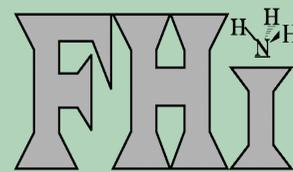


Comparison of in situ XAS and in situ PES in the soft X-ray range for the characterisation of heterogeneous catalytic processes



H. Bluhm¹, M. Hävecker¹, A. Knop-Gericke¹, R. Schlögl¹
F. Requejo², D. F. Ogletree², M. Salmeron²

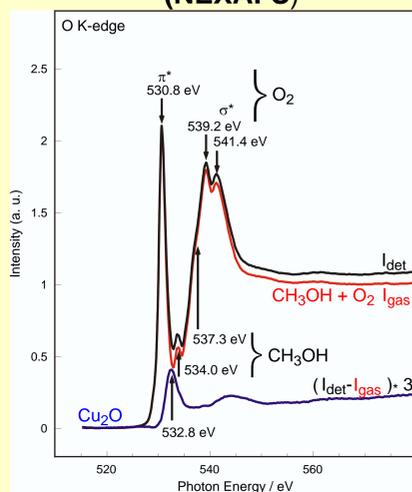
¹Fritz-Haber-Institut der MPG, Dept. Inorganic Chemistry, Faradayweg 4-6, 14195 Berlin, Germany
²Lawrence Berkeley Natl. Laboratory, University of California, Berkeley, California 94720 USA



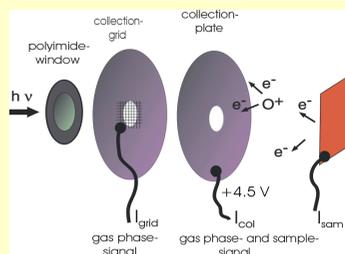
In situ NEXAFS of an active copper foil

The aim of the present project is to study the electronic structure of a catalyst under working conditions by using surface sensitive techniques to detect the really relevant electronic features. Therefore simultaneously to the catalyst surface NEXAFS and PES the conversion of the gas phase is determined by mass spectroscopy.

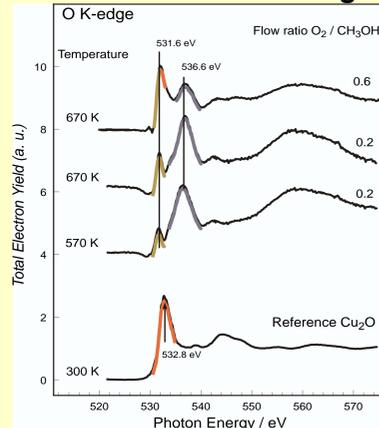
Analysis of the Near Edge X-ray Absorption Fine Structure (NEXAFS)



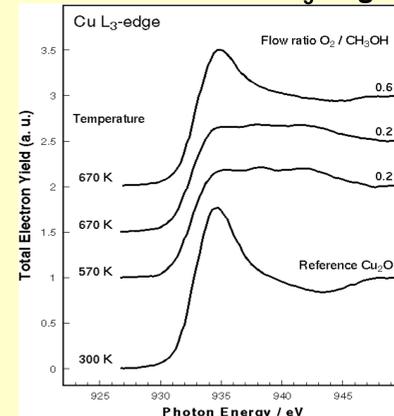
In situ XAS detector arrangement



NEXAFS at the O K-edge



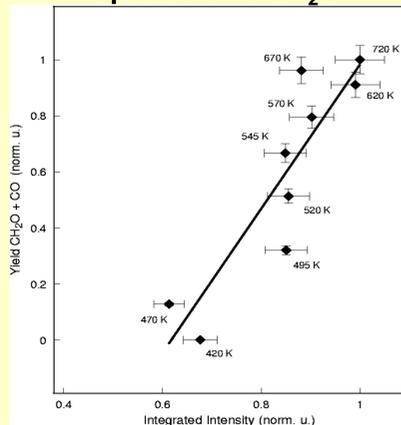
NEXAFS at the Cu L3-edge



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

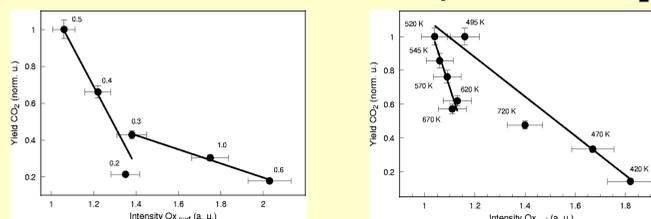
Transition from an oxidic copper-phase to the metallic state

