Modern Methods in Heterogeneous Catalysis Research

Axel Knop-Gericke, January 09, 2004

In situ X-ray photoelectron spectroscopy (XPS)
In situ near edge X-ray absorption fine structure (NEXAFS) in the soft energy range

Outline

In situ X-ray photoelectron spectroscopy (XPS)

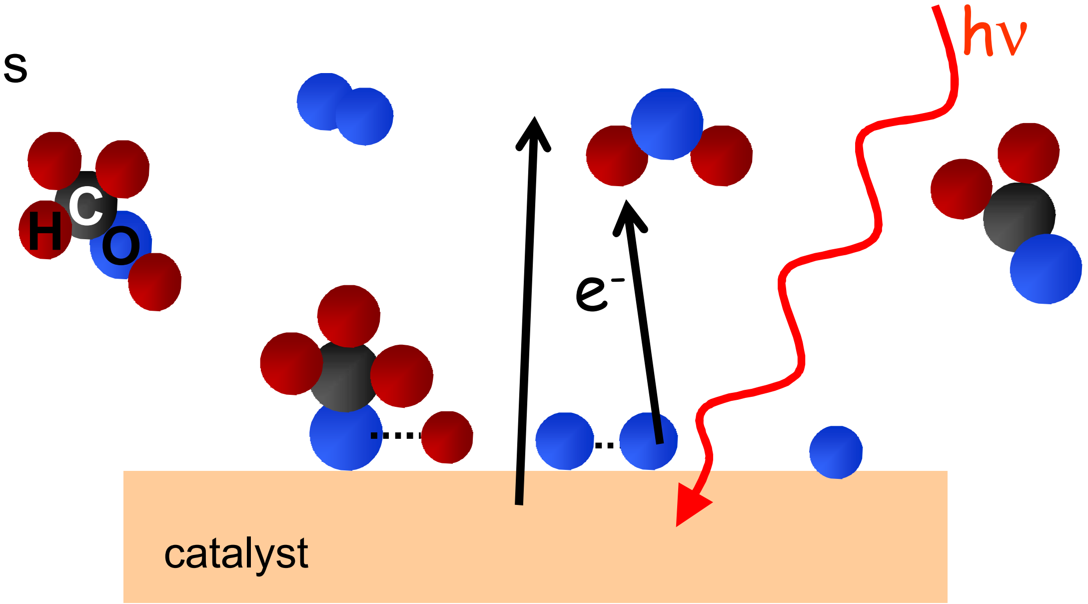
Basics (you heard an hour ago)
Experimental Set up
Examples: methanol oxidation on copper
pentene hydrogenation on Pd

In situ near edge X-ray absorption fine structure (NEXAFS) in the soft energy range

Basics
Experimental Set up
Examples: Methanol oxidation on copper
n-Butane oxidation on vanadium phosphorous oxide

Motivation

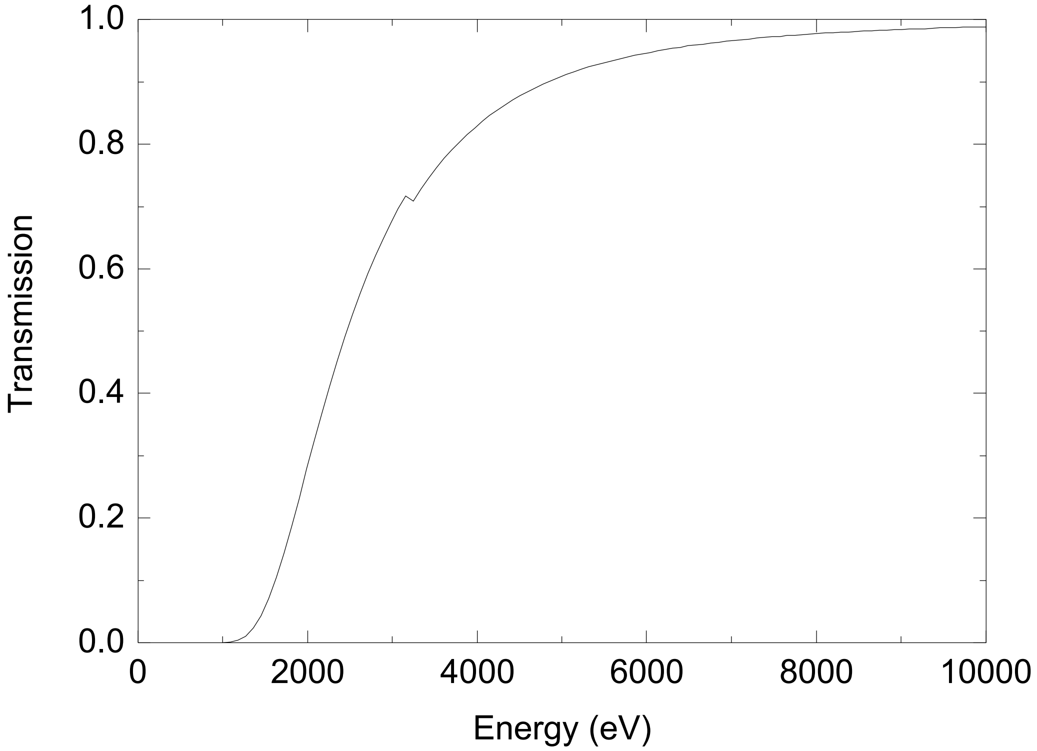
Example: catalysis



ex situ analysis
does not give
correct results!

- Many other processes cannot be studied in UHV:
  environmental chemistry, corrosion, electrochemistry
- Very few methods can investigate the solid-gas interface at high pressures – „Pressure Gap"
  (SFG, scanning probe microscopies, X-ray diffraction)
- Photoemission methods are very powerful

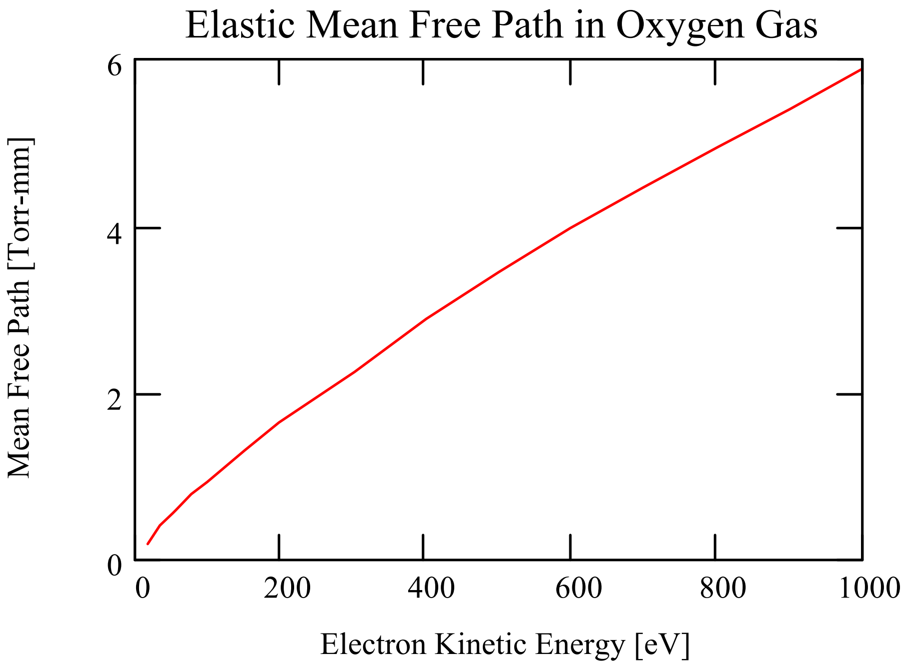
Transmission of 20 cm air



In situ XPS: obstacles

Fundamental limit:

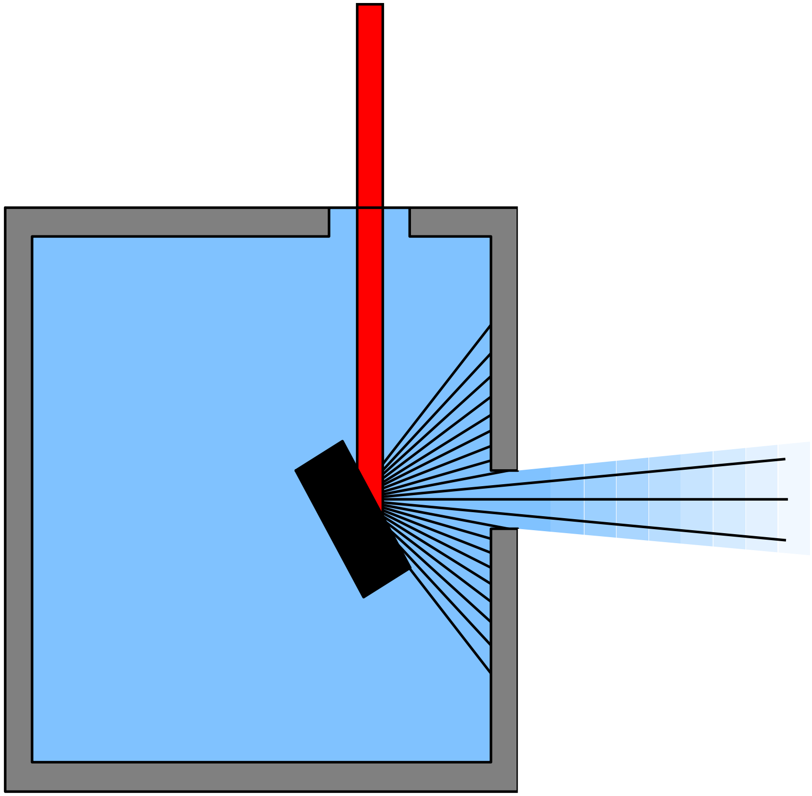
elastic and inelastic scattering of electrons in the gas phase



Technical issues:

