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High-Pressure Low-Energy X-Ray Absorption Spectroscopy:

A Tool to investigate heterogeneous catalytic Processes under Reaction Conditions

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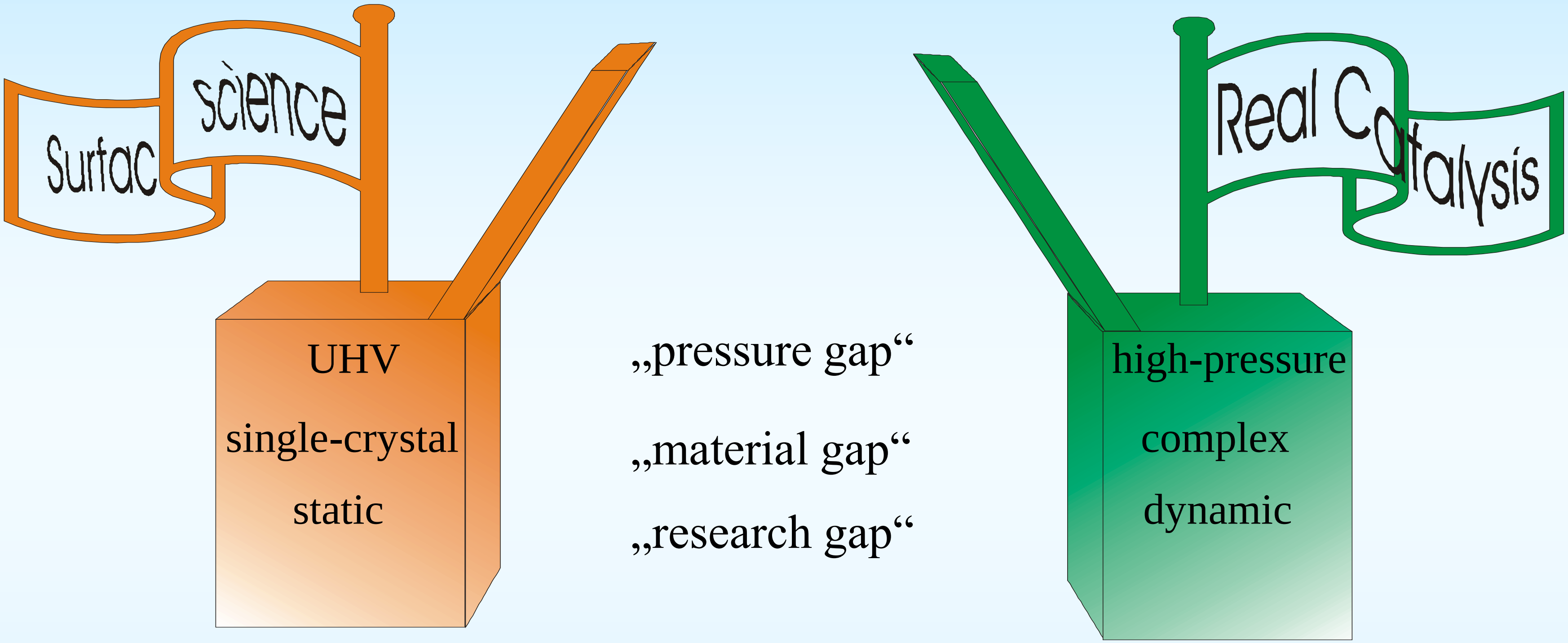
Target of the Project



Investigation of the electronic structure of a catalyst under working conditions using a surface-sensitive method

In situ X-ray absorption spectroscopy (XAS) in the soft X-ray range (E_{ph} = 200 eV - 1000 eV)

Demands

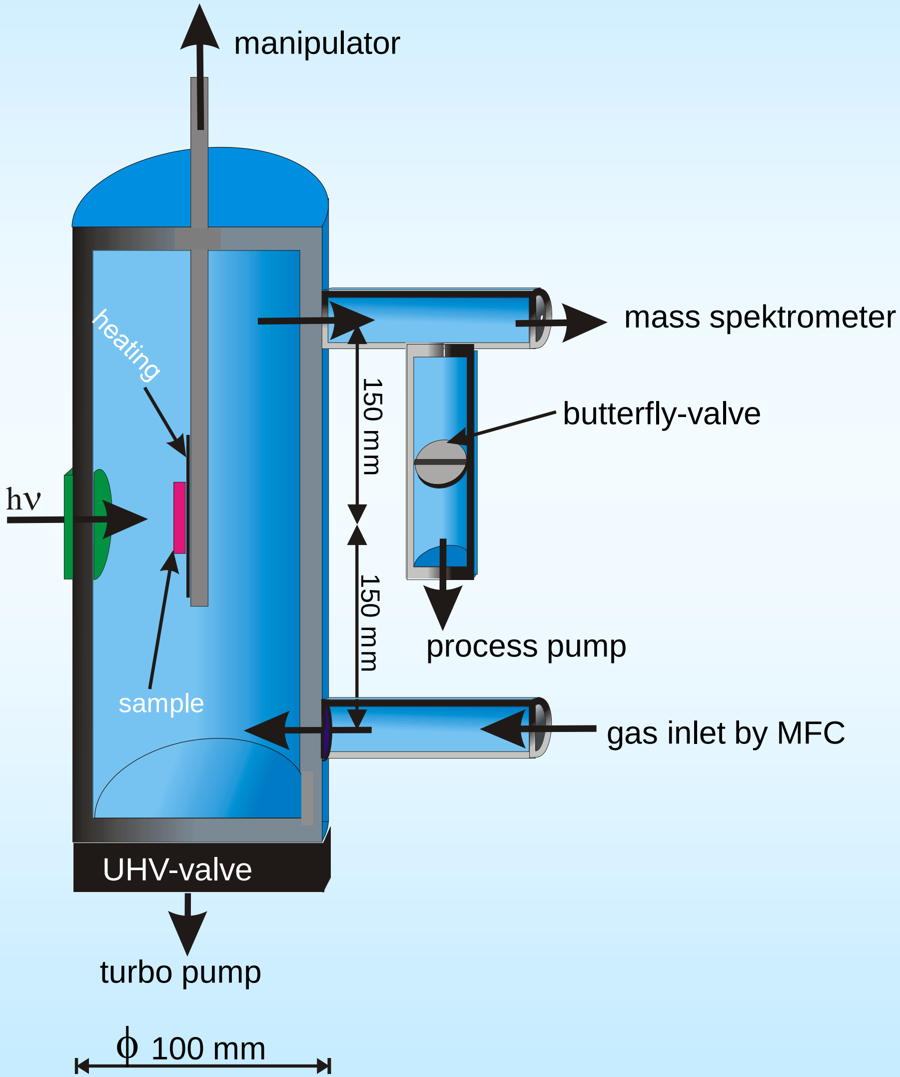
Simultaneous detection of Near Edge X-ray Absorption Fine Structure (NEXAFS) of the surface of the catalyst (C,N,O K-edge and L-edges of transition metals) and of the conversion of the gas phase

