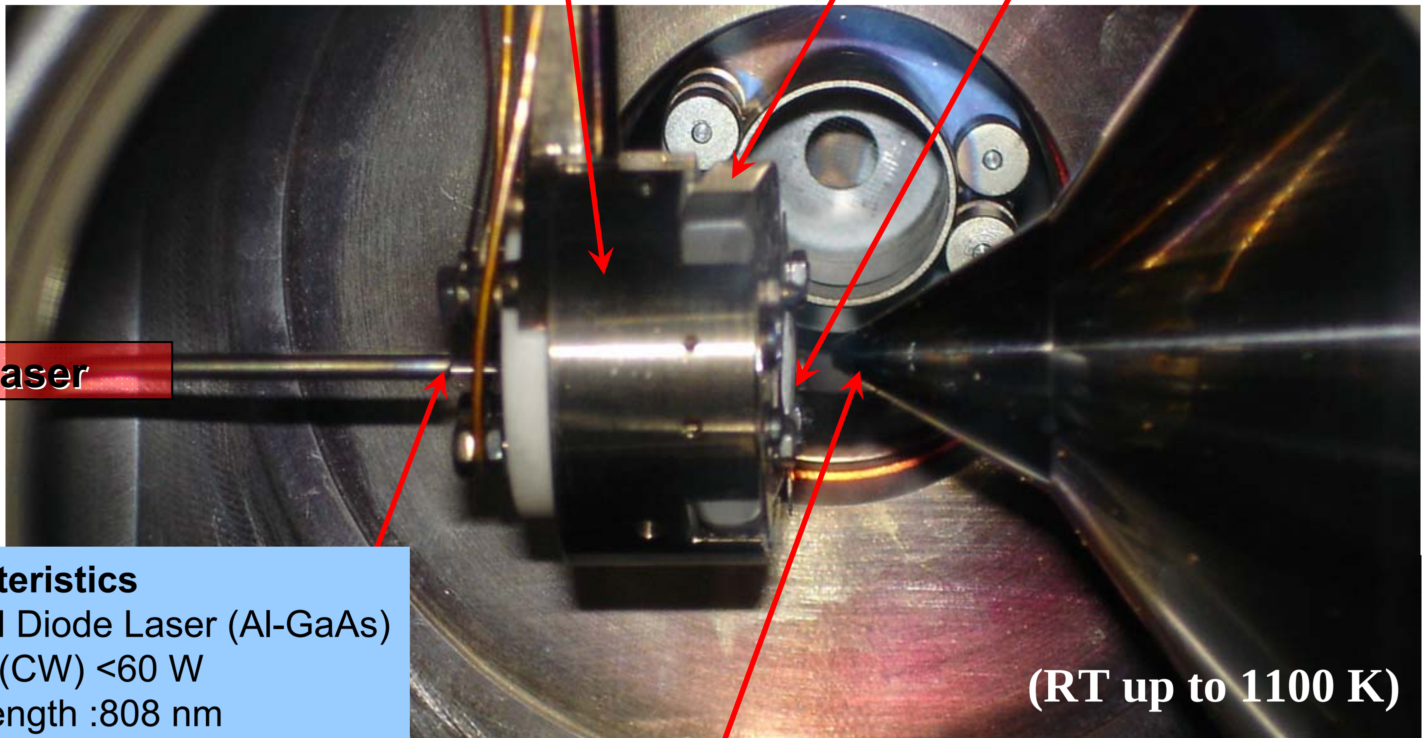
Sapphire

Sample
pellet

Stainless steel
clips



Sample Heating

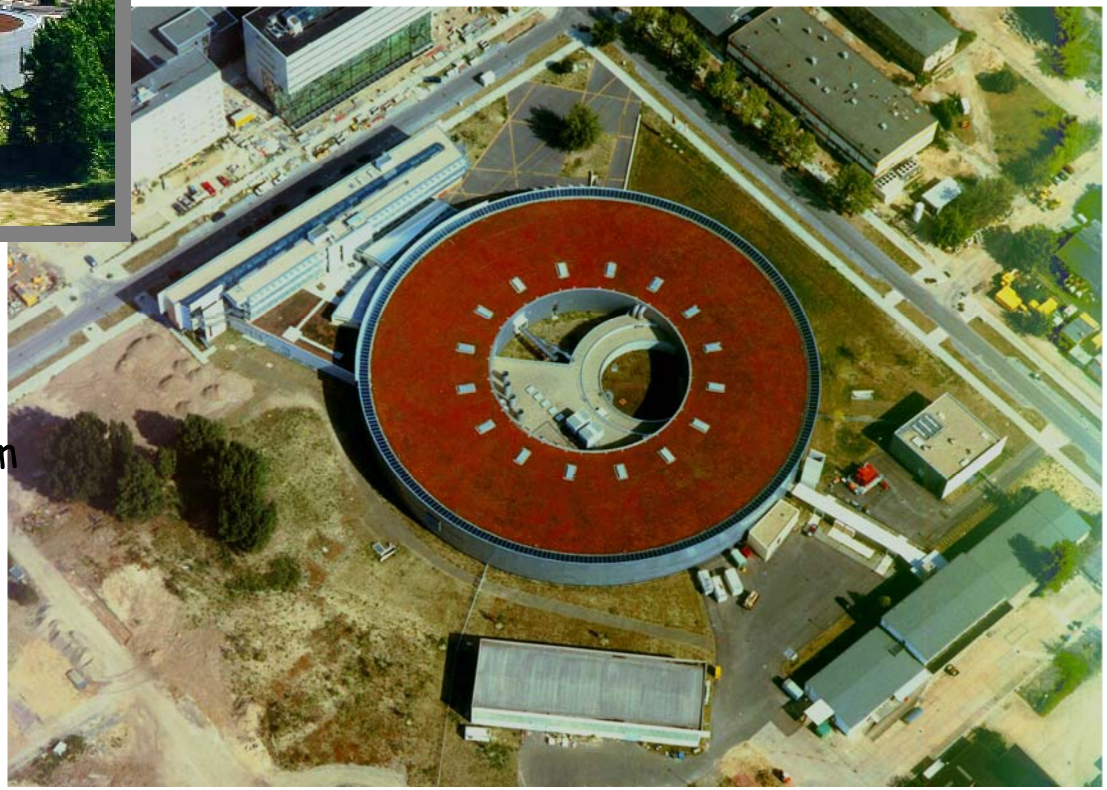


Laser Characteristics
Fibber coupled Diode Laser (Al-GaAs)
Output Power (CW) <60 W
Centre Wavelength :808 nm
Fibre Core diameter: 600 µm

Synchrotron Radiation

Experiments done at undulator 49/2, PGM1 at

BESSY

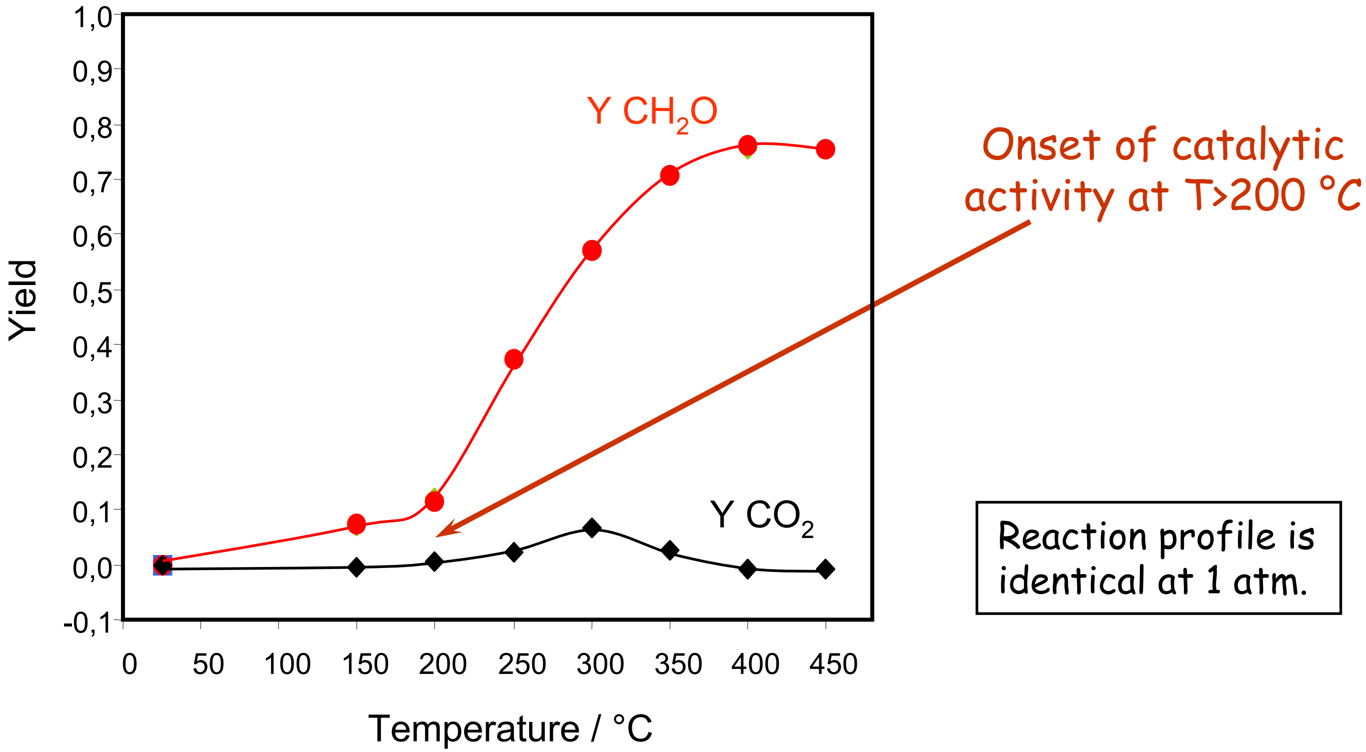


Electron Energy : 1.7 GeV
Storage ring circumference : 240m
Ring current : 0.25 A

Application of in situ XPS to catalysis: methanol oxidation on Cu

Partial oxidation: $CH_3OH + \frac{1}{2}O_2 \xrightarrow{Cu} CH_2O + H_2O$

Total oxidation: $CH_3OH + \frac{3}{2}O_2 \xrightarrow{Cu} CO_2 + 2H_2O$



Reaction profile is identical at 1 atm.

What is the state of the surface under reaction conditions?