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

In situ XPS : basic concept

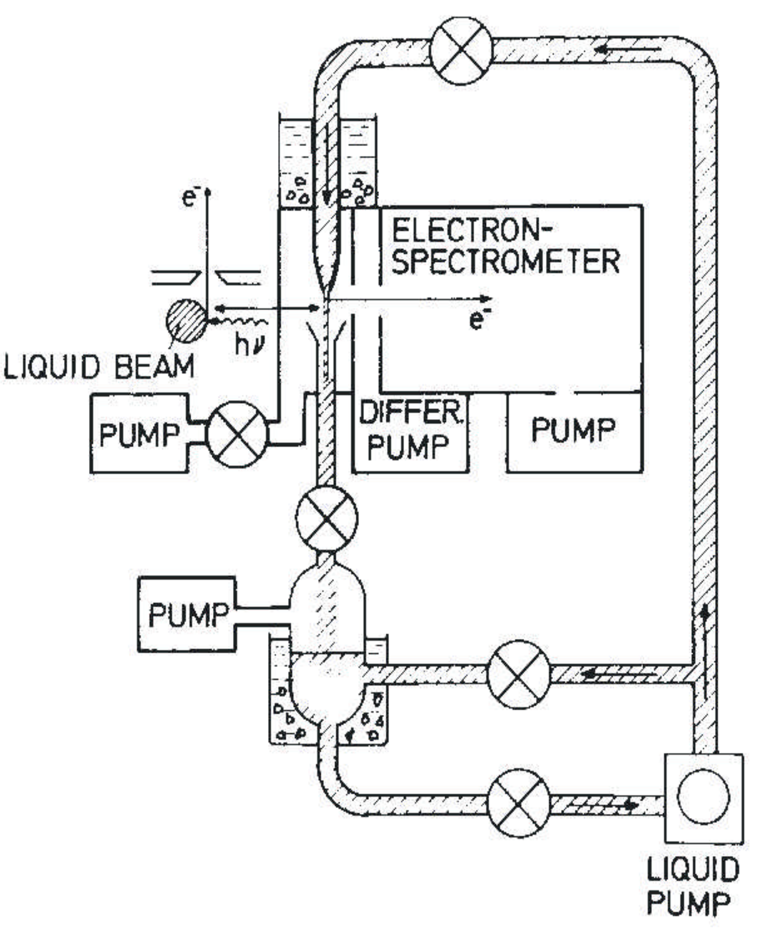


- Photons enter through a window

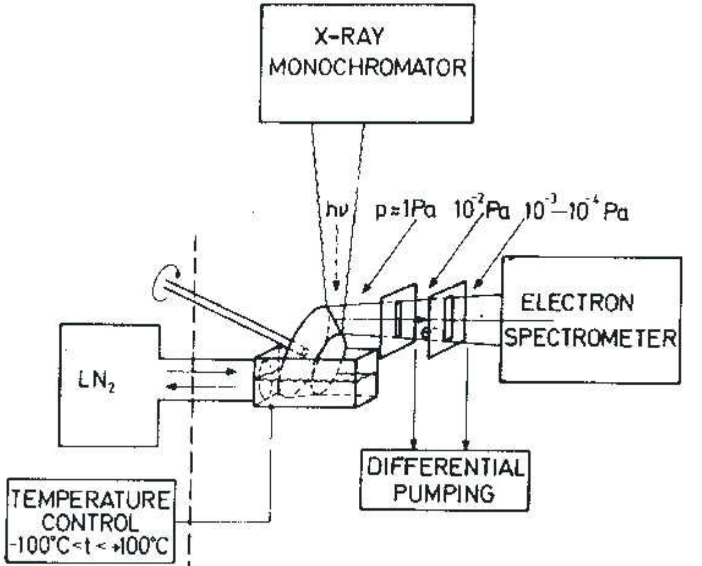
- Electrons and a gas jet escape through an aperture to vacuum

In situ XPS instruments: previous designs

- K. Siegbahn et al. (1968)
- K. Siegbahn et al. (1973)
- M.W. Roberts et al. (1979)
- M. Grunze et al. (1988)

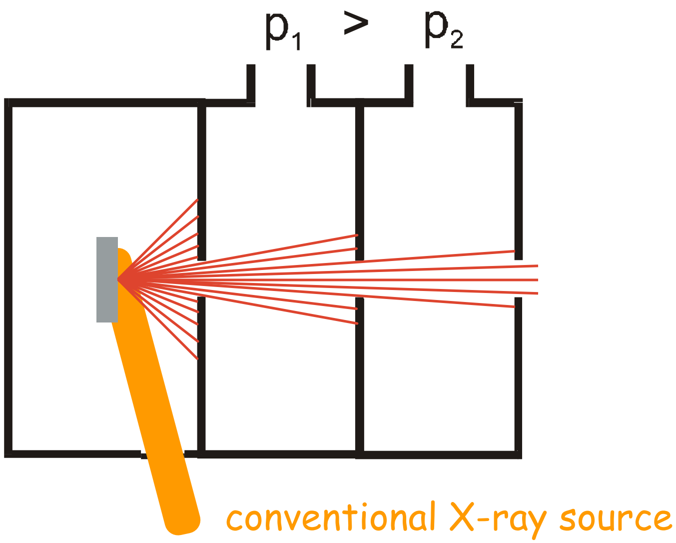


H. Siegbahn et al., J. Electron Spectrosc. Relat. Phenom. **2**, 319 (1973)

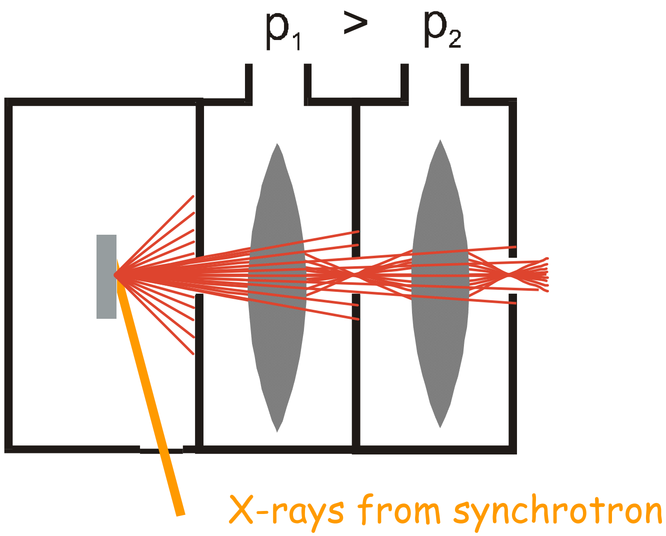


H. Siegbahn et al., J. Electron Spectrosc. Relat. Phenom. **24**, 205 (1981)

In situ XPS : differential pumping + electrostatic lens system

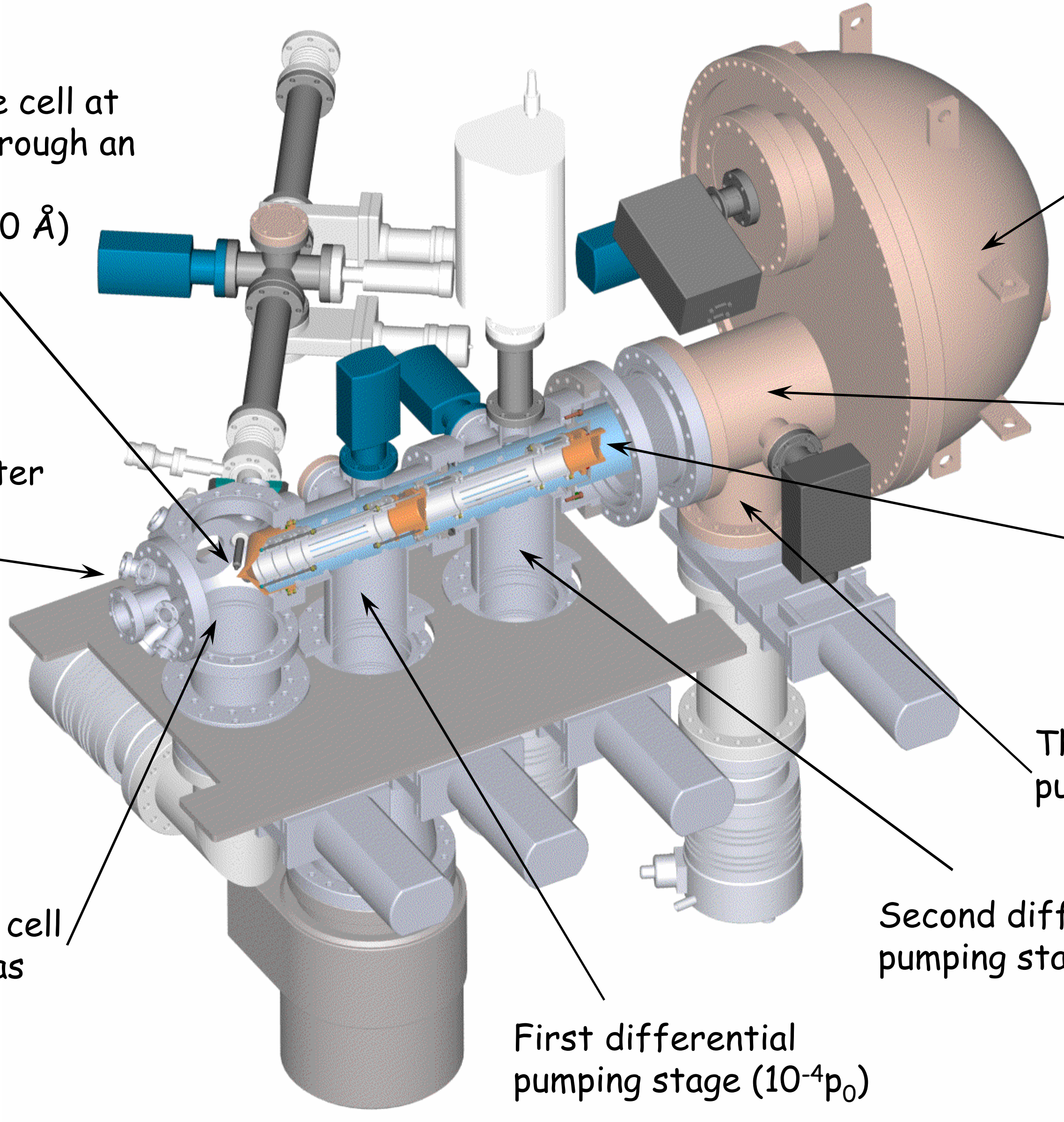


previous designs



our design

In situ XPS system



X-rays enter the cell at 55° incidence through an SiN_x window (thickness ~ 1000 Å)

Hemisphercal electron analyzer ($10^{-9}p_0$)