spectroscopic demands ⟷ kinetic demands

"robust" chemical reaction

$2\ CH_3OH + O_2$	→	$2\ CH_2O + 2\ H_2O$	oxidative dehydrogenation
CH_3OH	→	$CH_2O + H_2$	dehydrogenation
$2\ CH_3OH + 3\ O_2$	→	$2\ CO_2 + 4\ H_2O$	total oxidation

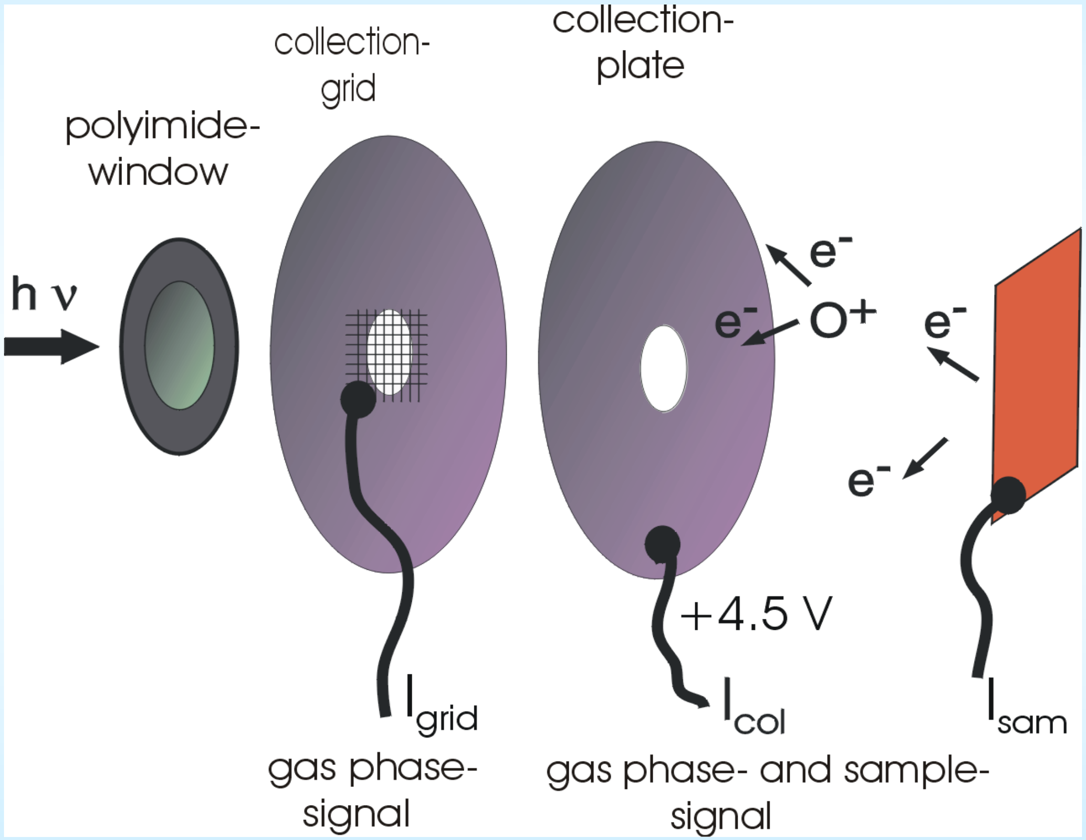
Experimental Set-Up

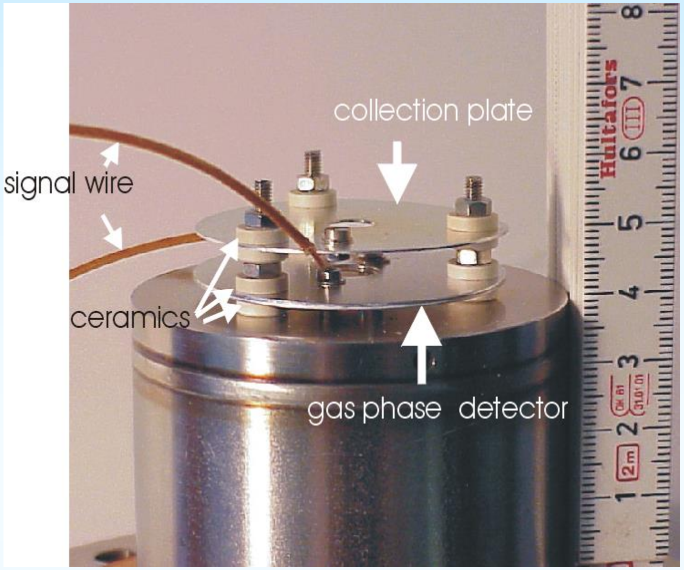


properties of the set-up

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

Arrangement of the Detector-System





Simultaneous detection of gas phase- and sample signal

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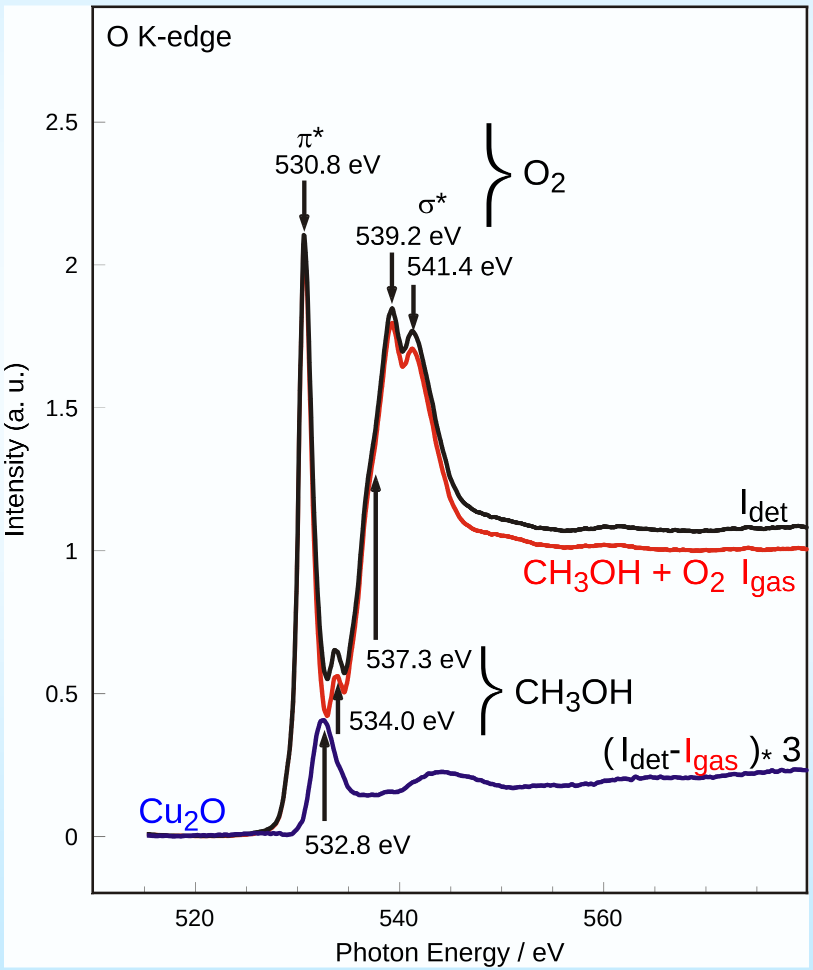
Treatment of the Detector Signals