Partial oxidation of methanol

UHV XPS

I.E. Wachs & R.J. Madix, Surf. Sci. 76, 531 (1978); A. F. Carley et al., Catal. Lett. 37, 79 (1996).

$$O^-(a) + 2CH_3OH(g) \longrightarrow 2CH_3O^-(a) + H_2O(g)$$

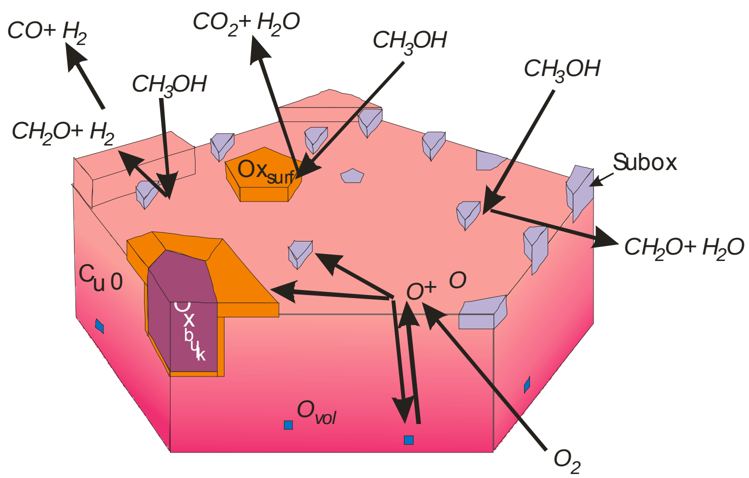
$$CH_3O^-(a) \longrightarrow CH_2O(g) + H^+(a)$$

In situ NEXAFS

A. Knop-Gericke et al., Topics Catal. 15, 27 (2001).

$CH_3OH + O_2$ ~ 0.5 mbar

<u>suboxide phase</u>:
- only present in situ



Questions for in situ XPS: - Quantitative analysis of surface species
- Carbon species on the surface
- Depth-dependent analysis

Experimental conditions

sample: polycrystalline Cu foil

Variations of mixing ratios: $CH_3OH : O_2$ = 1:2, 3:1, 6:1; T = 400 °C; p = 0.6 mbar

Temperature series: gas mixture at room temperature: $CH_3OH : O_2$ = 3:1;
p = 0.6 mbar; temperature: 25 °C → 450 °C

flow rates: 10 ... 20 sccm

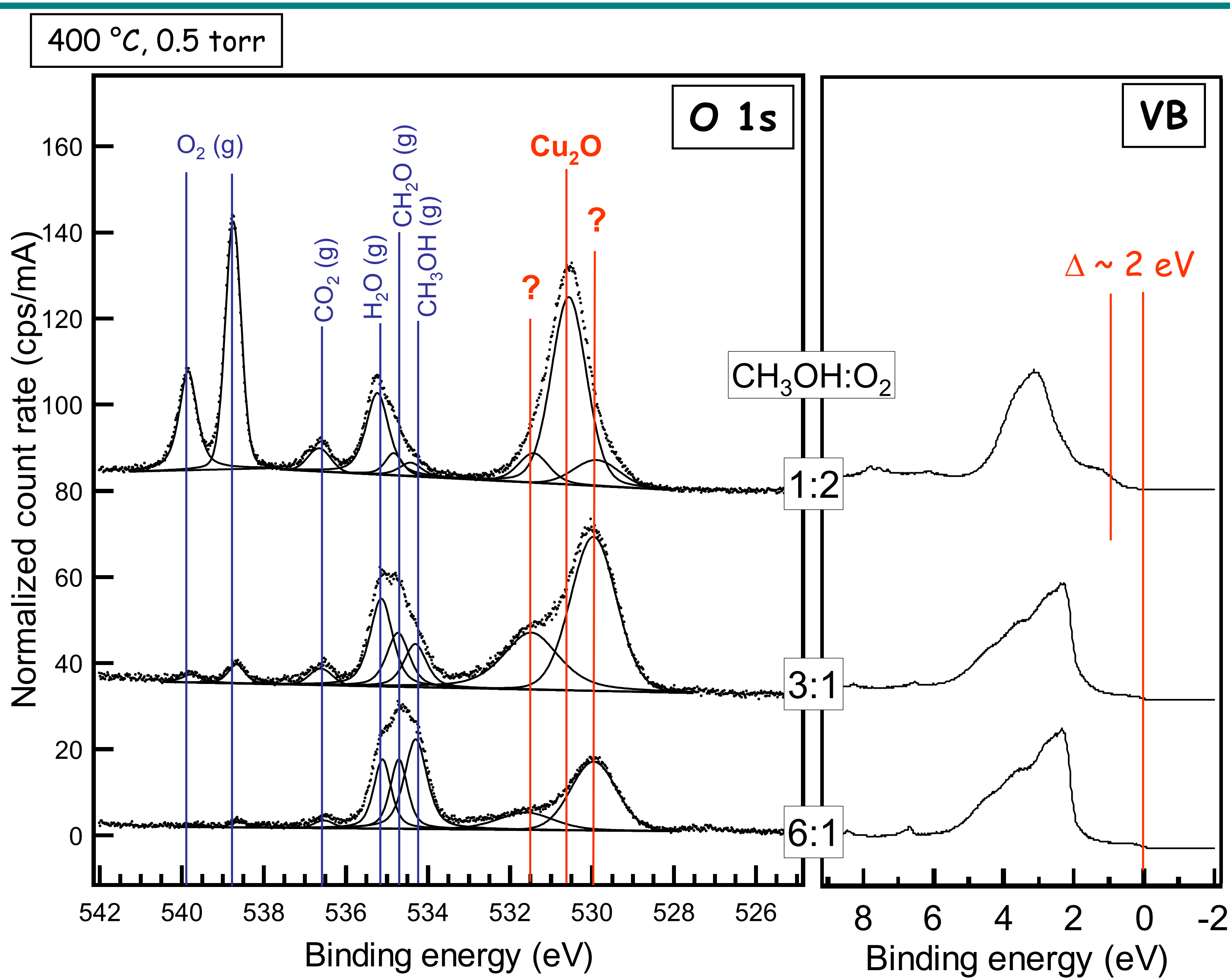
XPS measurements

Beam line U49/2-PGM1 at Bessy
Energy range 100...1500 eV
total spectral resolution 0.1 eV @ 500 eV

O 1s, C 1s, Cu 3p, Cu 2p: KE ~ 180 eV
Valence Band: KE ~ 260 eV

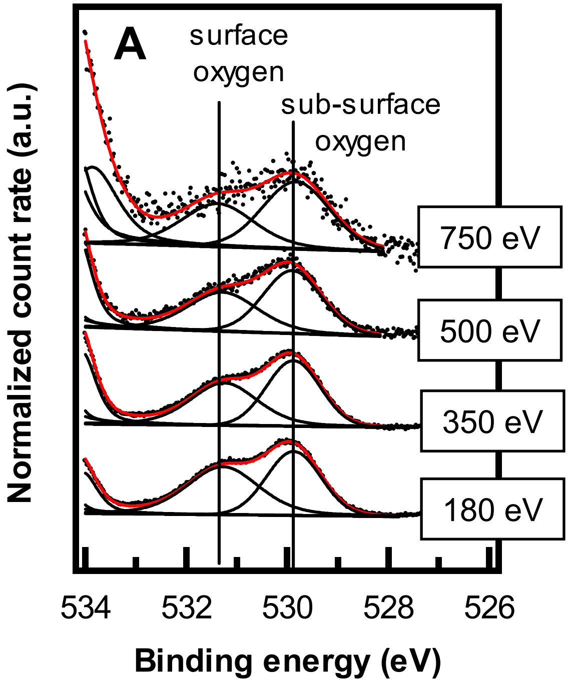
Depth profiling with KEs 180 eV, 350 eV, 500 eV, 750 eV

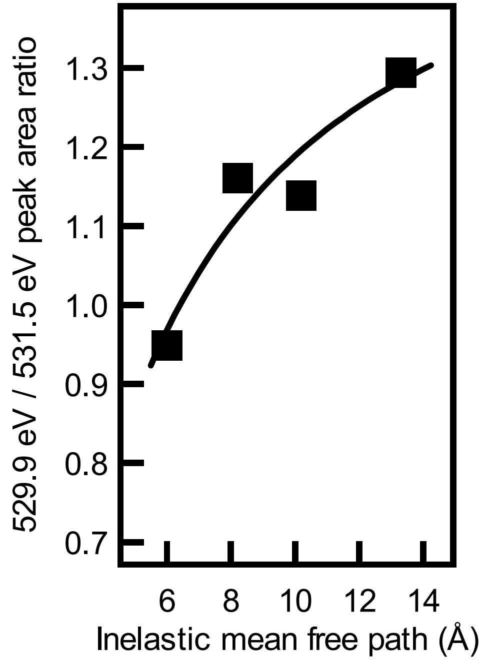
Methanol oxidation on Cu: O1s spectra

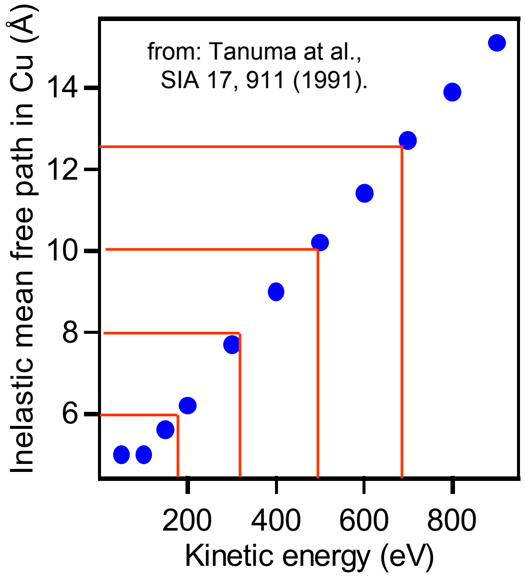


O1s depth profiling

$CH_3OH : O_2 = 3:1$





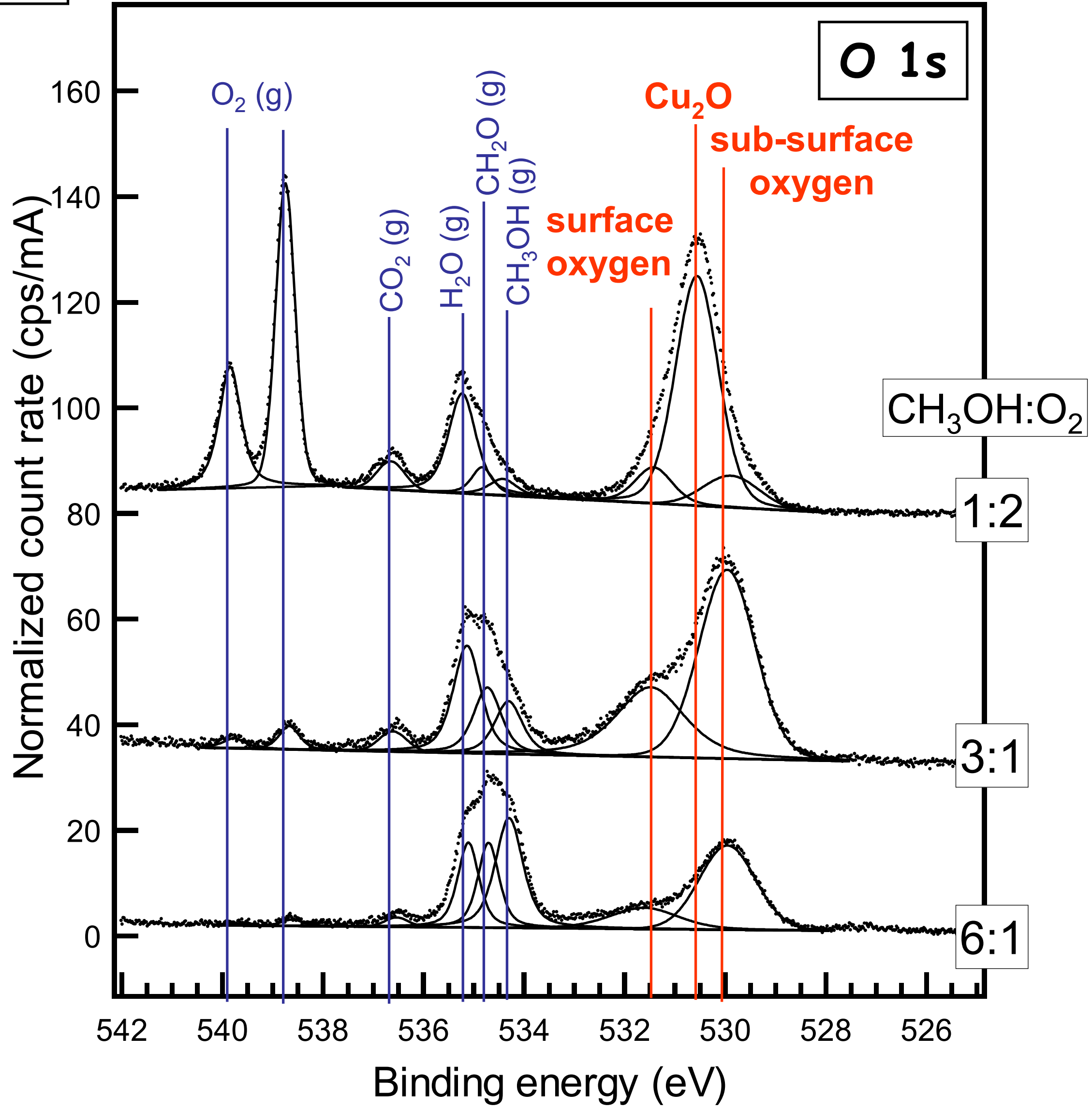


$$I_{529.9}/I_{531.5}=n_{529.9}/n_{531.5}\cdot\exp[-(z_{531.5}-z_{529.9})/\lambda]$$