Analyzer input lens

Focal point of analyzer input lens

mass spectrometer and additional pumping

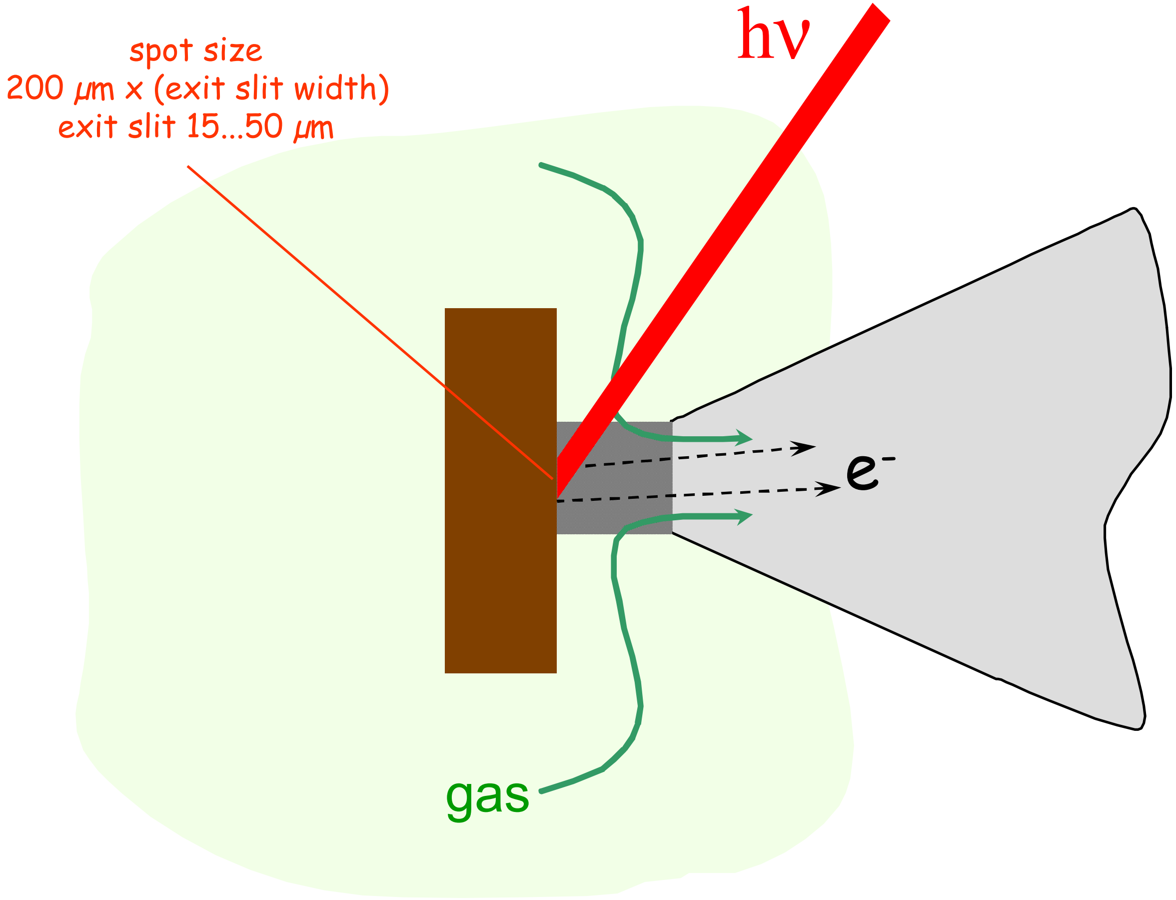
Experimental cell supplied by gas lines (p_0)

First differential pumping stage ($10^{-4}p_0$)

Second differential pumping stage ($10^{-6}p_0$)

Third differential pumping stage ($10^{-8}p_0$)

Gas phase analysis using XPS



<u>gas phase signal:</u> 1 mbar·mm ~ a few monolayers

Photon scource

Berliner**E**lektronen**s**peicherringgesellschaft für **Sy**nchrotronstrahlung

BESSY

Application of in situ XPS to catalysis

Catalytic oxidation of methanol

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

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

What is the state of the surface under reaction conditions?

surface properties ⇔ catalytic activity

⇨ In situ measurements are necessary

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).

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

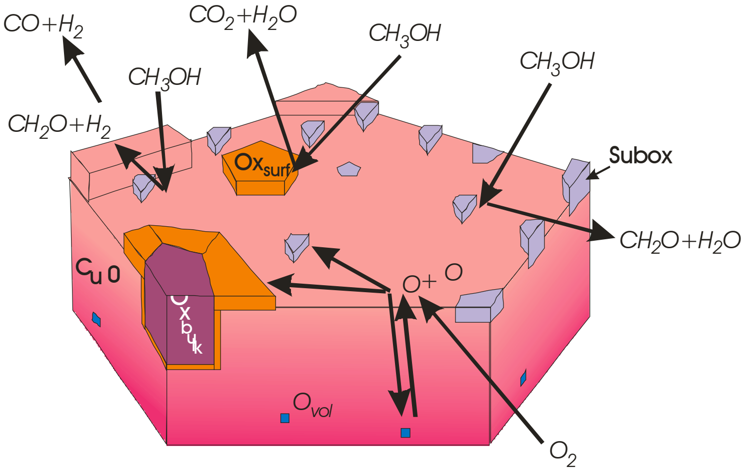
$$CH_3O^-(a) \longrightarrow CH_2O(g) + H^+(a)$$

In situ NEXAFS

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

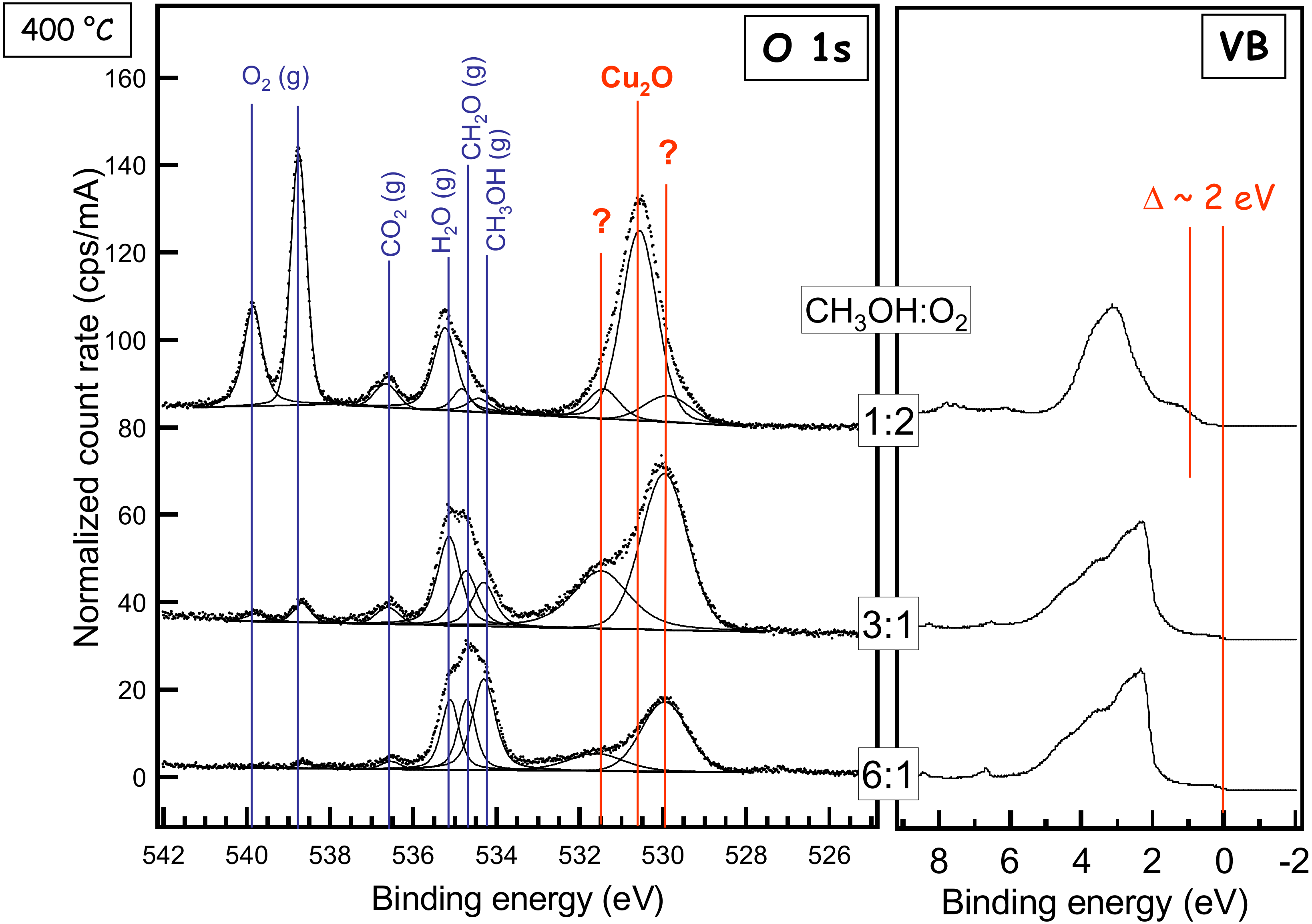
$CH_3OH + O_2 \sim$ 0.5 mbar

suboxide phase:
- only present in situ



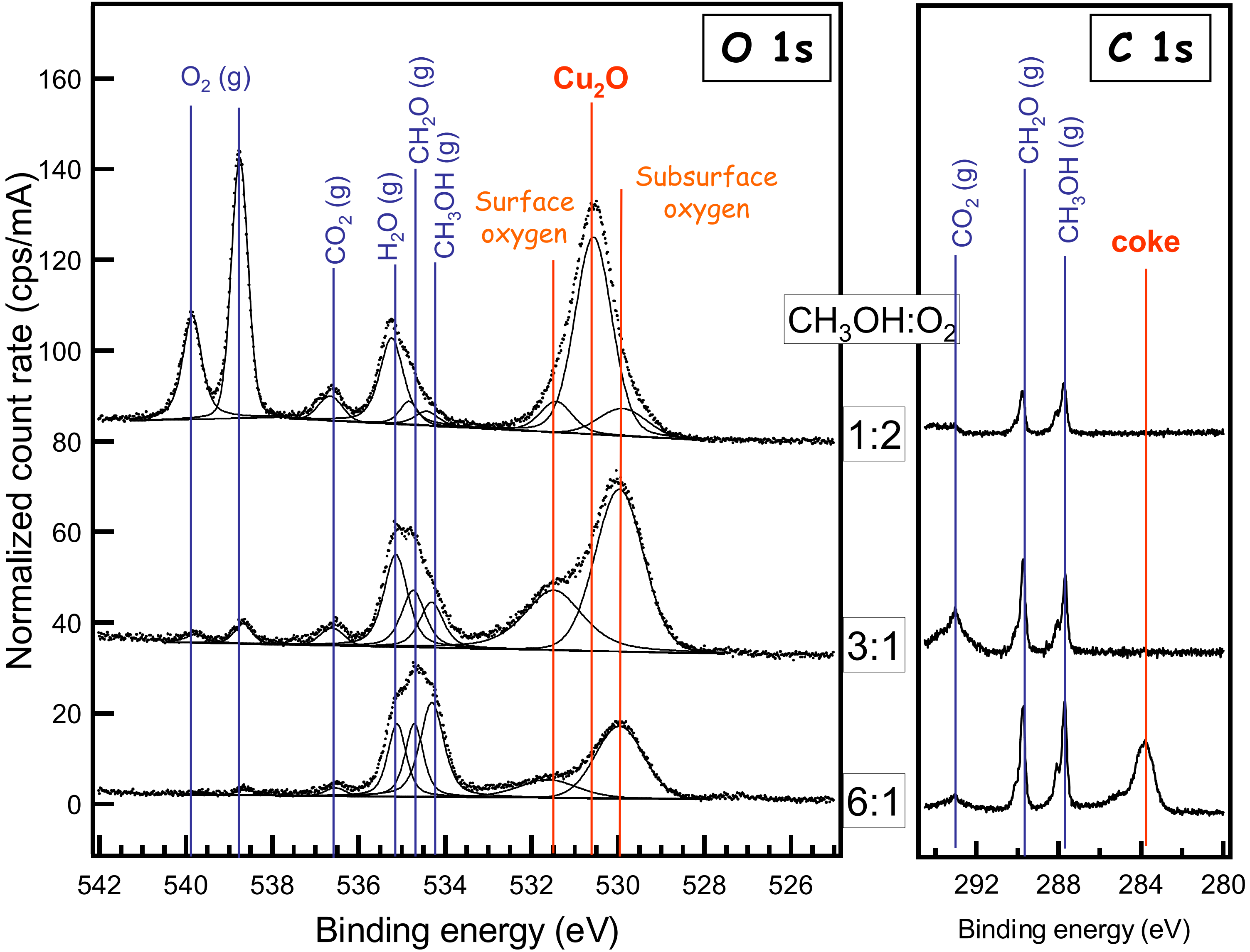
Questions for in situ XPS:
- Quantitative analysis of surface species
- Carbon species on the surface
- Depth-dependent analysis