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

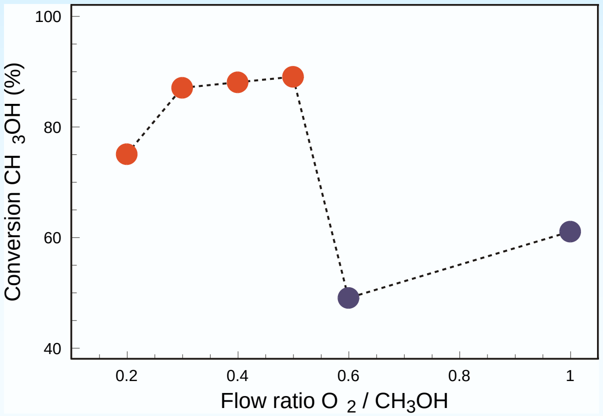


NEXAFS of the O K-edge

- 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

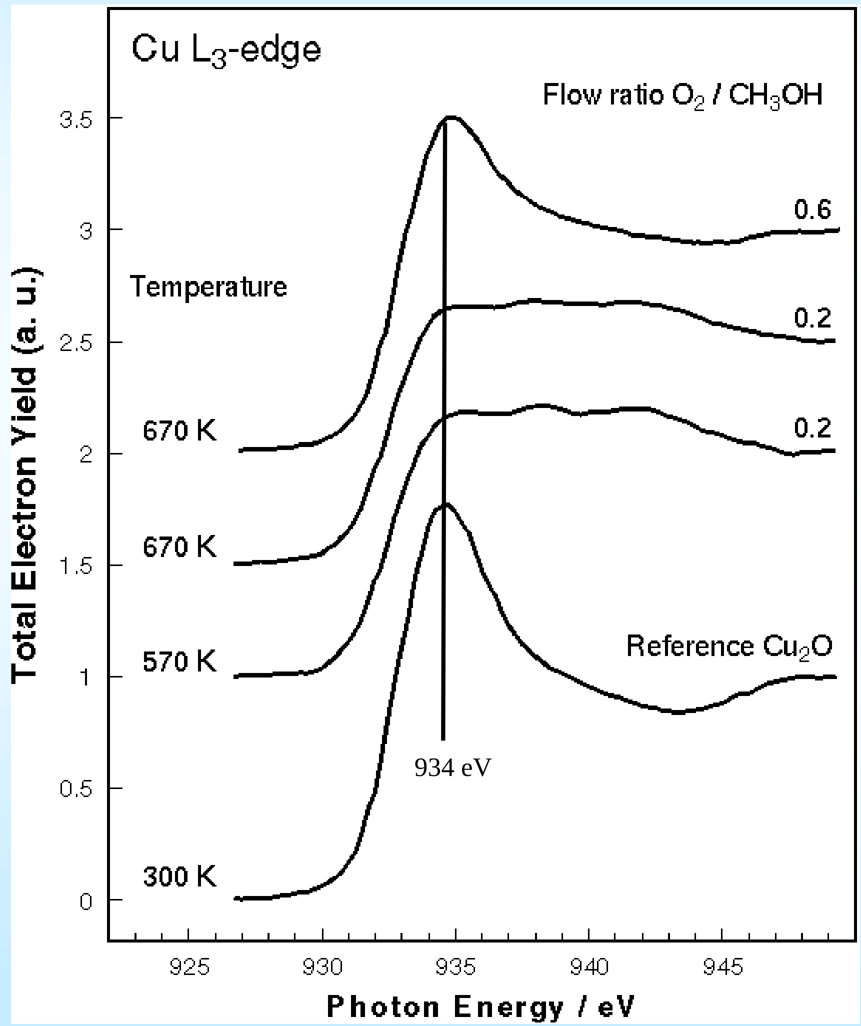
Results

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

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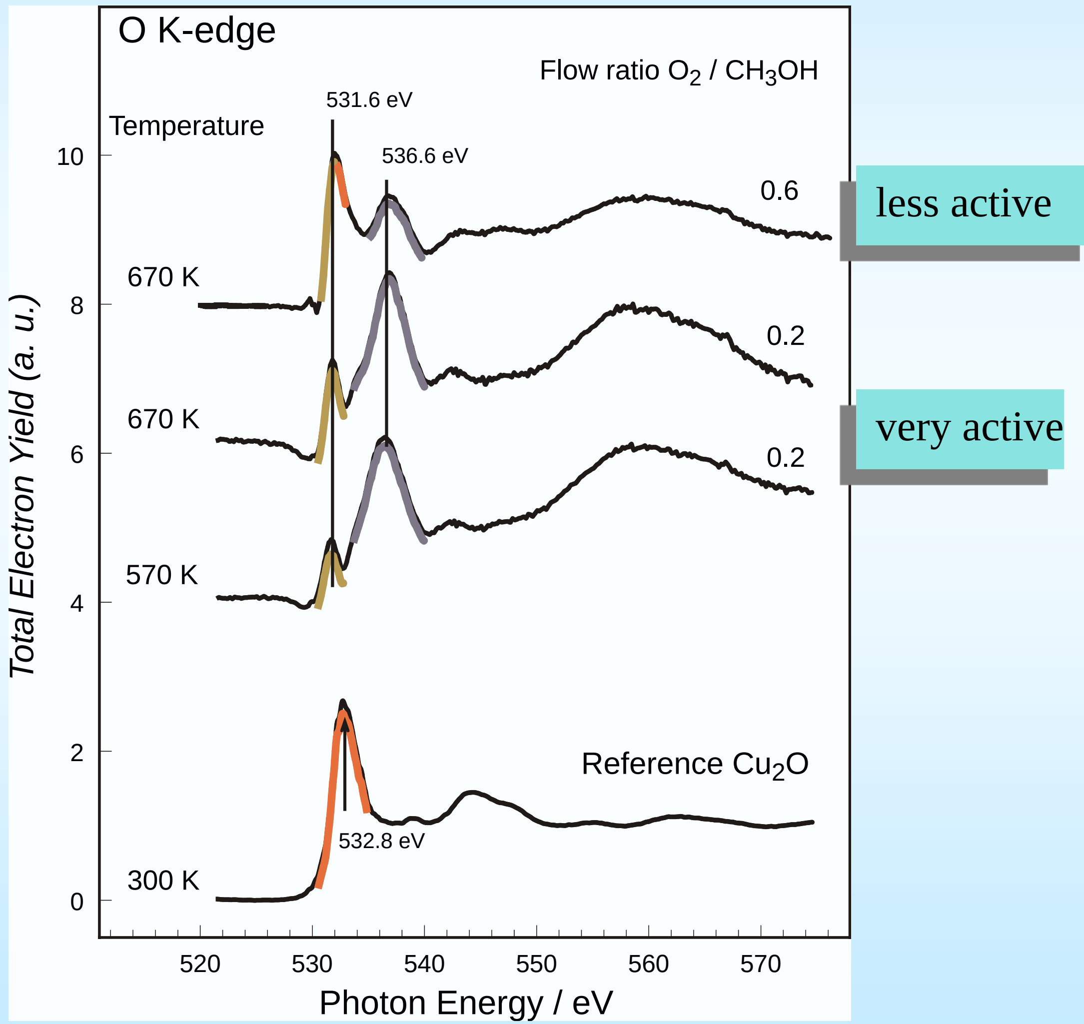
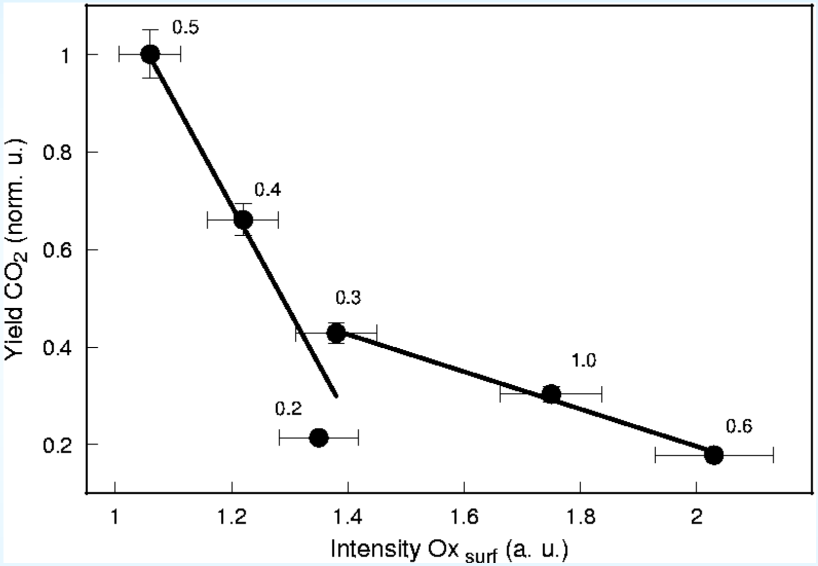
Results