Δz = 3 Å, $n_{529.9}/n_{531.5} = 1.6$

Variation of the gas phase composition

400 °C

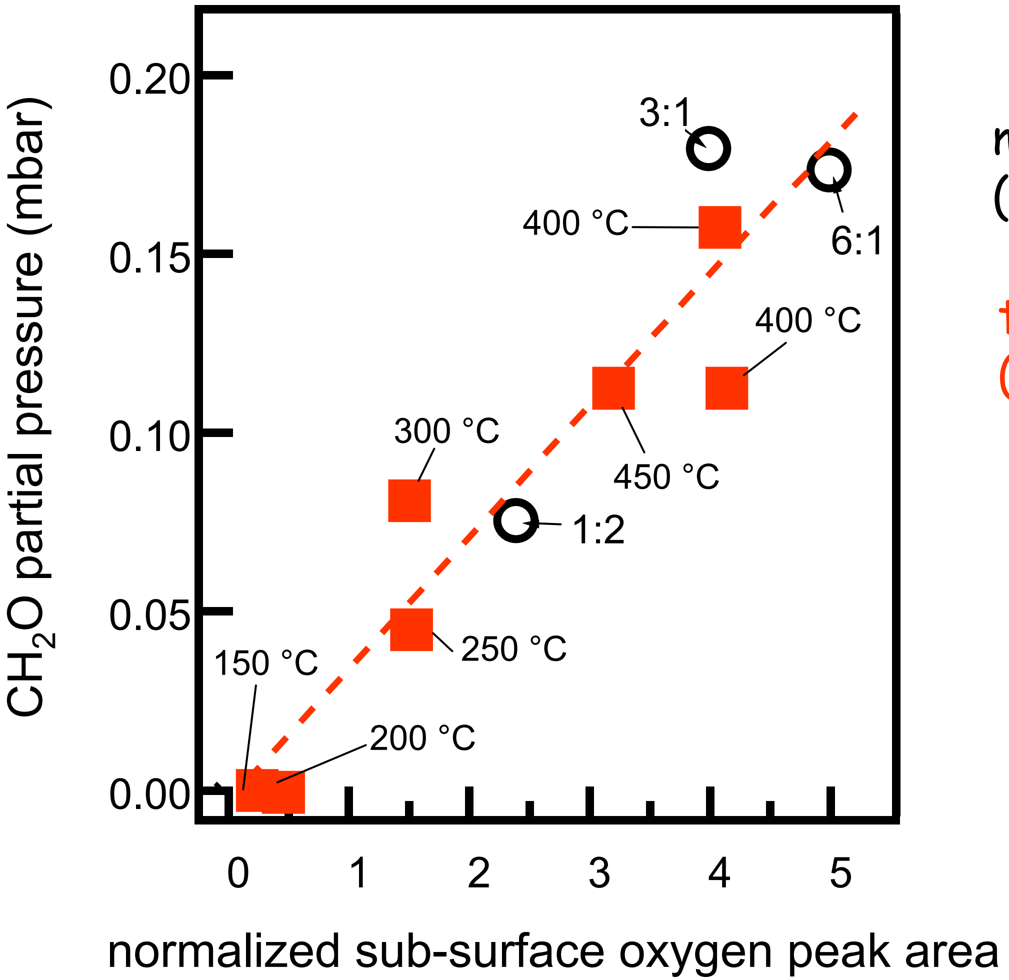


conversion CH_3OH (part. press. CH_3OH)	yield CH_2O (part. press. CH_2O)	yield CO_2 (part. press. CO_2)
0.68 0.053	0.46 0.075	0.22 0.072
0.58 0.167	0.45 0.179	0.13 0.103
0.38 0.307	0.35 0.173	0.03 0.030

partial pressures in mbar

Correlation of catalytic activity and surface species

CH_2O yield vs sub-surface oxygen peak area



mixing ratio series
(T = 400 °C)

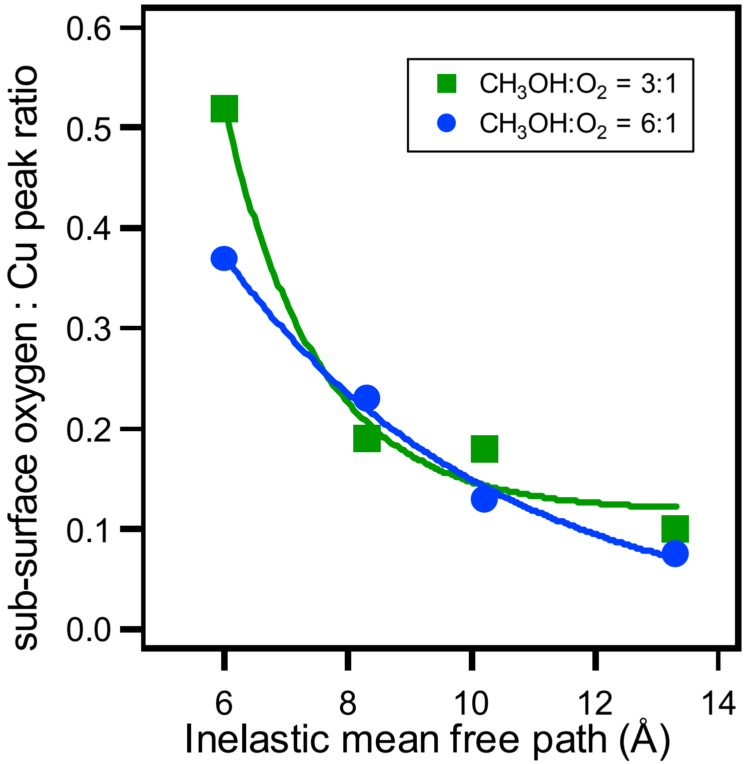
temperature series
(CH_3OH:O_2=3:1)

Open questions:
What is the nature of the sub-surface oxygen species?
What is its role in the catalytic reaction?

Depth profiling

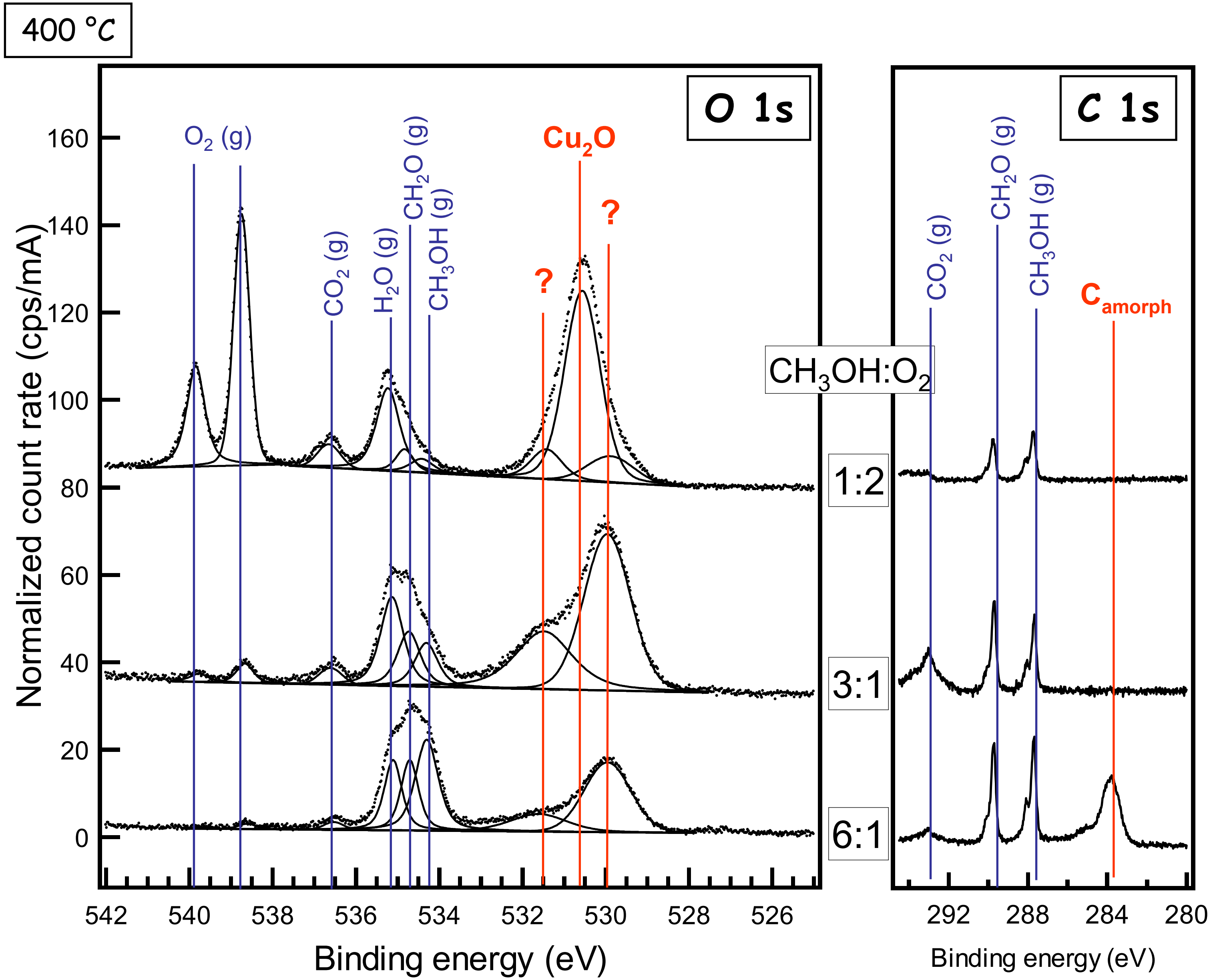
(calculated from Cu 3*p* and sub-surface O 1*s*)

Reducing conditions



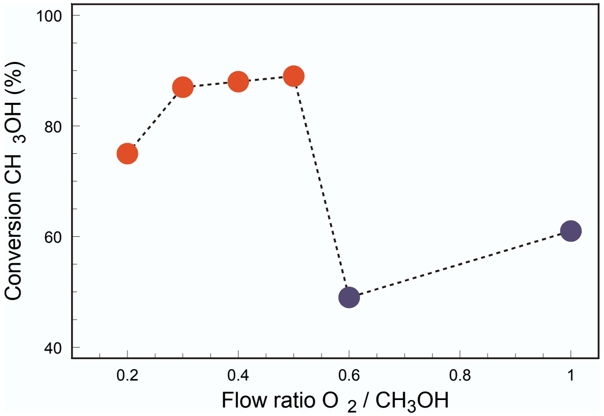
Open questions: What is the nature of the sub-surface oxygen species?
What is its role in the catalytic reaction?