Methanol oxidation on Cu: O1s spectra



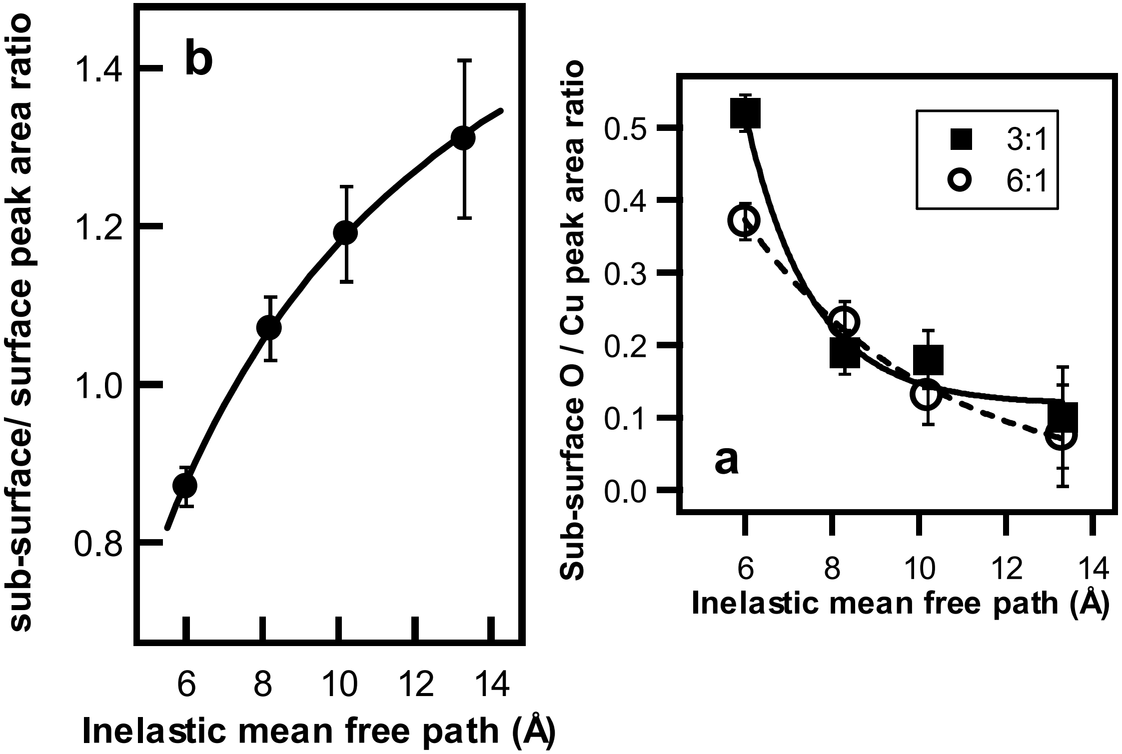
Methanol oxidation on Cu: O1s spectra

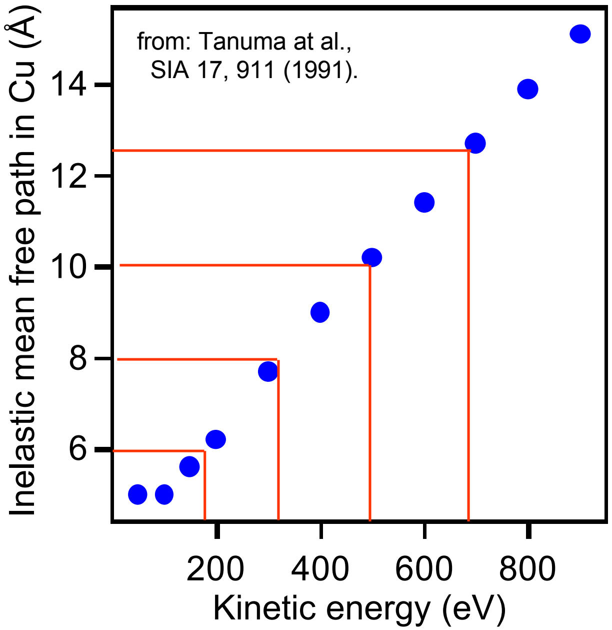
400 °C



O 1s depth profile

$CH_3OH : O_2 = 3:1$



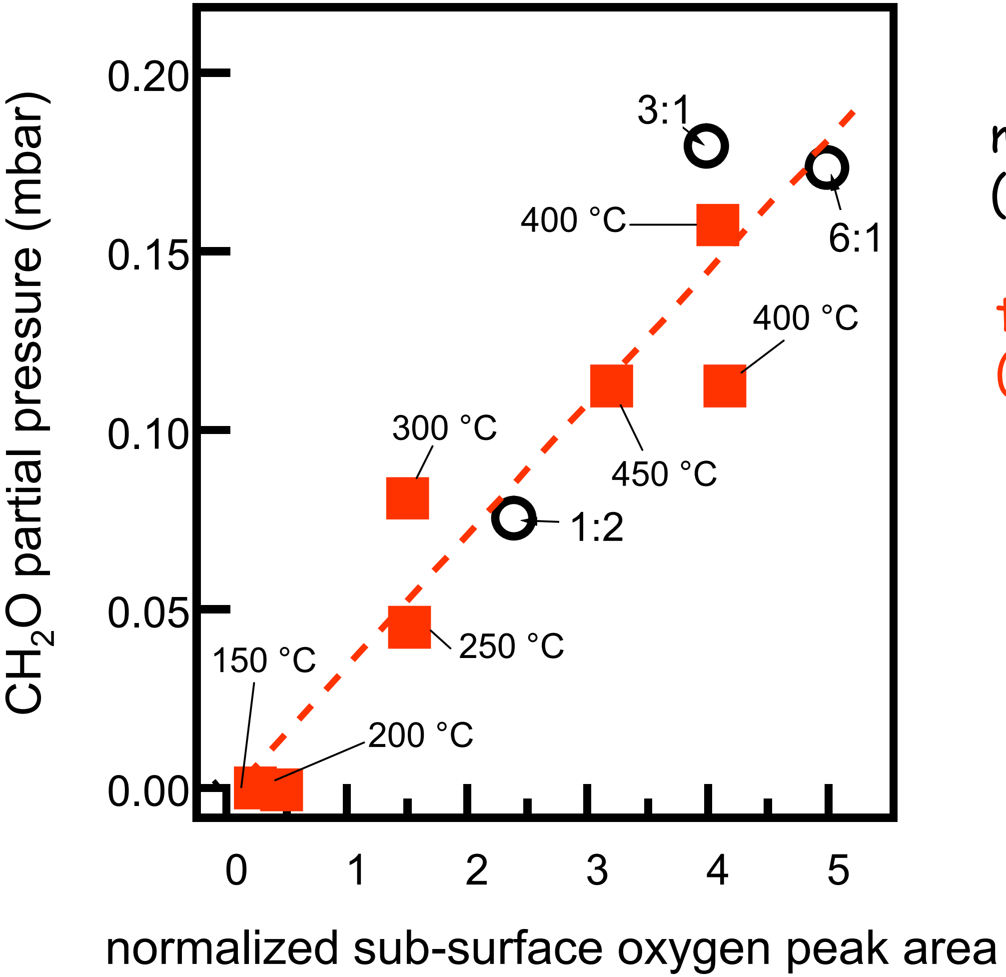

from: Tanuma at al., SIA 17, 911 (1991).

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

$\Delta z = 4$ Å, $n_{529.9}/n_{531.5} = 1.6$

Correlation of catalytic activity and surface species

CH_2O yield vs sub-surface oxygen peak area



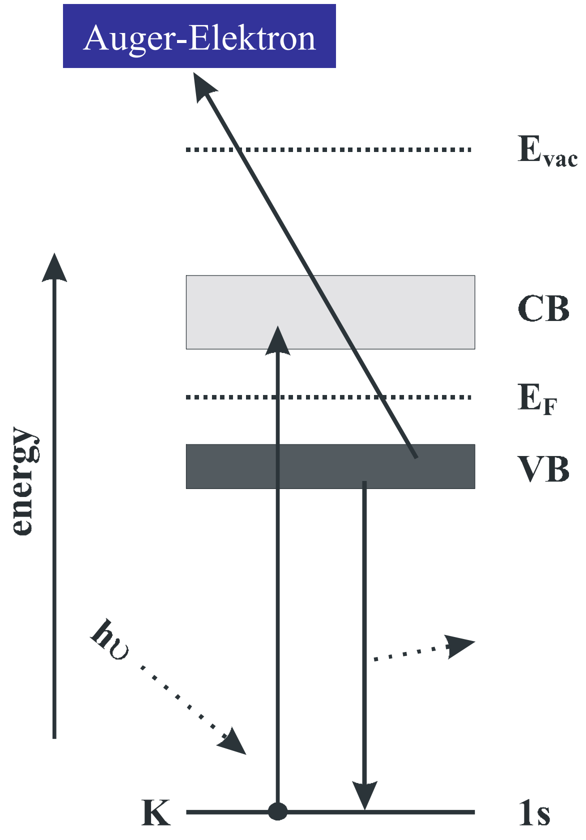
mixing ratio series
(T = 400 °C)

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?