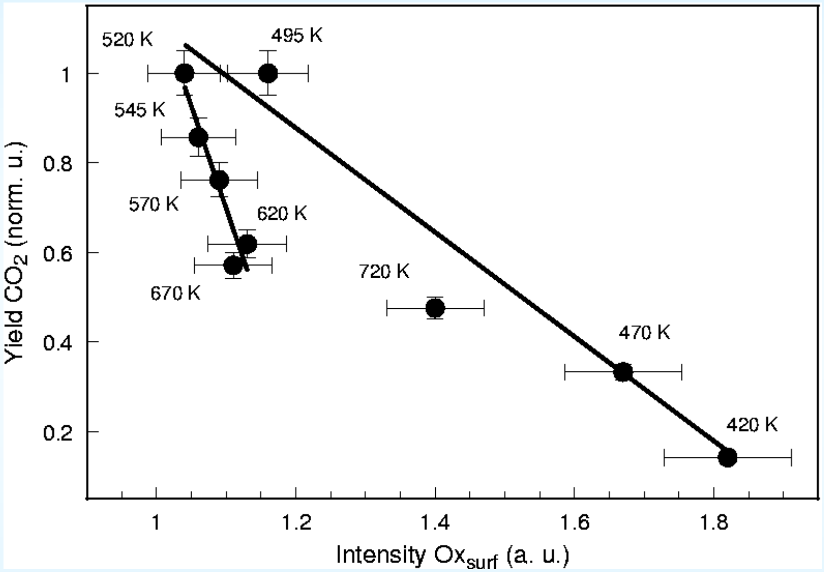
NEXAFS at the O K-edge

- 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



Correlations between oxidic species and CO_2

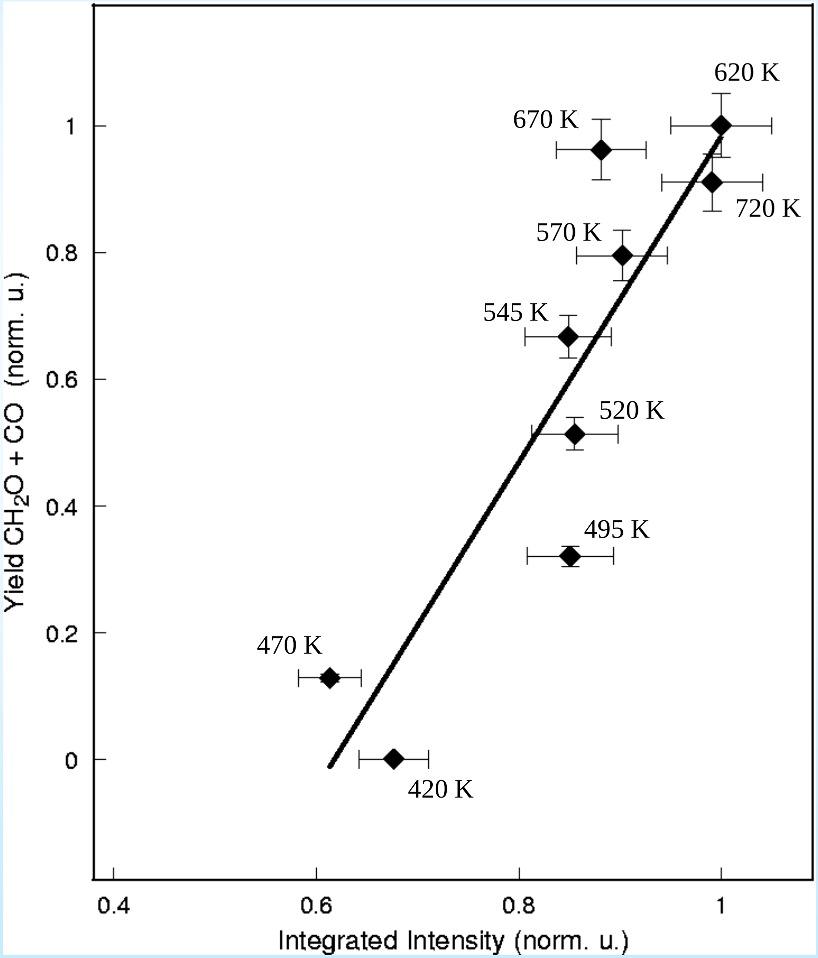




- Intensity of the oxidic species Ox_{surf} decreases with increasing CO_2-yield
- 2 areas of activity can be distinguished

Correlation between the Suboxide Species and CH_2O

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

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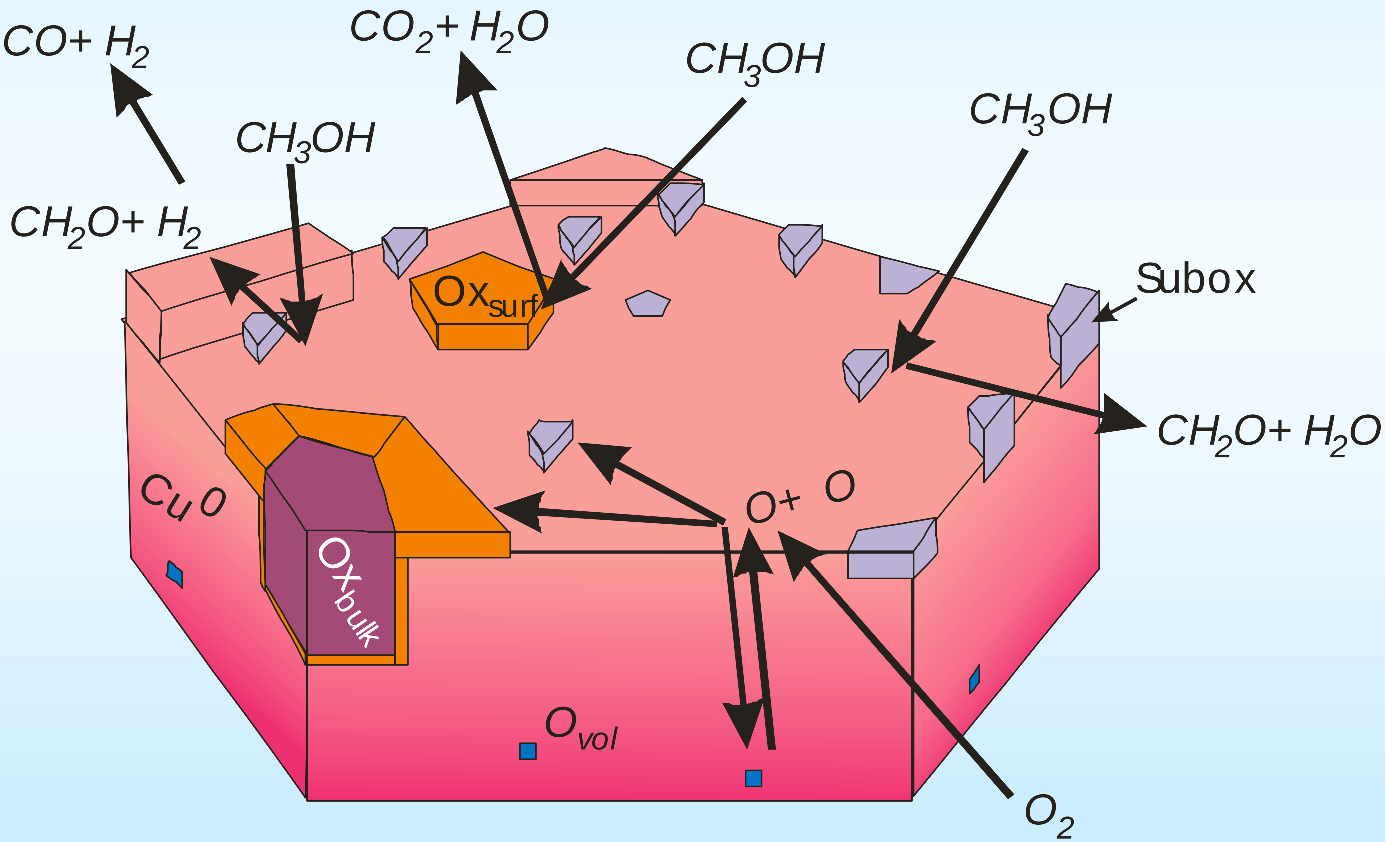
Model