Methanol oxidation on Cu: C1s spectra



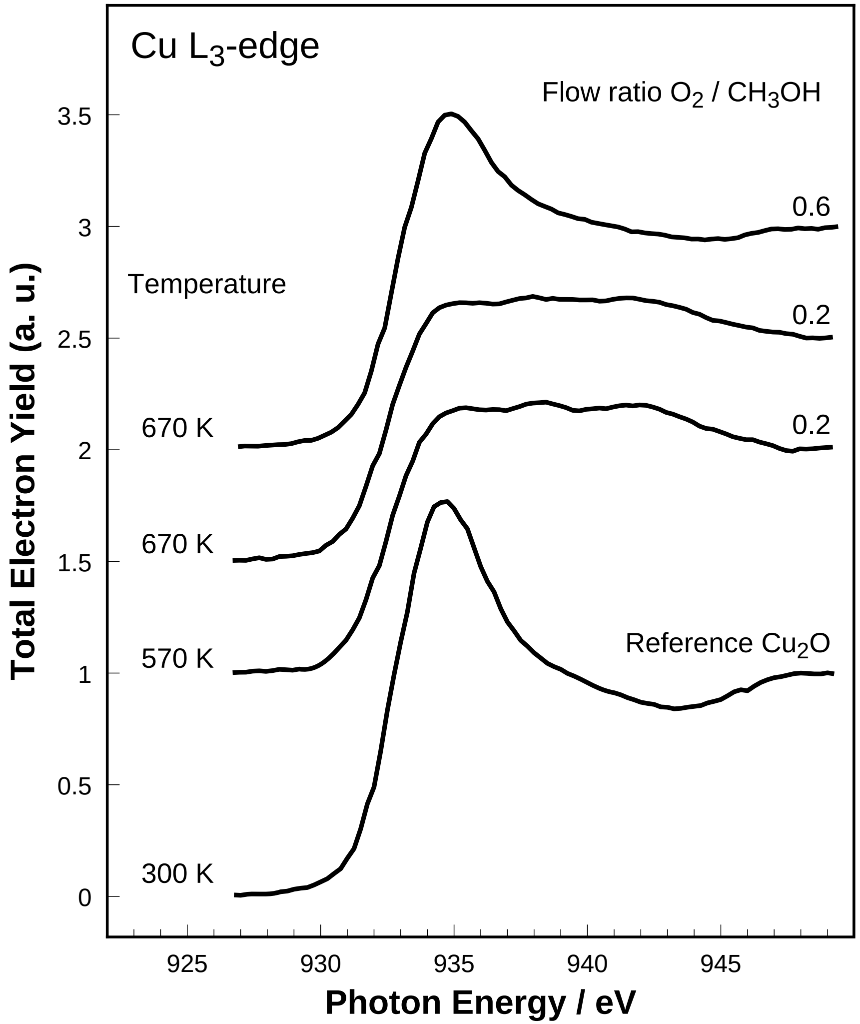
Cu L_3- NEXAFS

Catalytic Activity



Increased activity for gas flow ratios: O_2 / $CH_3OH \leq 0.5$

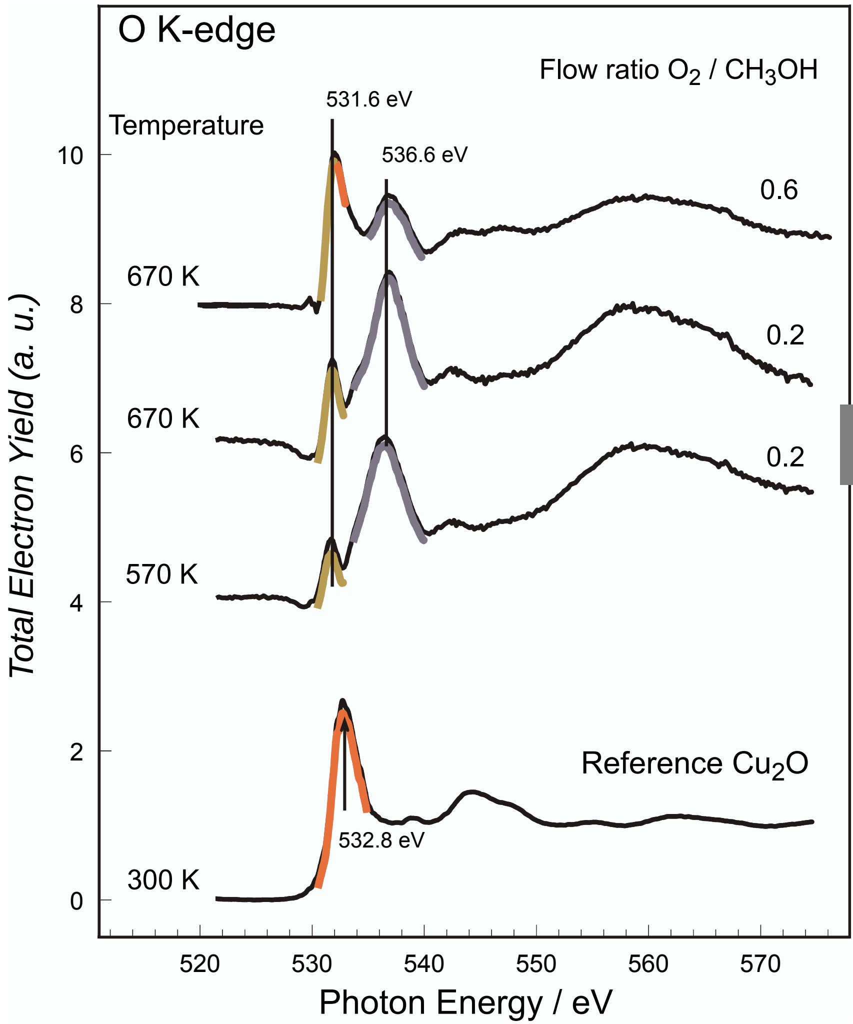
NEXAFS at the Cu L_3-edge



Transition from an oxidic copper-phase to the metallic state

NEXAFS at the O K-edge

- NEXAFS of the active state is completly different from the NEXAFS of the known copper-oxides
- 2 oxidic- and 1 suboxidic species can be distinguished

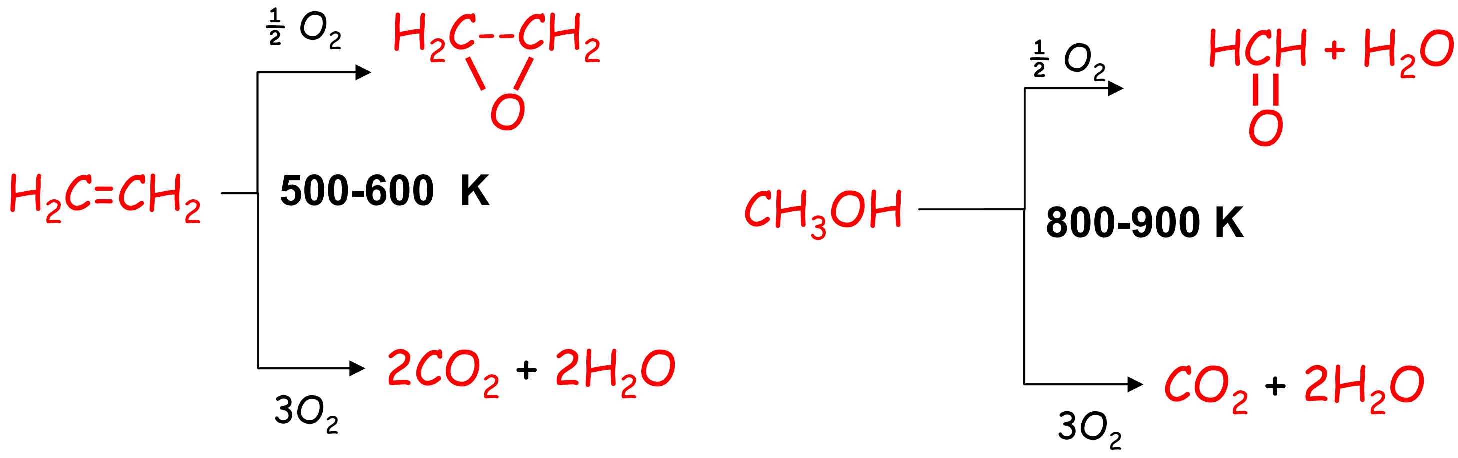


less active

very active

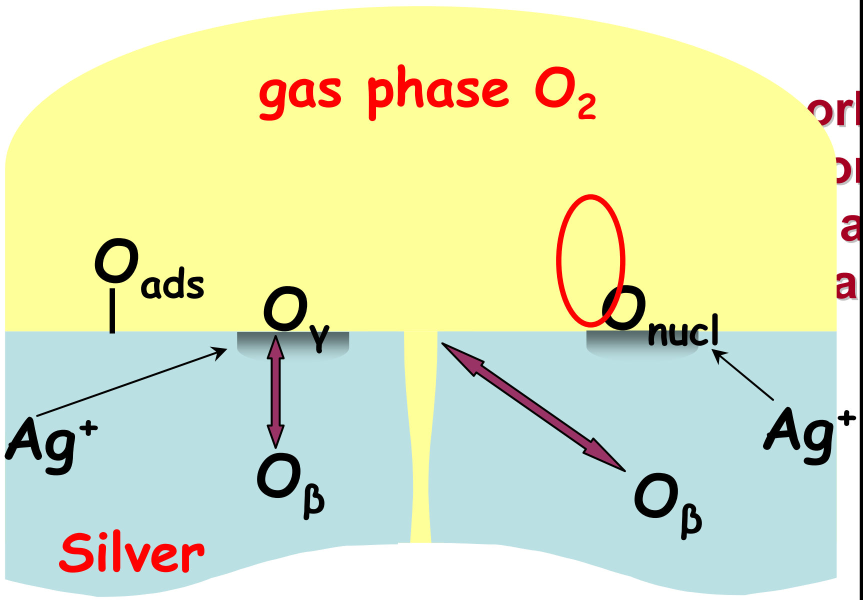
Oxygen species on Ag (111)
Motivation

Important Industrial Applications :