Basics of X-ray absorption spectroscopy

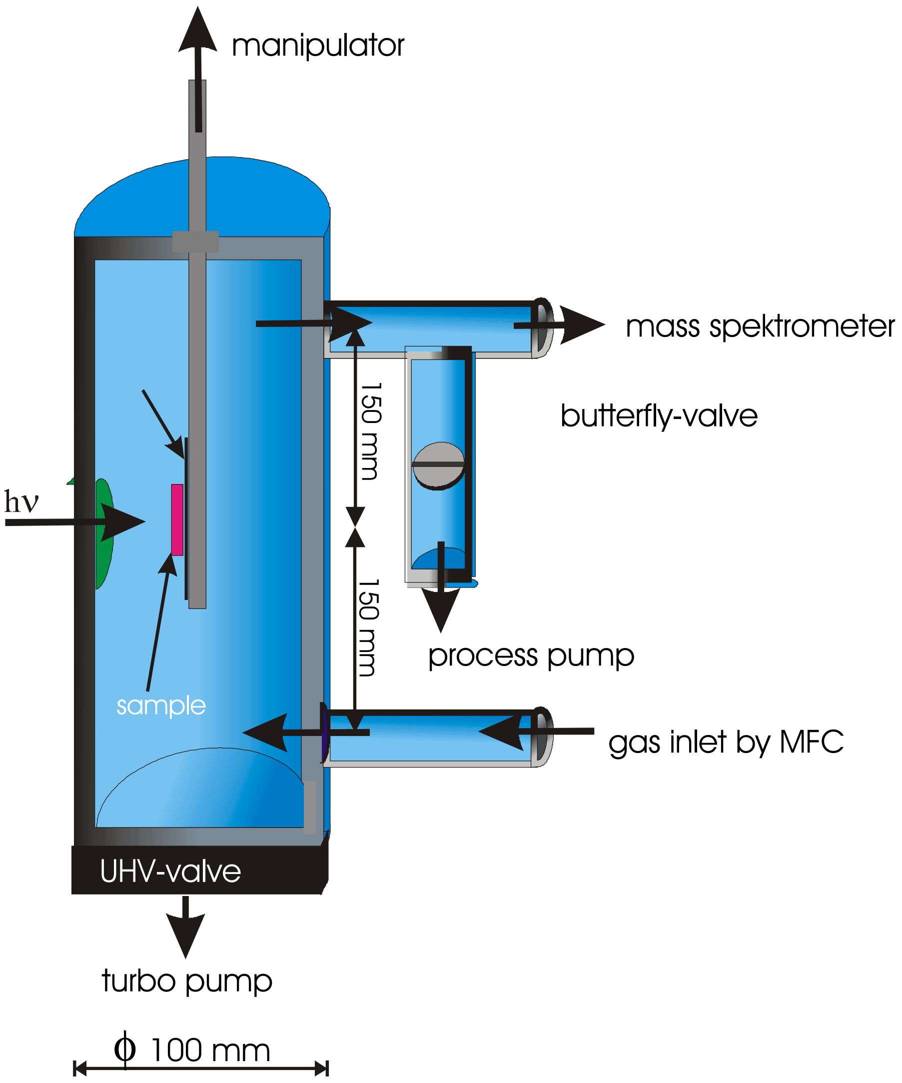
Prinzip der Röntgenabsorptionsspektroskopie (XAS)



- Anregung von Rumpfniveauelektronen mittels Röntgenstrahlung
- Relaxation mittels Fluoreszenzstrahlung oder durch Aussenden eines Auger-Elektrons (**TEY**, PEY, AEY)
- Untersuchung der unbesetzten Zustände

$$I \propto \left|\langle f|\vec{p}|i\rangle\right|^2$$

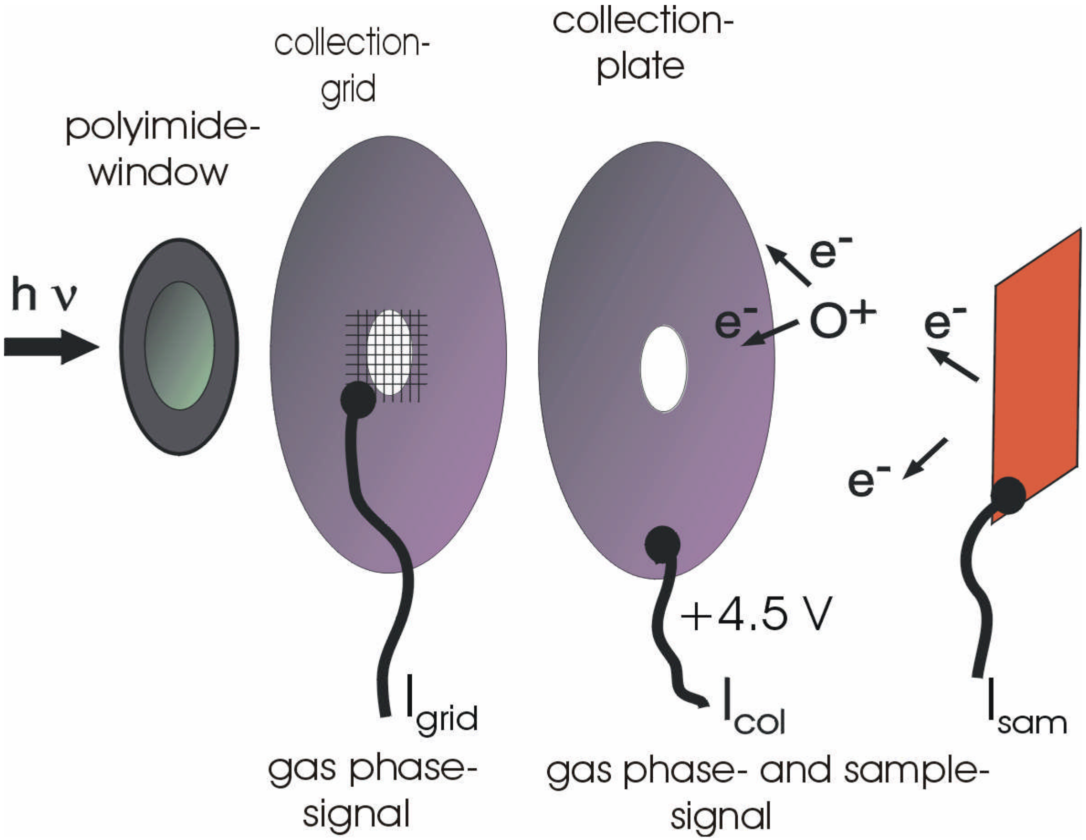
Experimental set up for in situ XAS investigations

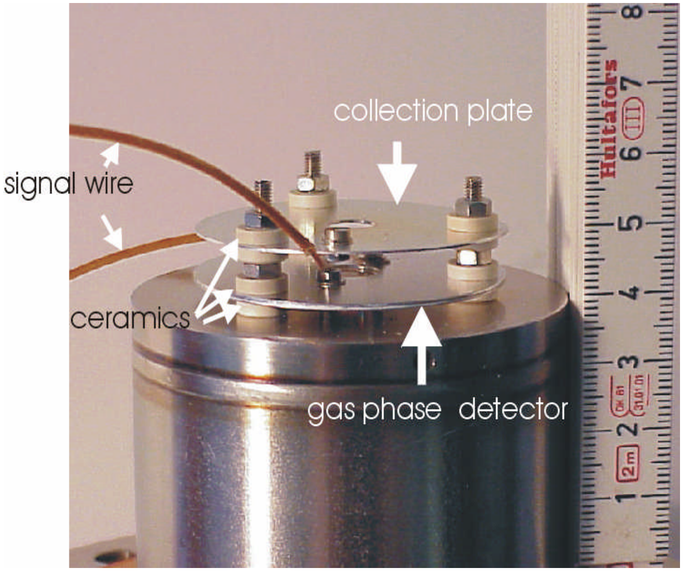


properties of the set-up

- heating up to 900 K
- pressure up to 20 mbar
- batch- and flow-through-mode
- angular dependent measurements

In situ XAS detector system

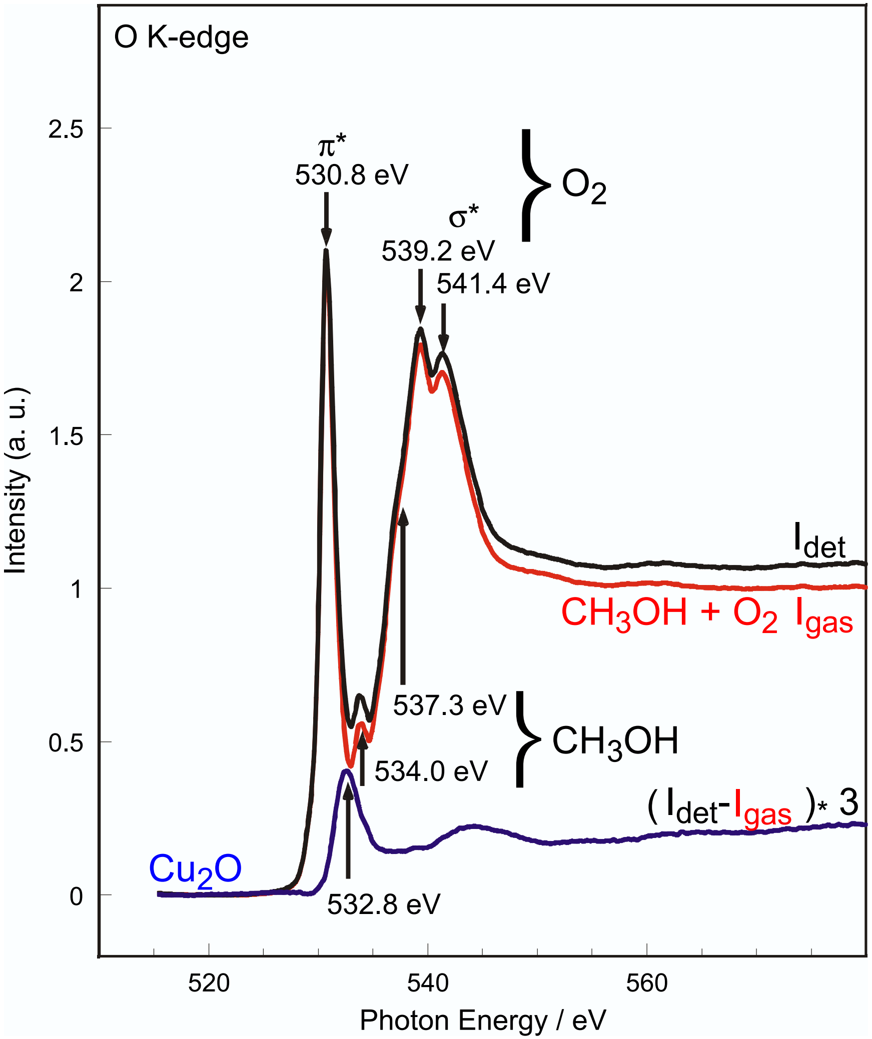




Simultaneous detection of gas phase- and sample signal

Gas phase substraction

Analysis of the **N**ear **E**dge **X**-ray **A**bsorption **F**ine **S**tructure (NEXAFS)