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



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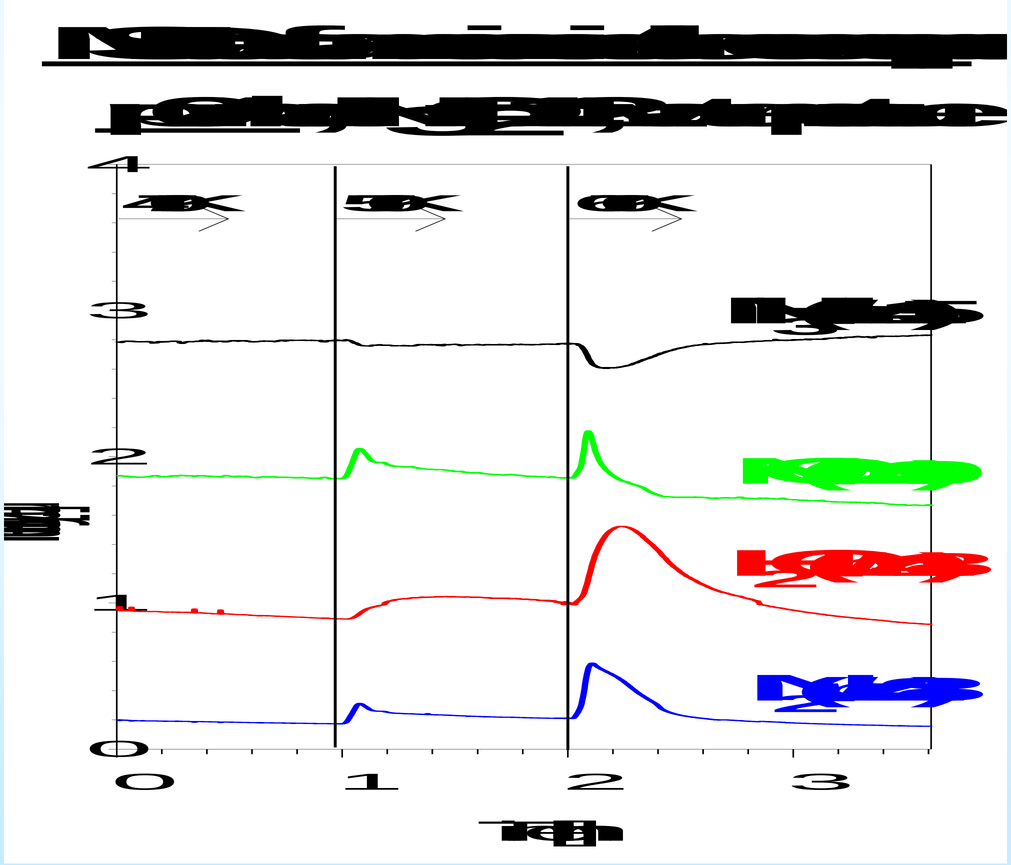
Ammonia Oxidation over Copper
Temperature Dependence @ 0.4 mbar

$4\ NH_3 + 3O_2 \rightarrow 2N_2 + 2\ H_2O$ (partial oxidation)

$4\ NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$ (total oxidation)