"Simple" Model adsorption system for theoretical studies

Literature review :Oxygen species reported on silver

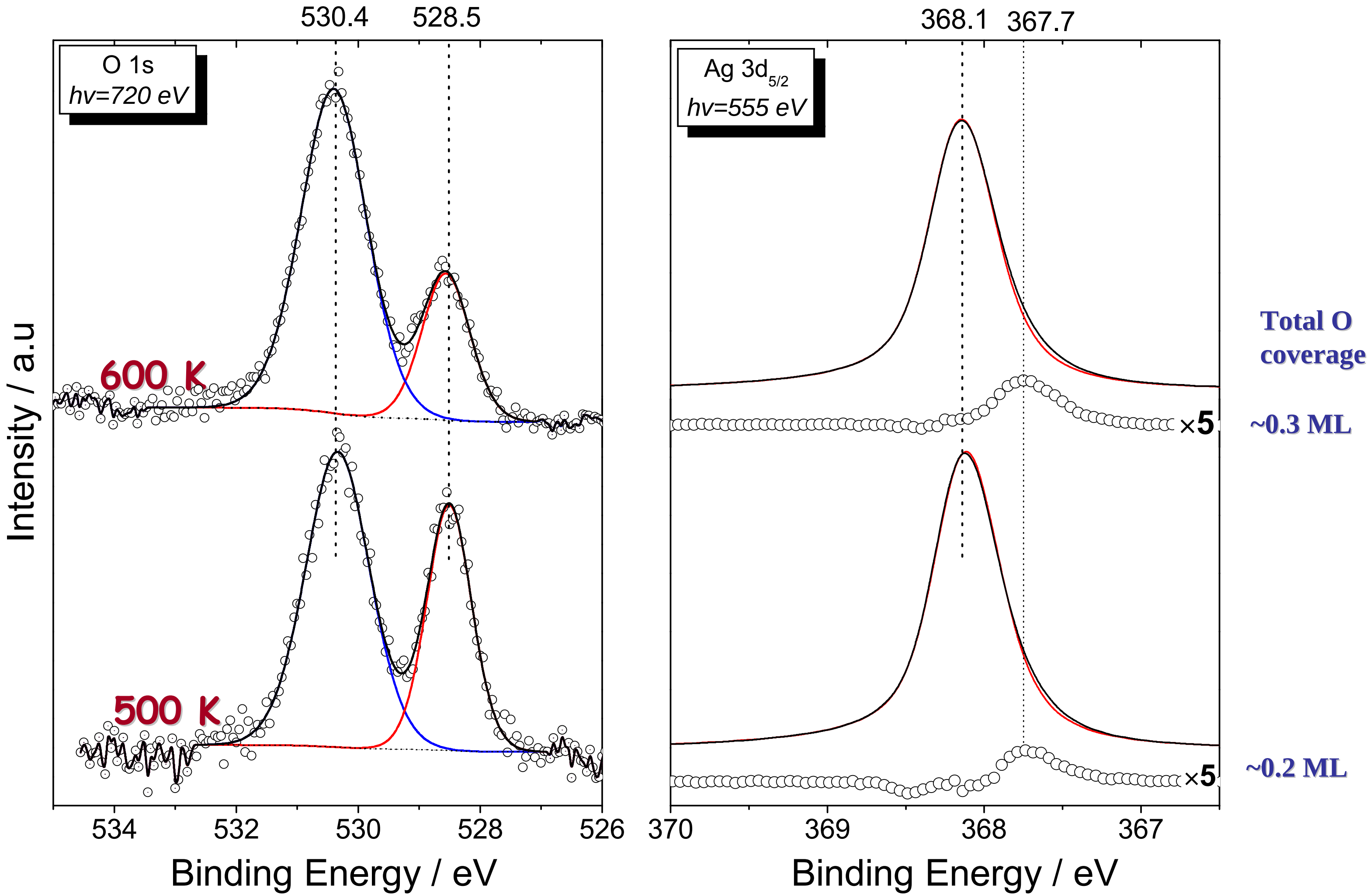


Species	Description	BE (eV)	Formation of ionic Ag
O_{nucl} or $p(4\times4)$-O	Atomic oxygen embedded on Ag	528.3±0.2	Yes
O_γ	Atomic oxygen strongly chemisorbed on Ag	529.2±0.2	no
O_{ads} or O_{elec}	Atomic oxygen adsorbed on Ag surface	53[illegible].4±0.2	no
O_β	Atomic oxygen incorporated in the Ag subsurface/bulk	530.5 ±0.5	no
OH_{ads}	Hydroxyl species	531.5 ±0.4	no
H_2O_{ads}	H_2O adsorbed	533.2 ±0.3	no
$CO_{3,ads}$	Surface carbonates	530.2 ±0.3	no

orbed O_2
orbed O_2
adsorbed atomic O
ace or bulk-dissolved atomic O

1. O_2 Pressure
2. Temperature
3. Silver surface crystallographic orientation
4. Defect density
5. Pre-treatment history

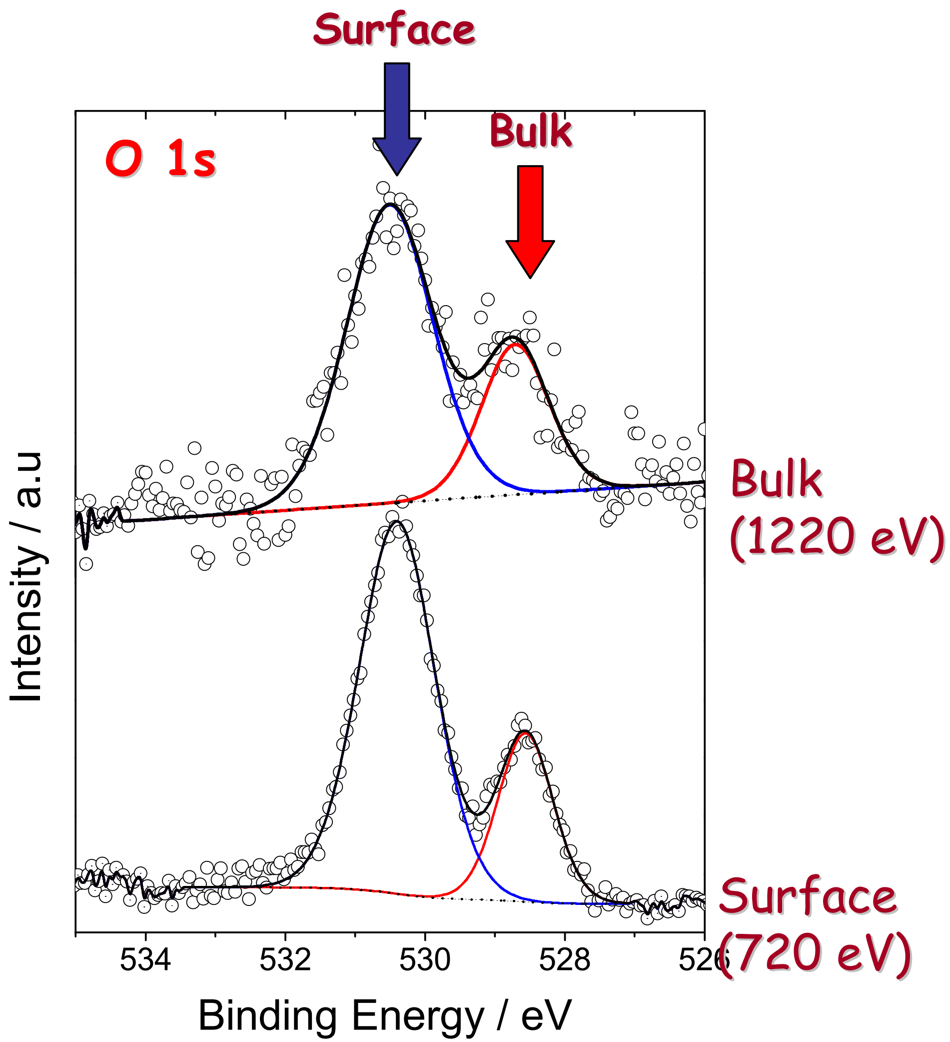
Oxygen species on Ag (111) at 500 and 600 K in 0.13 mbar O_2

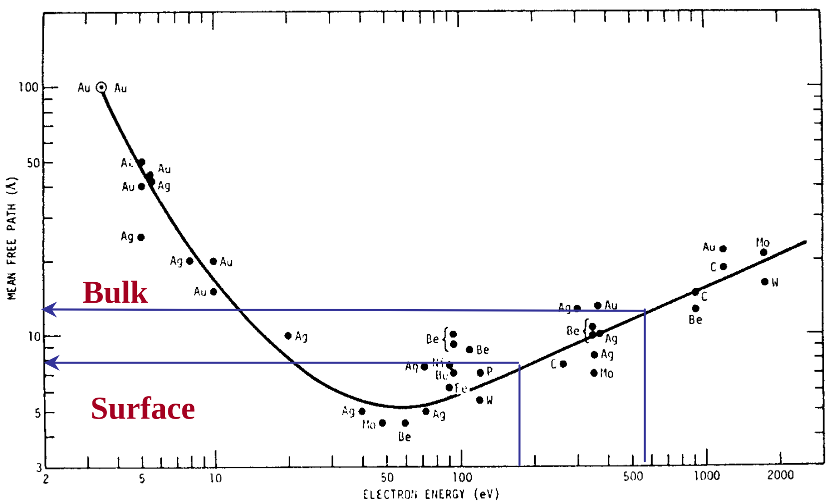


*Sample was first cleaned (sputtered-annealed) then temp. raised and 0.13 mbar O_2 introduced

Oxygen species on Ag (111) at 600 K in 0.13 mbar O_2

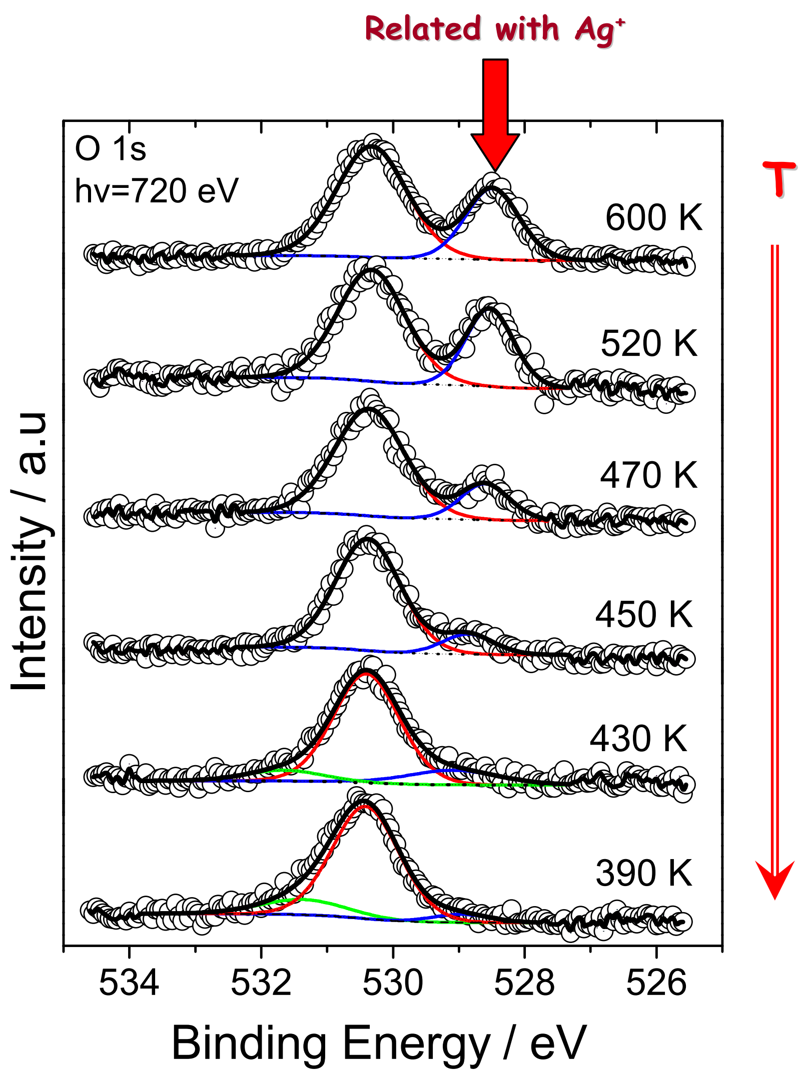
Comparison between O 1s spectra recorded using different excitation energies