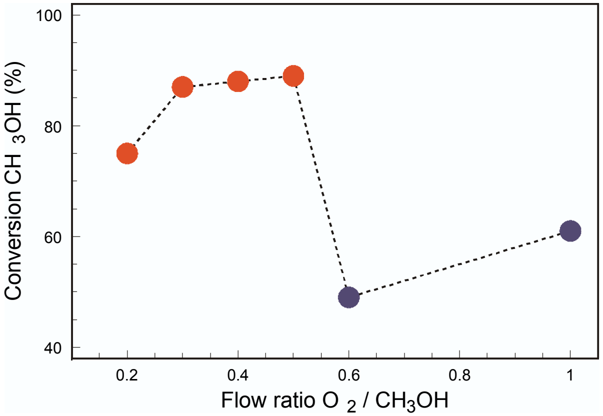
NEXAFS of the O K-edge

- Total electron yield of the gas phase dominates all signals, therefore only small differences in the detector signals

- Substraction allows to separate the absorption signal of the surface of the catalyst

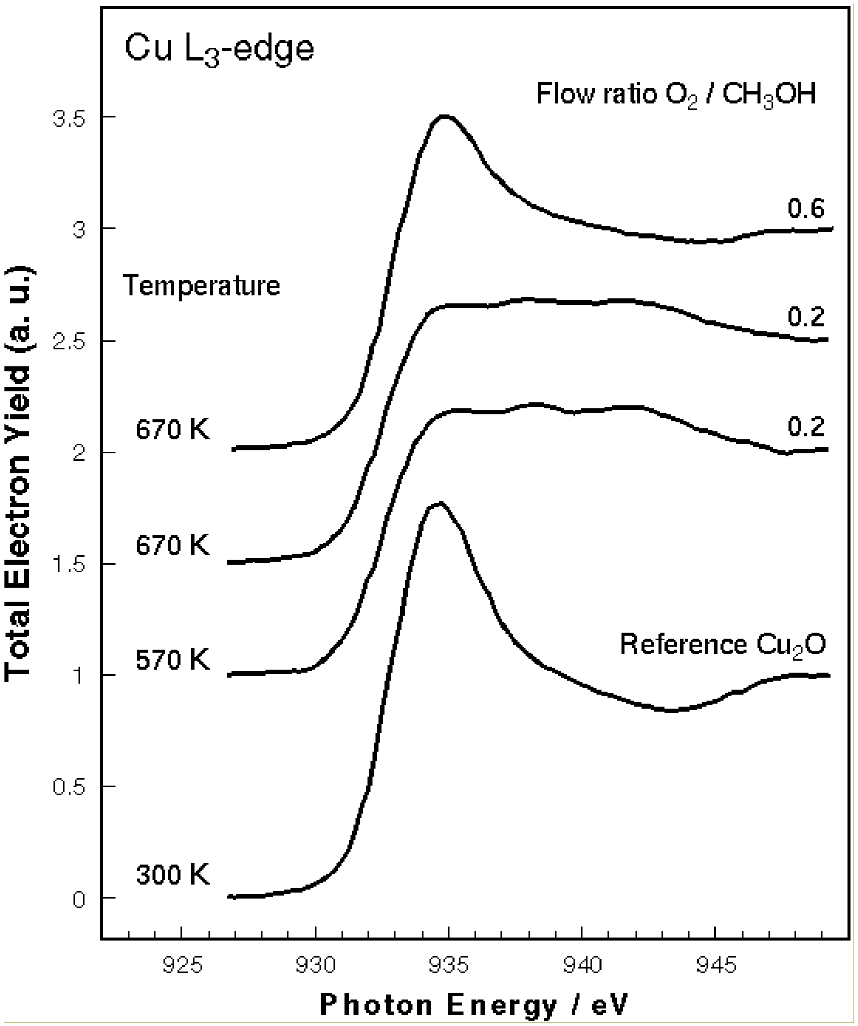
Cu L_3-NEXAFS

Catalytic Activity



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

NEXAFS at the Cu L_3-edge

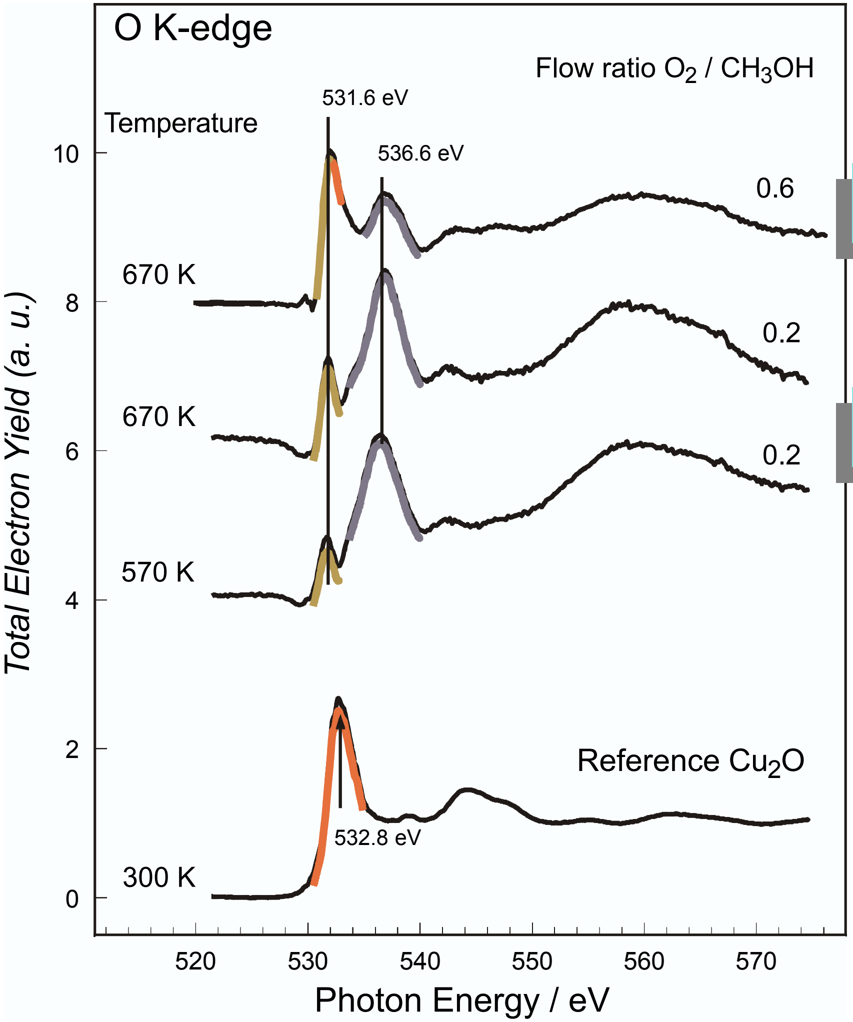


Transition from an oxidic copper-phase to the metallic state

NEXAFS at the O-K edge

- NEXAFS of the active state is complety different from the NEXAFS of the known copper-oxides

- 2 oxidic- and 1 suboxidic species can be distinguished

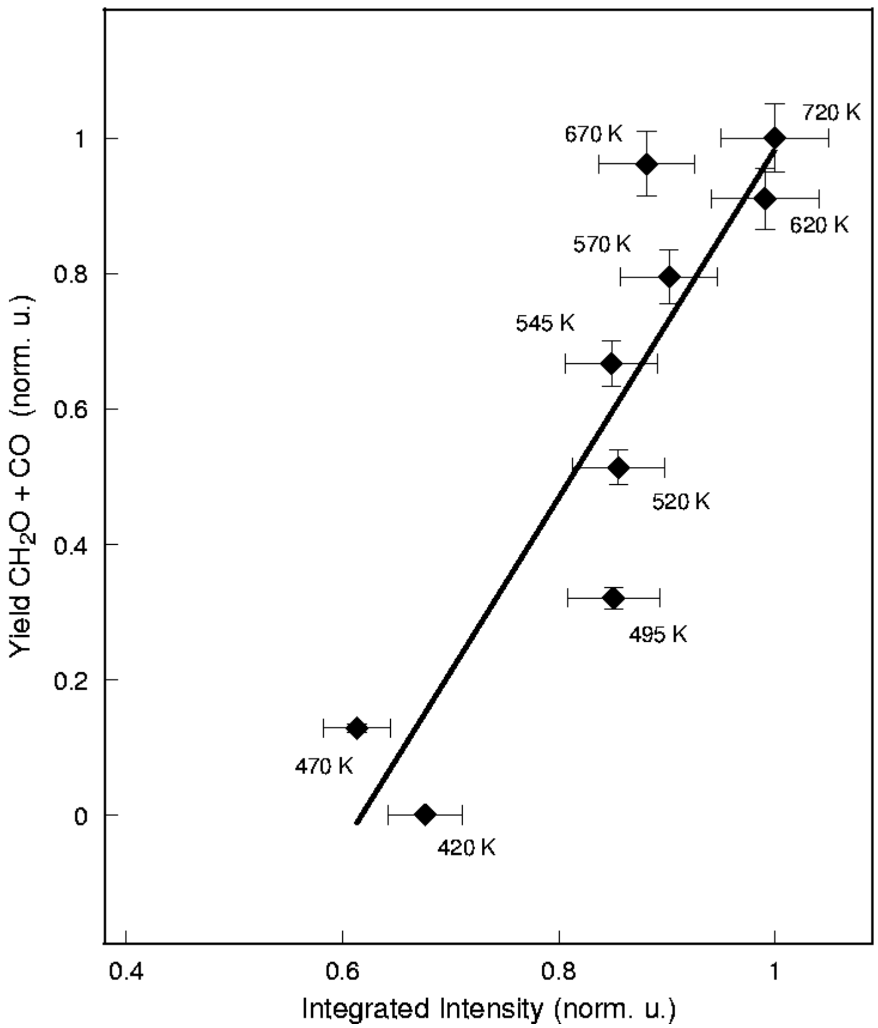


less active

very active

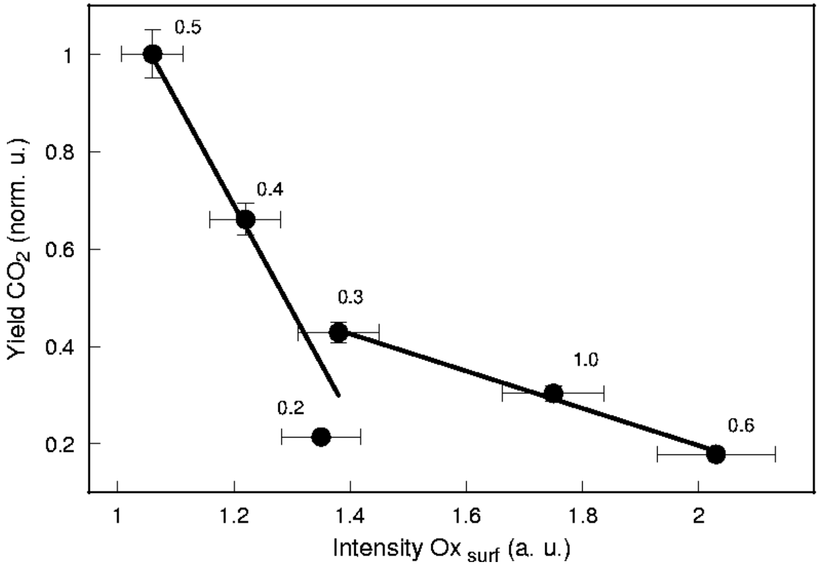
Correlation between the suboxide species and CH_2O yield