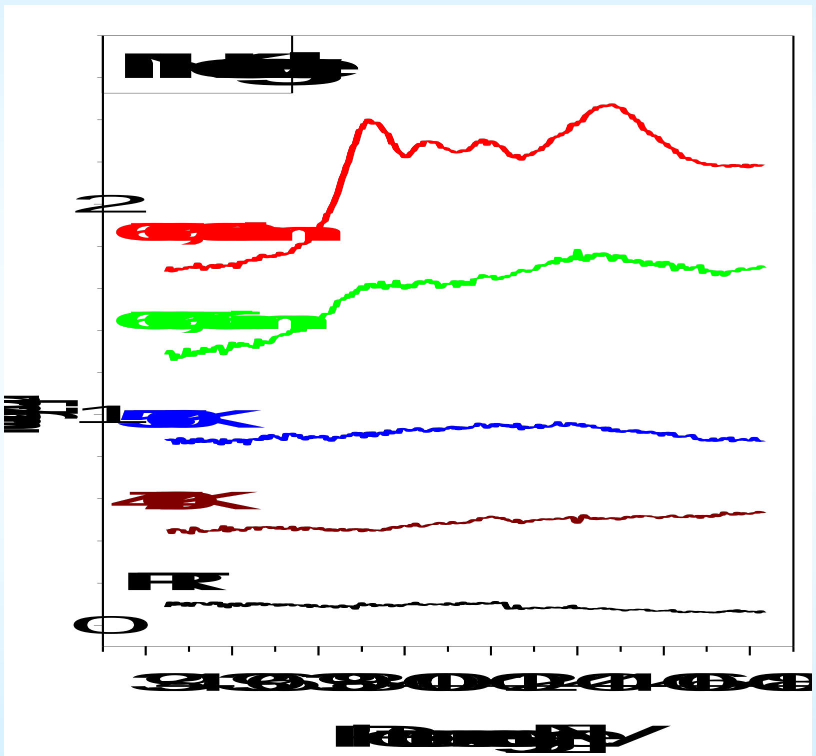
- no / low activity below 570K
- initial higher activity with increasing temperature
- but: deactivation of the catalyst