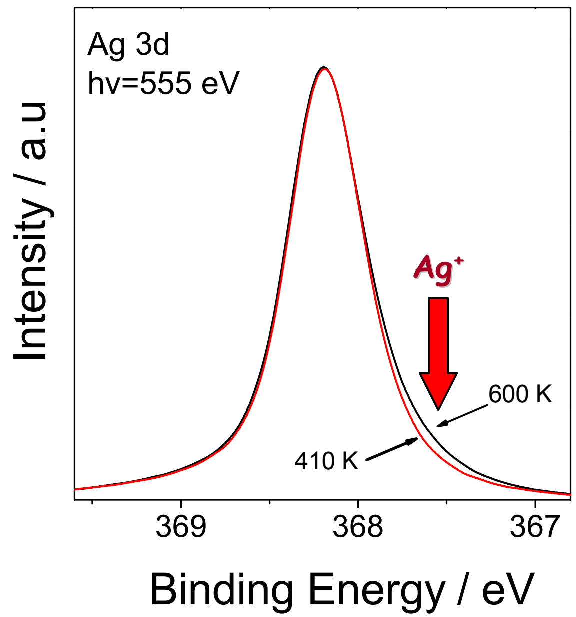




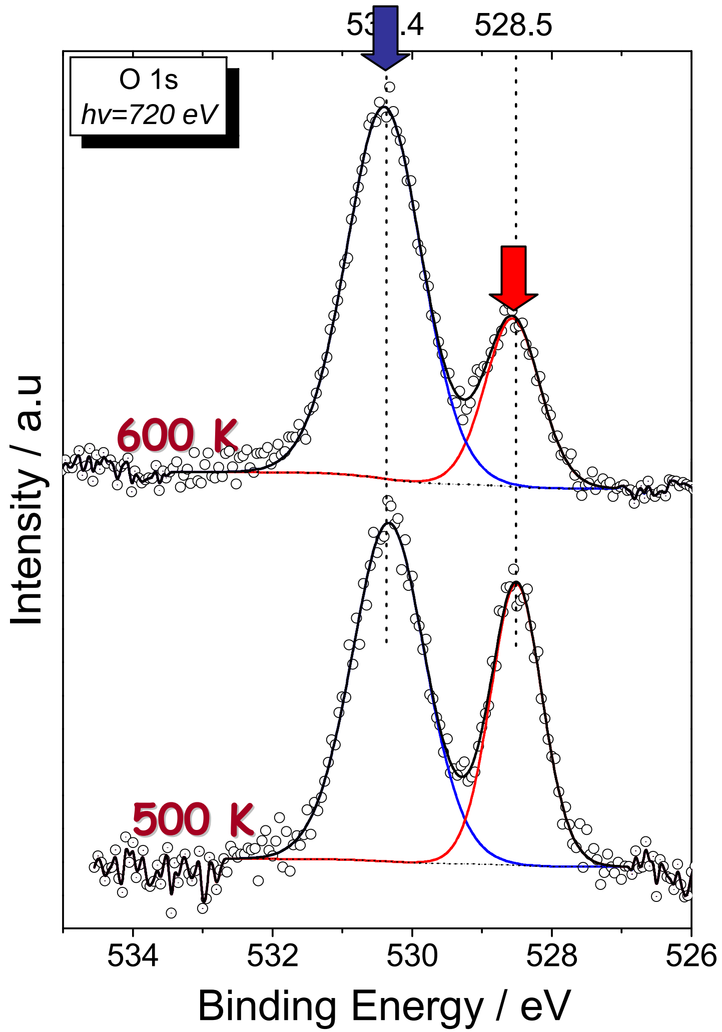
Oxygen species on Ag (111) in 0.13 mbar O_2

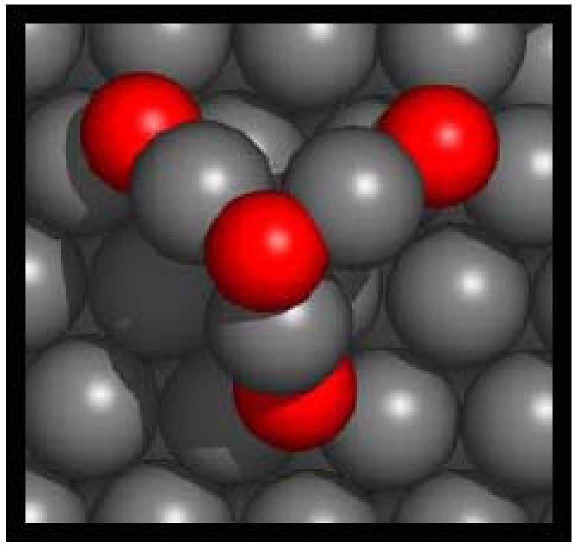
Oxygen Species related with ionic silver formation





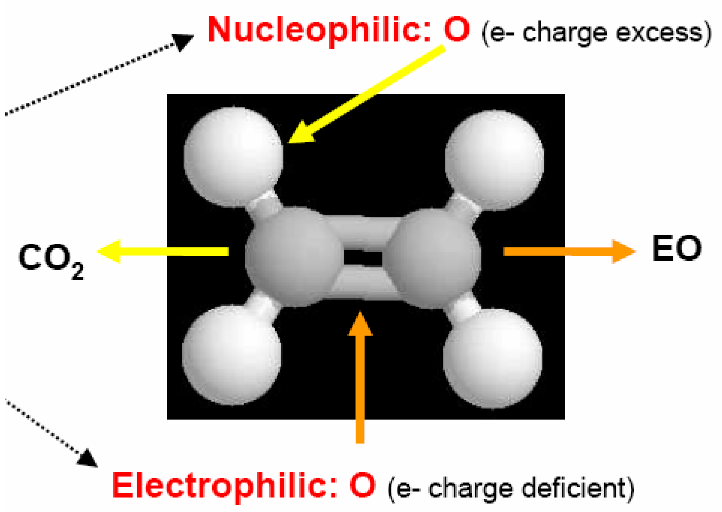
Oxygen species on Ag (111) at 500 and 600 K in 0.13 mbar O_2





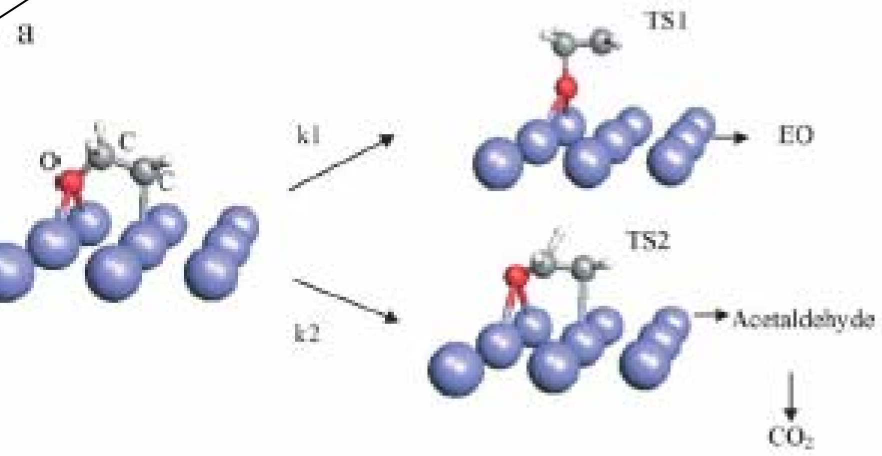
J. Schnadt et.al PRL 96, 146101 (2006)

Ethylene Epoxidation : Existing reaction models



R. A. van Santen, R. Lambert, C. Campbell (1985)

Ag-O interaction determines atomic oxygen charge



Oxametallacycle (reaction intermediate)

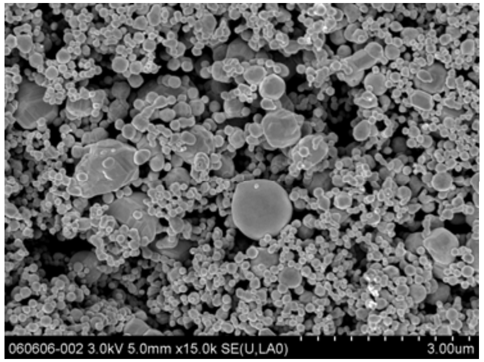
M. A. Barteau (2004)

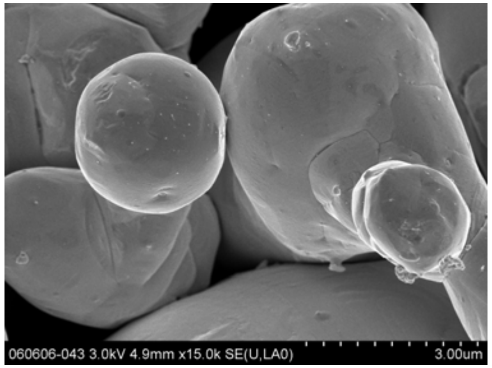
Ethylene epoxidation on Silver Powder Samples

SEM pictures*

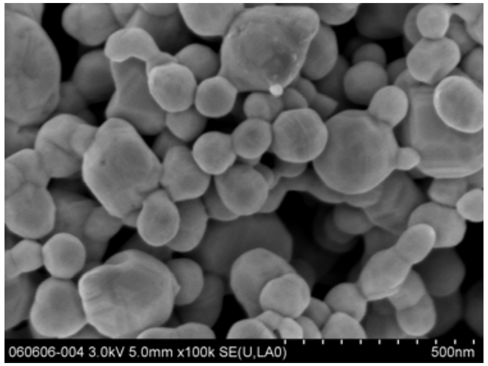
SAMPLE 1 : Ag-nano

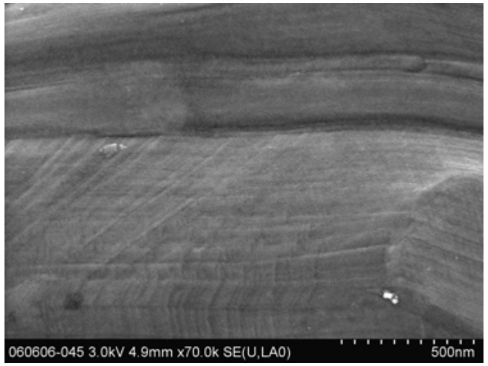
SAMPLE 2 : Ag-powder





3 µm





500 nm

Activated Ag Nano-powder
(~100 nm, high defect structure)

Ag powder
(<600 µm)