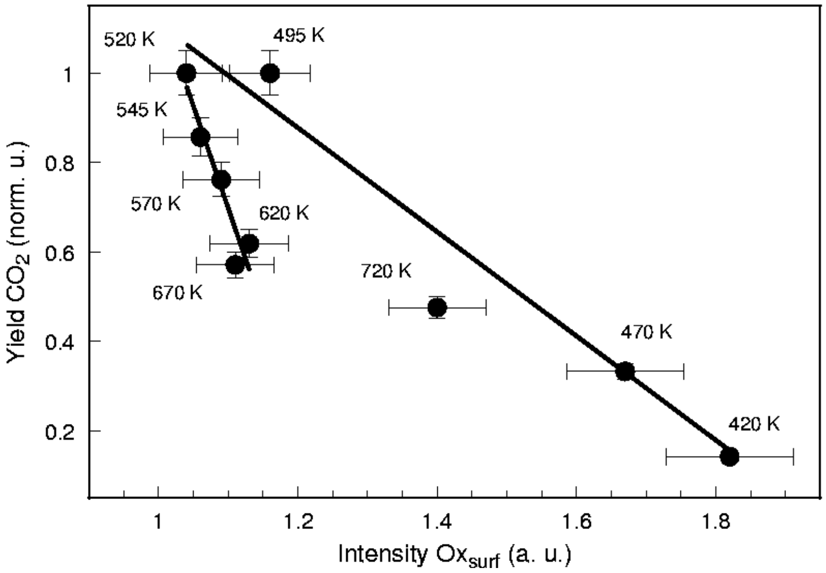
Variation of temperature at
O_2 / CH_3OH = 0.2



- Intensity of the suboxide species increases with increasing temperature
- Intensity of the suboxide species is positively correlated to the yield of CH_2O and CO

Correlation between oxidic species and CO_2

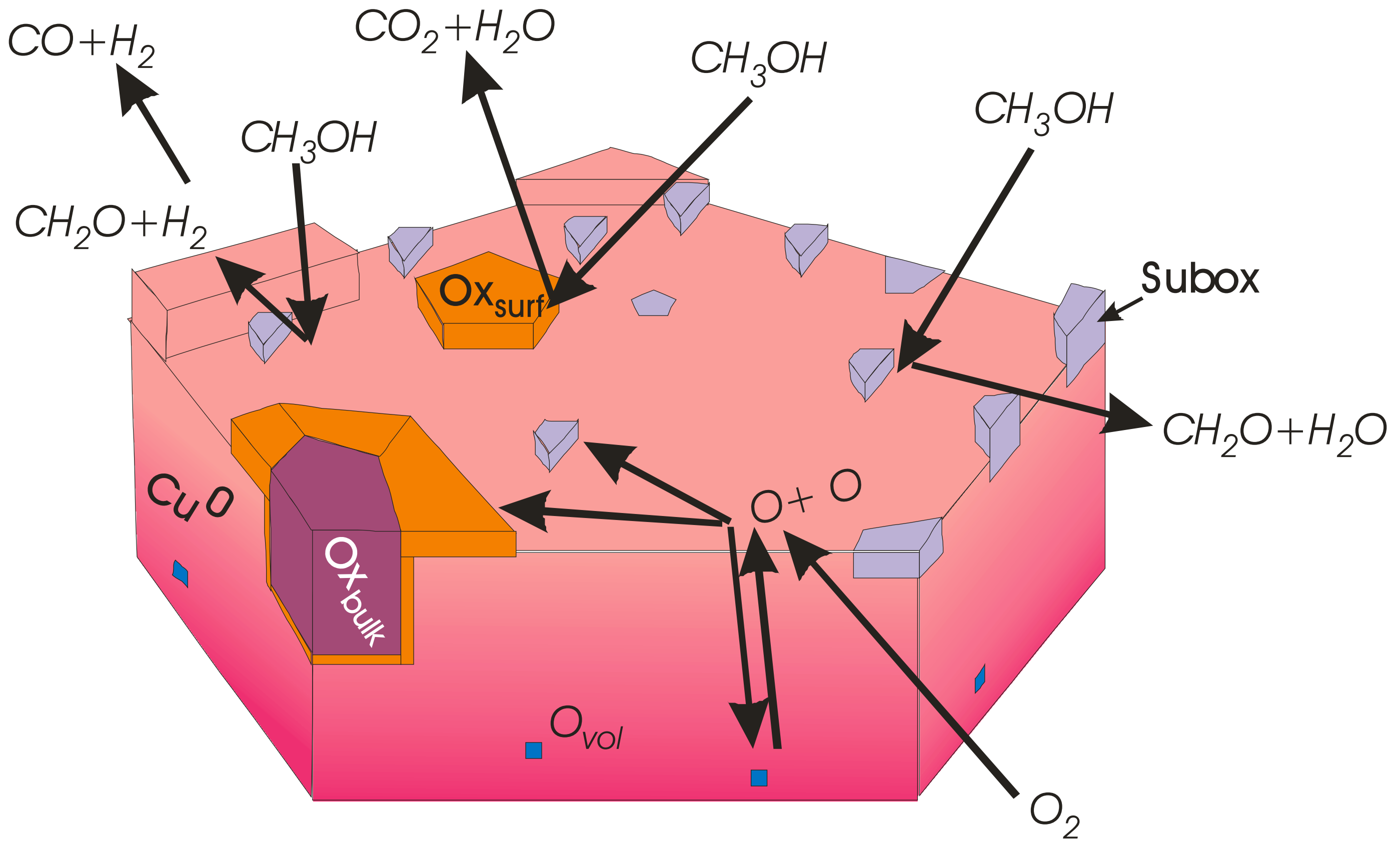




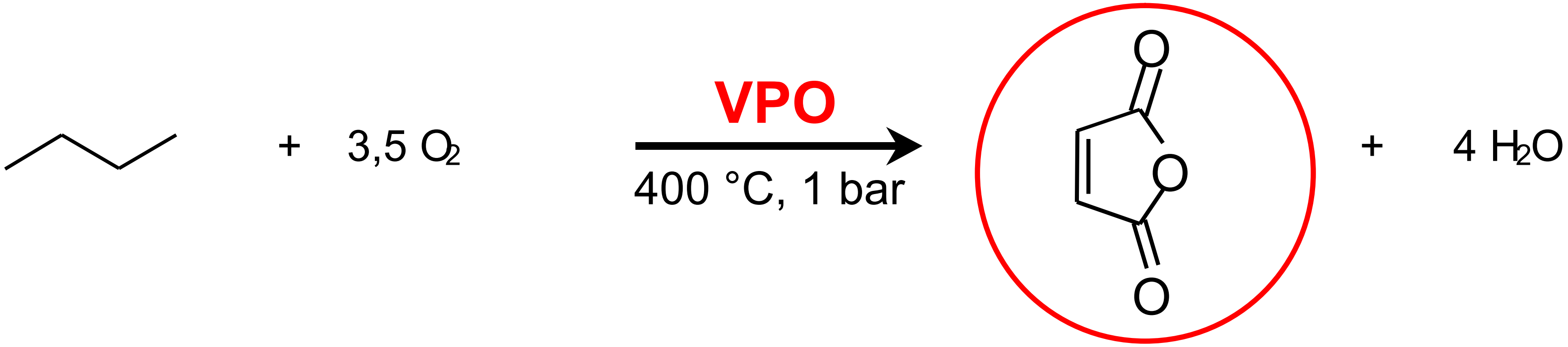
- Intensity of the oxidic species Ox_{surf} decreases with increasing CO_2-yield
- 2 areas of activity can be distinguished

Model

Proposed model of the copper surface under reaction conditions for methanol oxidation



n-Butane Oxidation to MA by Vanadium Phosphorus Catalysts



1,5 Vol% air Maleic Anhydride (MA)

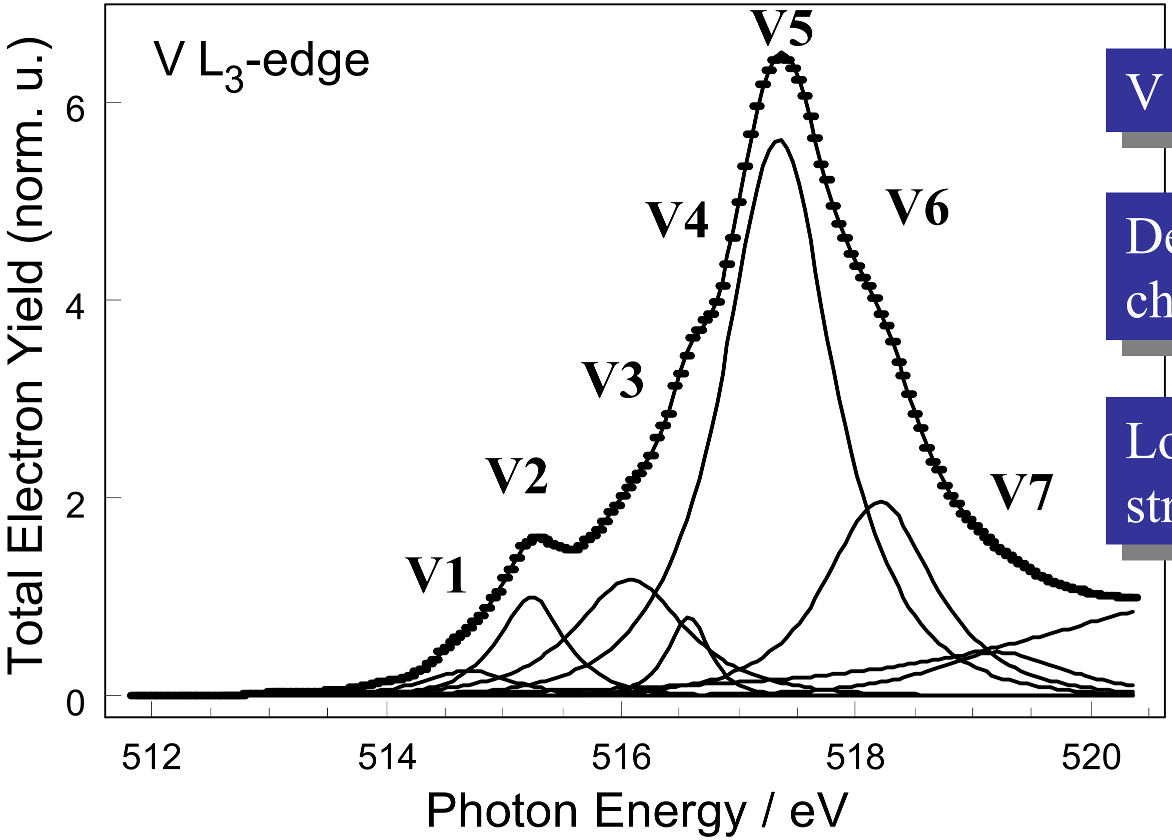
$$C_4H_{10} + 6{,}5\ O_2 \longrightarrow 4\ CO_2 + 5\ H_2O$$

$$C_4H_{10} + 4{,}5\ O_2 \longrightarrow 4\ CO + 5\ H_2O$$

Active phase: highly ordered vanadyl pyrophosphate $(VO)_2P_2O_7$?