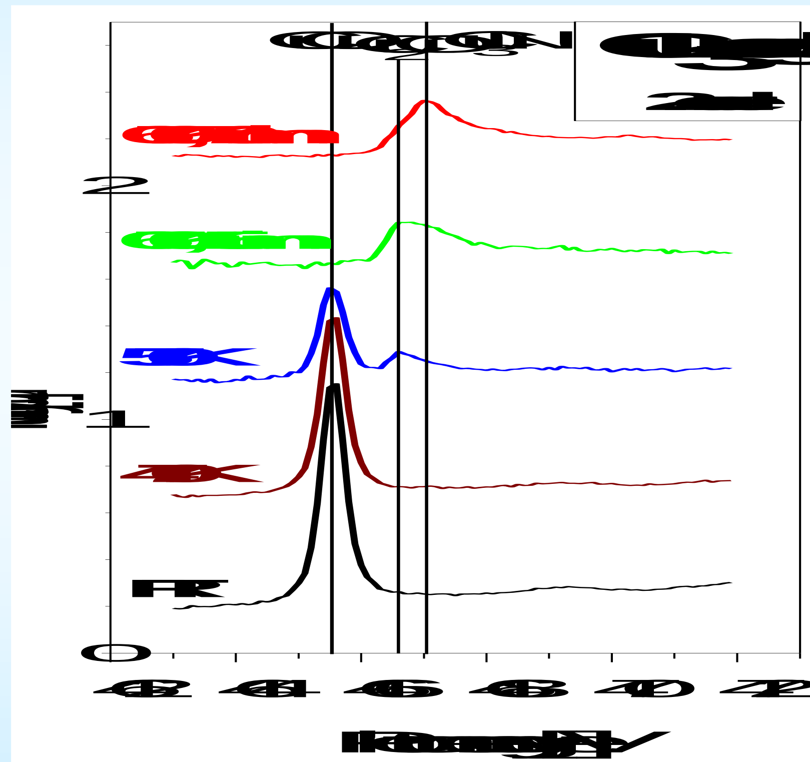


Deactivation

NEXAFS-spectra

@ p=0.4mbar, NH_3:O_2=1:12, var. temperature

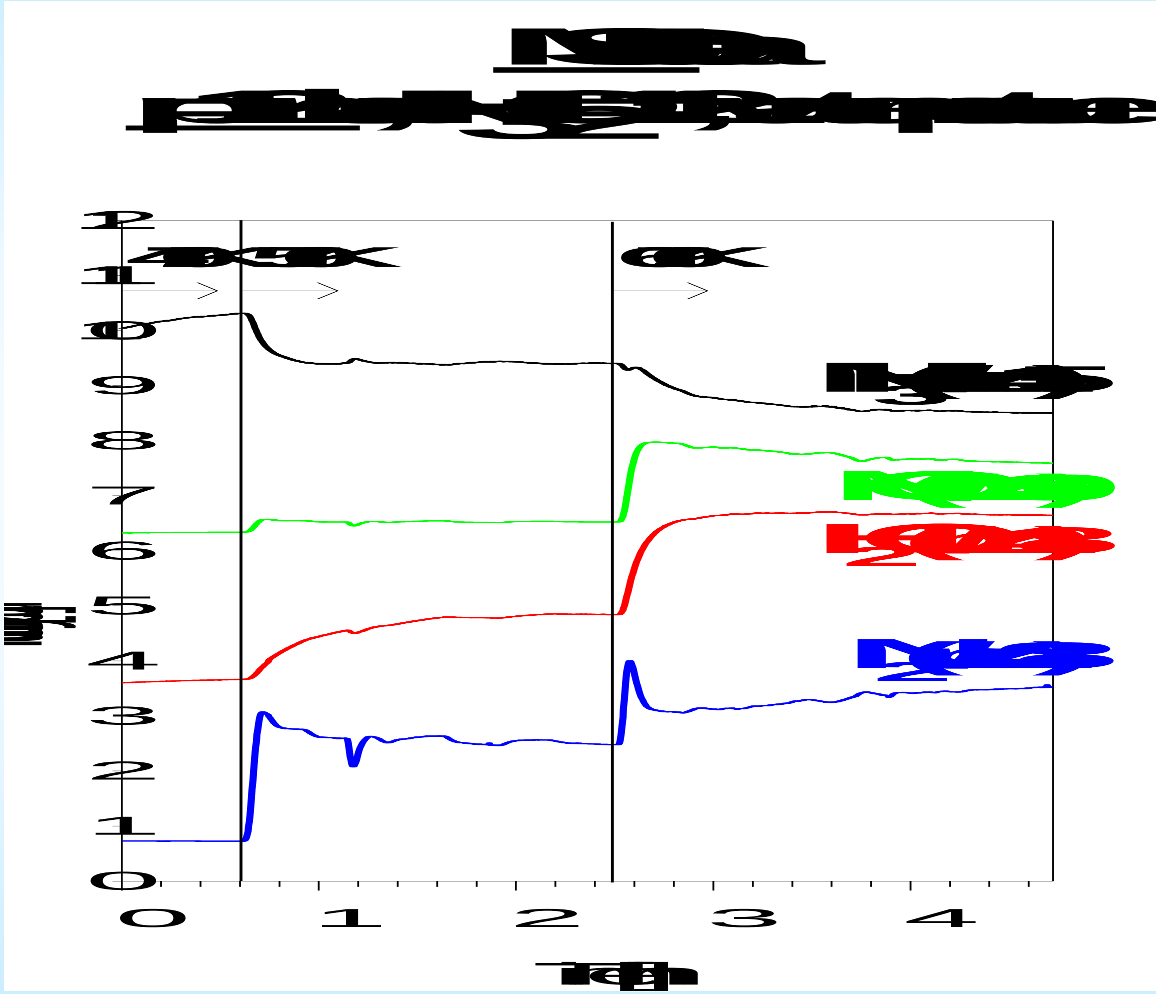




- **Deactivation due to formation of some N-species on the surface**
- **Cp. with reference spectra shows: Formation of Cu_3N**

Temperature dependence @ p=1.2mbar

- also no / low activity below 570K
- at T≥570K significant higher activity than at p=0.4mbar