Correlation between the Suboxide Species and CH₂O

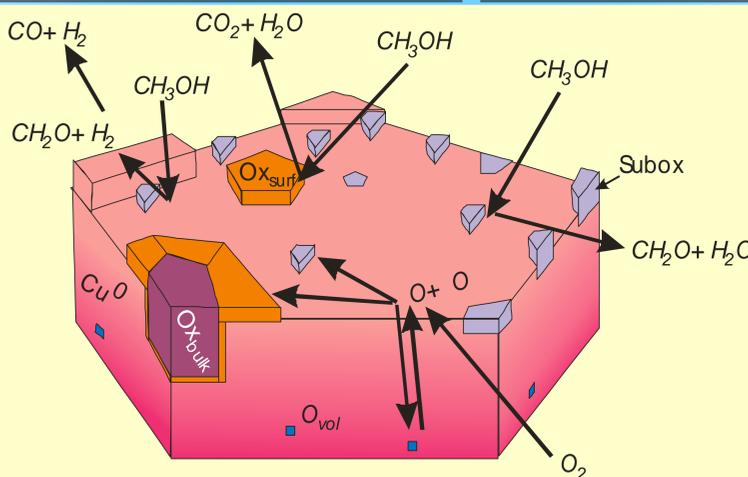


• Intensity of the suboxide species increases with increasing temperature
• Intensity of the suboxide species is positively correlated to the yield of CH₂O and CO

Correlations between oxidic species and CO₂



• Intensity of the oxidic species Ox_{surf} decreases with increasing CO₂-yield
• 2 areas of activity can be distinguished



Defect rich copper surface created by incorporation of oxygen from the gas phase
Stress and strain have influence on electronic states and catalytic activity [1]

Suboxide is marker for defects which are active sites for partial oxidation of methanol (role of suboxide in the reaction: spectator/participant ?)

Ox_{surf} is an oxide-like species on the disturbed surface (like thin surface oxide [2])
Ox_{surf} catalyses the total oxidation path of methanol

Coverage of the surface with oxide types inhibits the catalytic activity [3]
3D-growth of surface oxide creates bulk oxide Ox_{bulk}[4]

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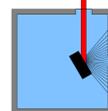
Acknowledgement

The staff of BESSY II and the staff of the ALS are gratefully acknowledged for their support in beamline operation.

In situ PES of an active copper foil

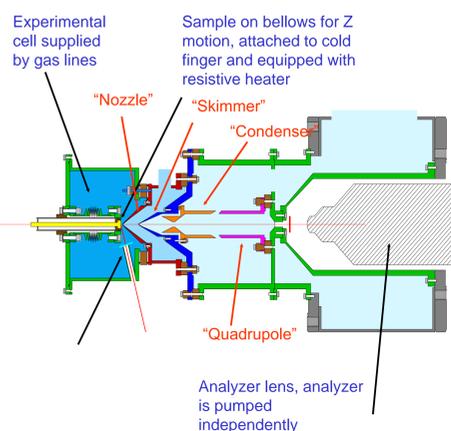
Set up of the in situ PES reaction-cell

Basic Concept



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

- Fundamental limit
 - Elastic and Inelastic scattering of electrons by gas molecules
- Technical Issues
 - Electron optics to transport electrons to an energy analyzer
 - Differential pumping to keep analyzer in high vacuum
 - Sample preparation and control in a flow reactor



In situ PES in a mixture of CH₃OH and O₂ @ 0.5 mbar