The VPO V L_3-NEXAFS

Analysis of spectral shape by unconstrained least squares fit



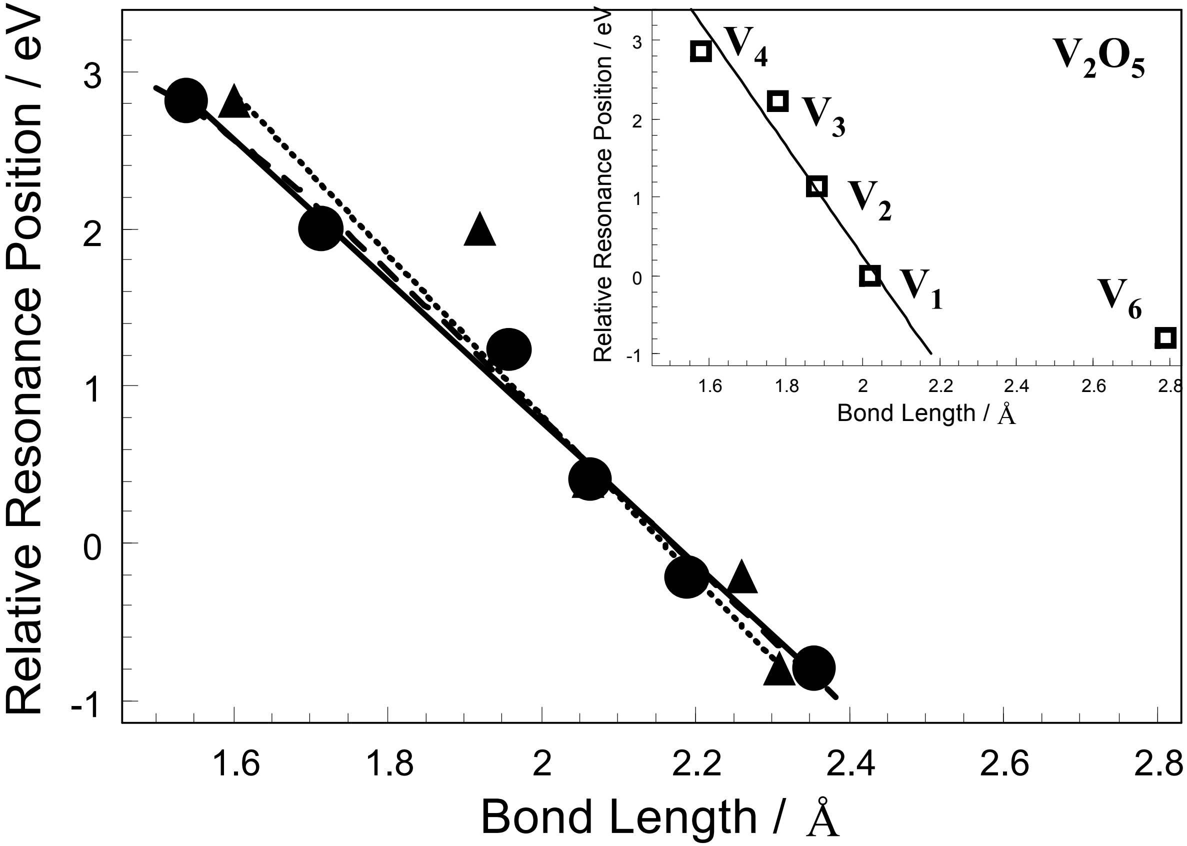
V valence

Details of the local chemical bonding

Local geometric structure

Interpretation of V L_3 NEXAFS

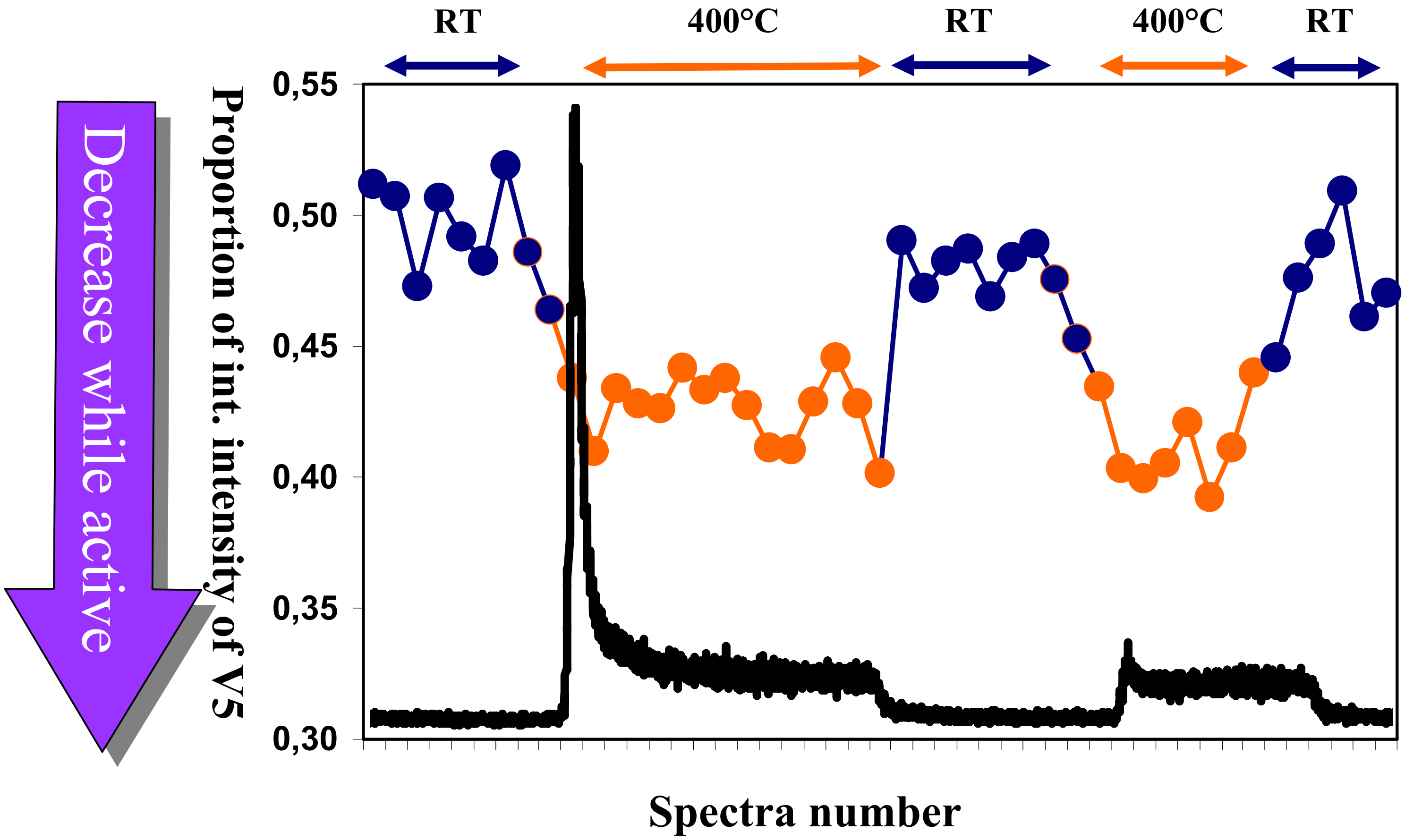
Experimental finding:

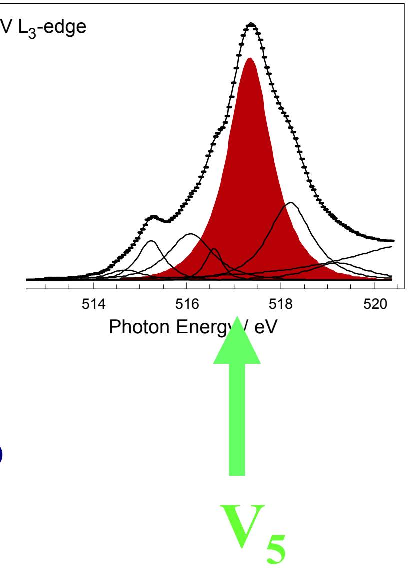


⇒ NEXAFS resonances appear in a sequence of V-O bond lengths

Changes of NEXAFS while heating

Relative spectral Intensity of V_5 at V L_3-edge

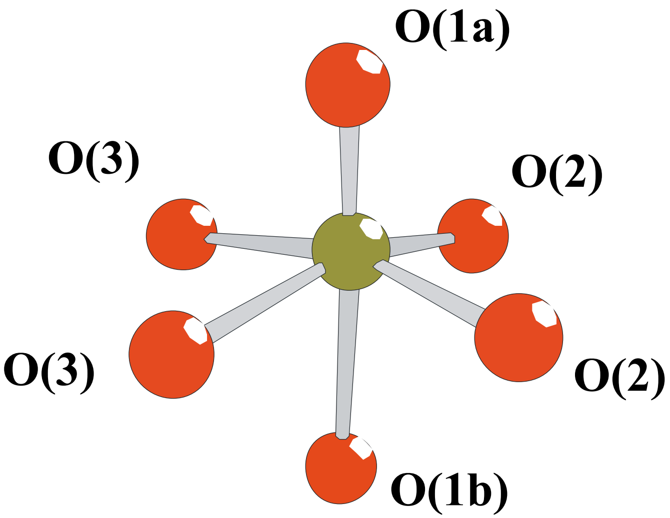




Interpretation of V L_3 NEXAFS

Identification of resonances (V5, V6):

V_2O_5 as model substance for VPO



DFT calculation of DOS (V_2O_5 !)*:

V_2O_5: Close relationship between geometric and electronic structure at V L_3-absorption edge

⇒ main contributions to NEXAFS resonances appear in a sequence of V-O bond length

⇒ V6: O(1a)
⇒ V5: ? (estimated value of bond length between O(2) and O(1a): 1.72 Å)

Summary

In situ XPS:

Estimation of stoichiometry, valence, depth profiles (using a tuneable photon scource), information depth can be reduced to 0.5 nm (depends on the kinetic energy)

In situ XAS

Information depth of about 50 nm in TEY, details of chemical bonding, local geometric structure, calculations or refrence samples are required

Methanol oxidation: a non oxidic subsurface oxygen species correlates with the yield of formaldehyde

Pentene hydrogenation: different carbon species were detected under reaction conditions, C-H correlates with activity

n-butane oxidation: indication that $(VO)_2P_2O_7$ is not the active phase