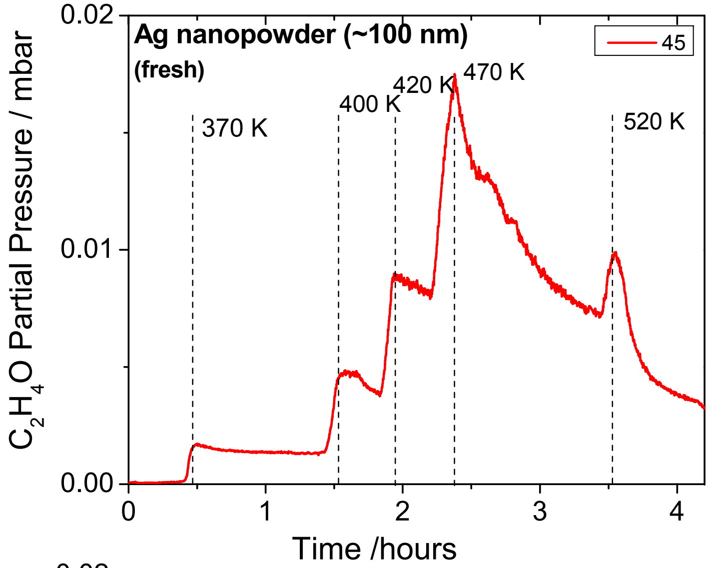
*Commercially available samples (Sigma-Aldrich)

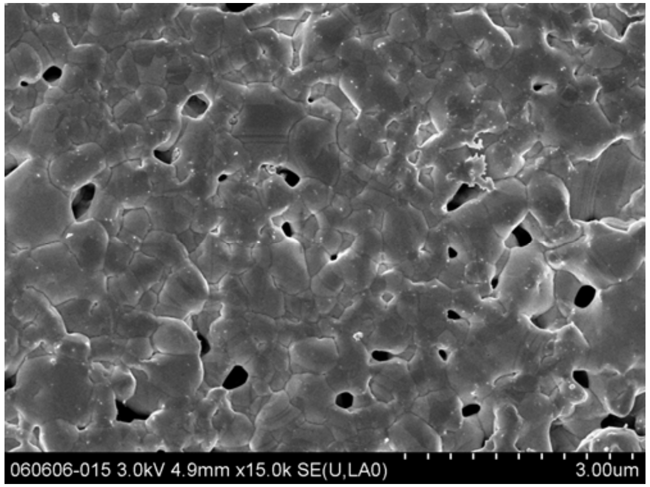
Powder Samples : Catalytic results

Detection of C_2H_4O (PTRMS) : Reaction conditions : C_2H_4/O_2 (1/2), P=0.5 mbar

Ag nano

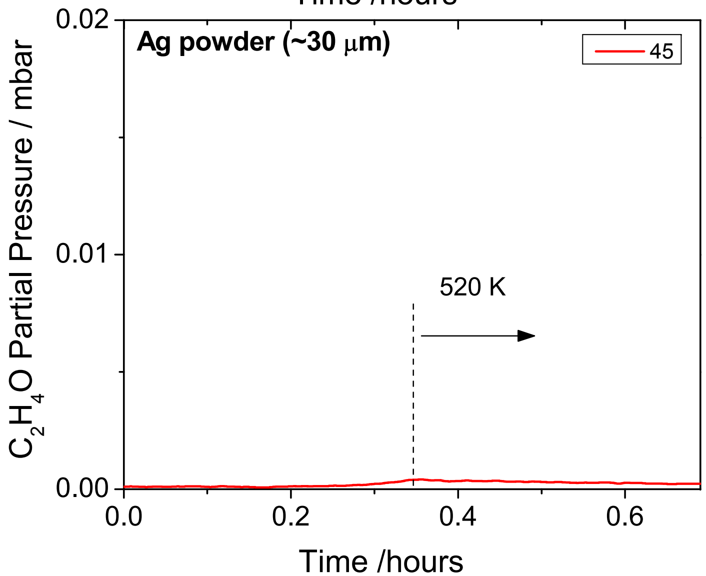
Highly active for ethylene epoxidation

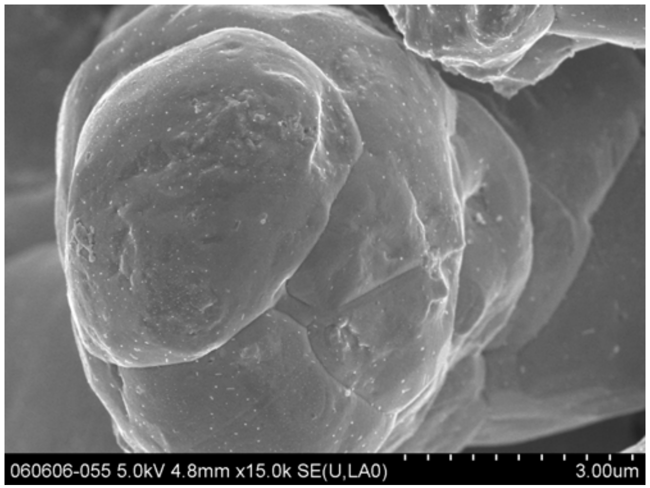




Ag powder

Inactive for ethylene epoxidation under our conditions





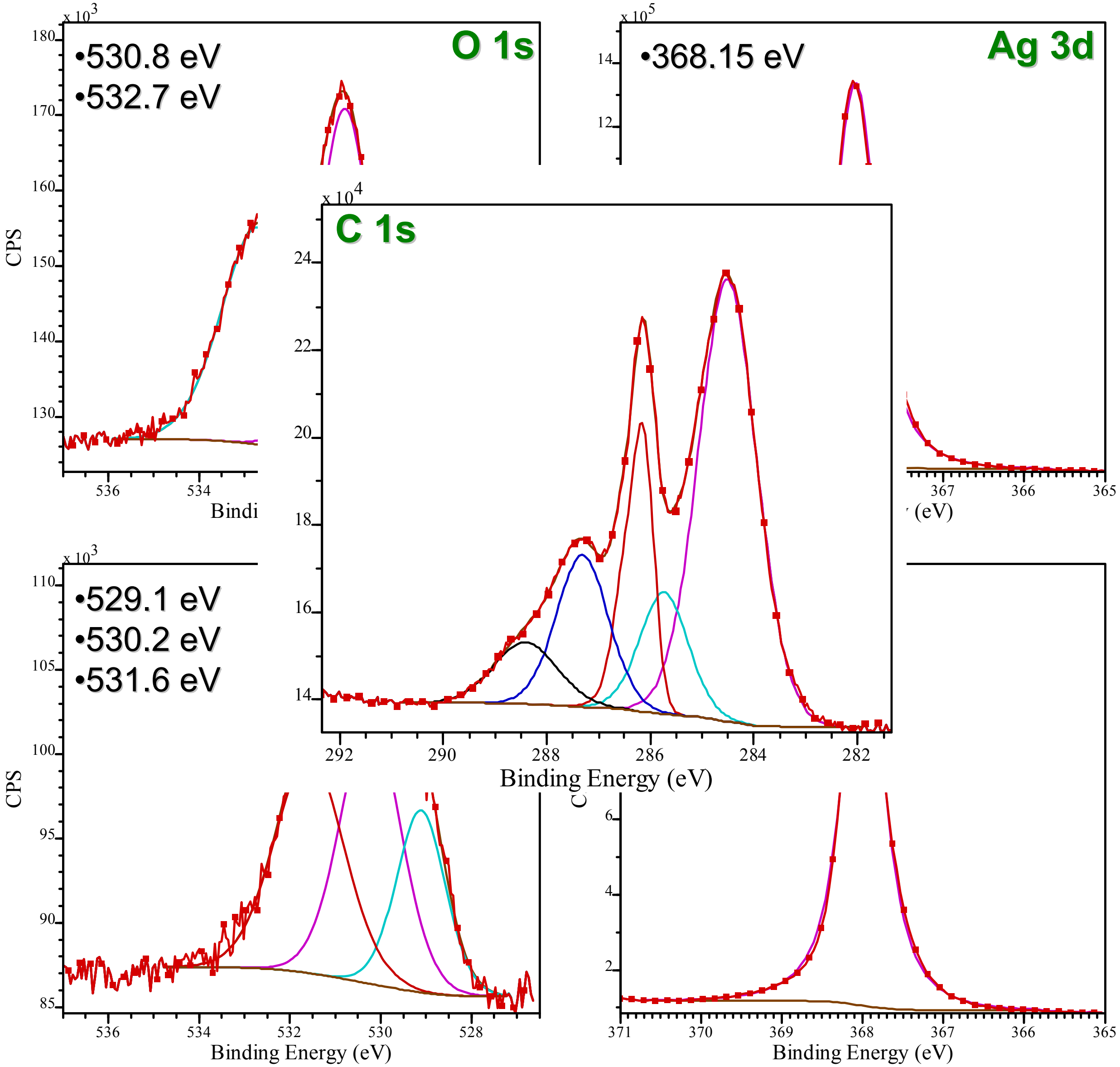
Silver particles agglomeration
→ loss of surface area

Powder Samples : Post reaction characterization

(C_2H_4/O_2 (1/2), P=0.5 mbar, @300 K)

Ag nano

Ag powder



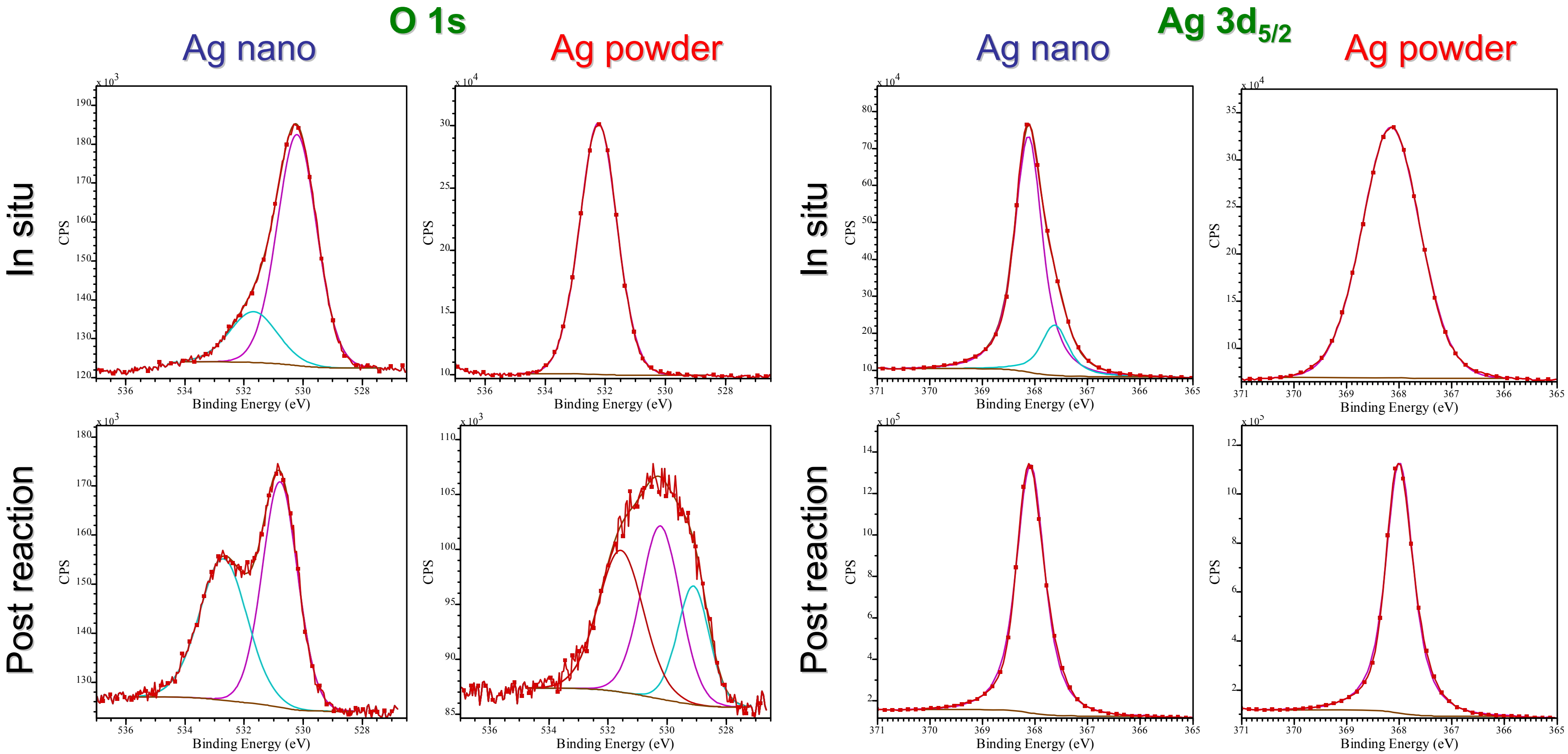
Intensity ratio

O/Ag =0.138

O/Ag = 0.084

EK=220 eV

Powder Samples : Comparison Post and in-situ characterization



Differences between *in situ* and *post reaction* spectra :

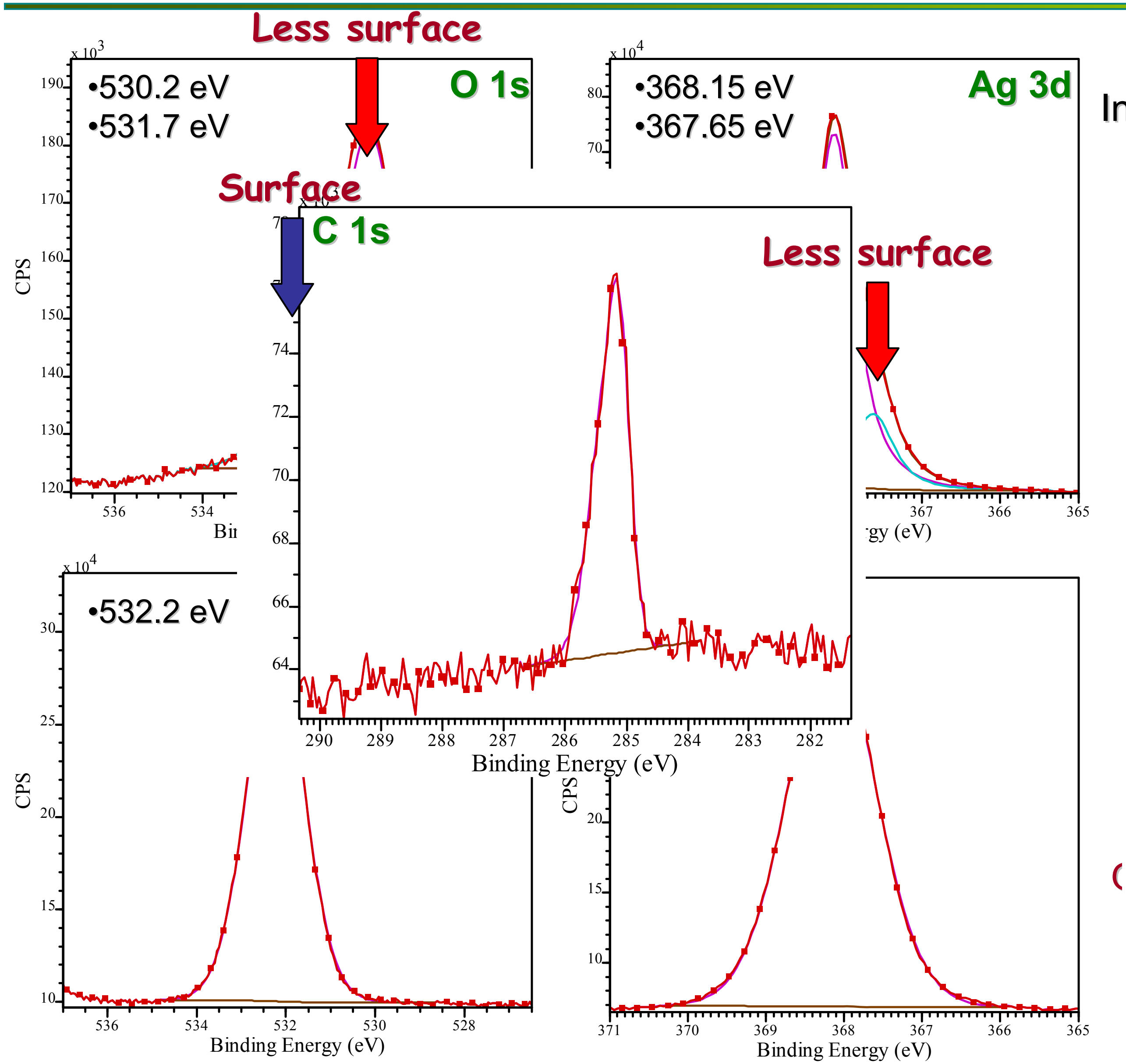
- Oxygen species
- Silver species
- Oxygen amount
- Adsorbed carbon

Differences between *active* and *non-active* catalyst :

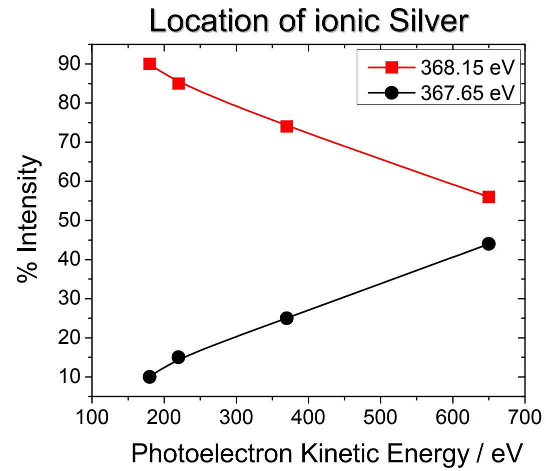
- Oxygen species
- Silver species
- Oxygen amount

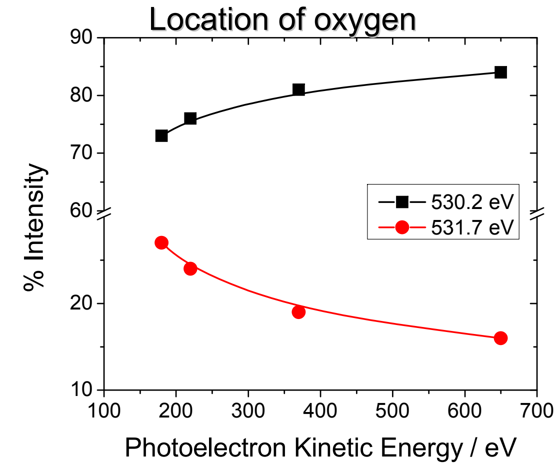
Powder Samples : In situ reaction characterization

(Reaction conditions : C_2H_4/O_2 (1/2), P=0.5 mbar, @520 K)

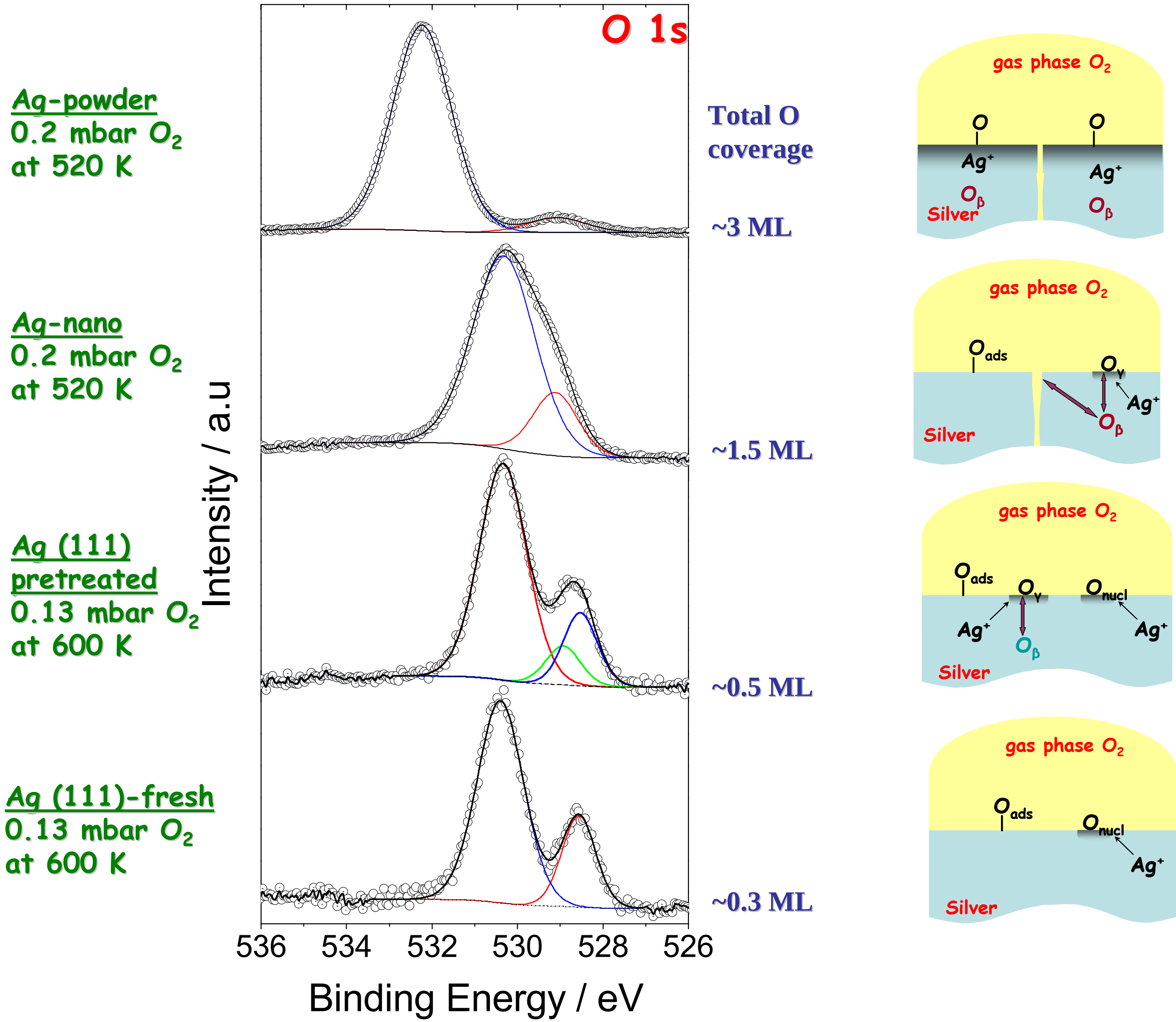


Intensity ratio





Comparison of oxygen species in all samples



Surface Analysis

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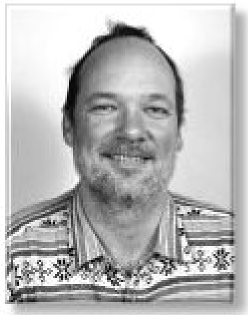

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