- **<u>no deactivation of the catalyst detectable</u>**



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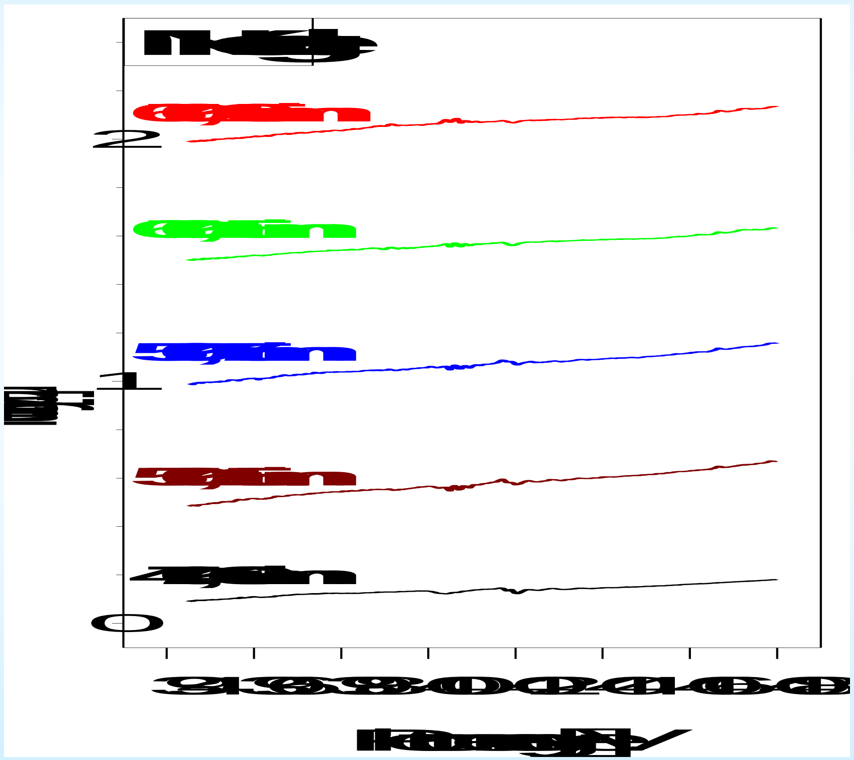
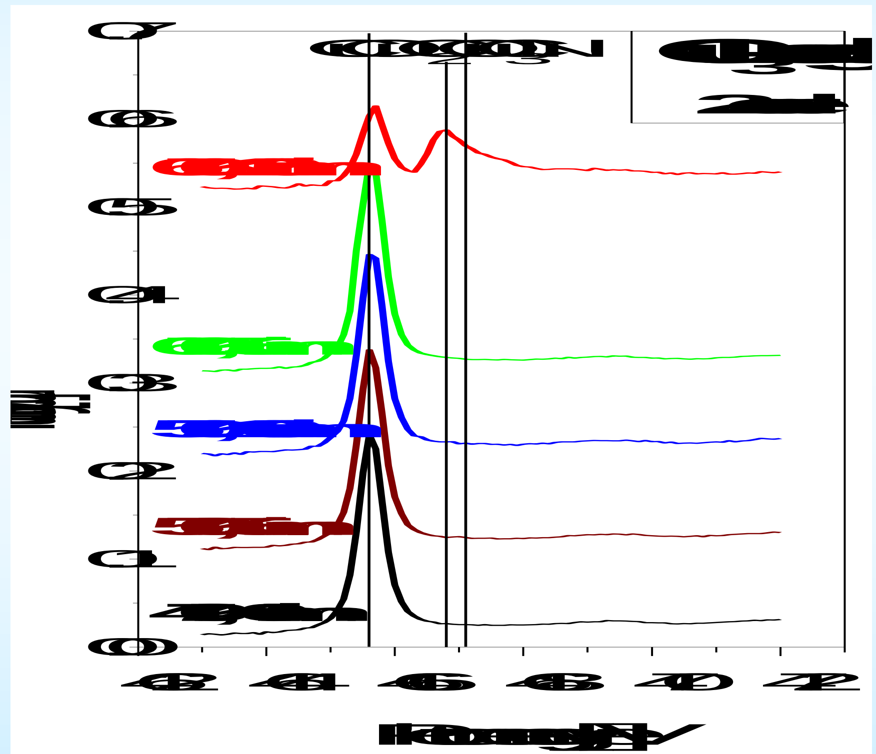
Deactivation at p=1.2 mbar ?

NEXAFS-spectra

@ <u>p=1.2mbar</u>, NH_3:O_2=1:12, var. temperature





- **No deactivation**
- **No formation of Cu_3N or other nitrogen species**

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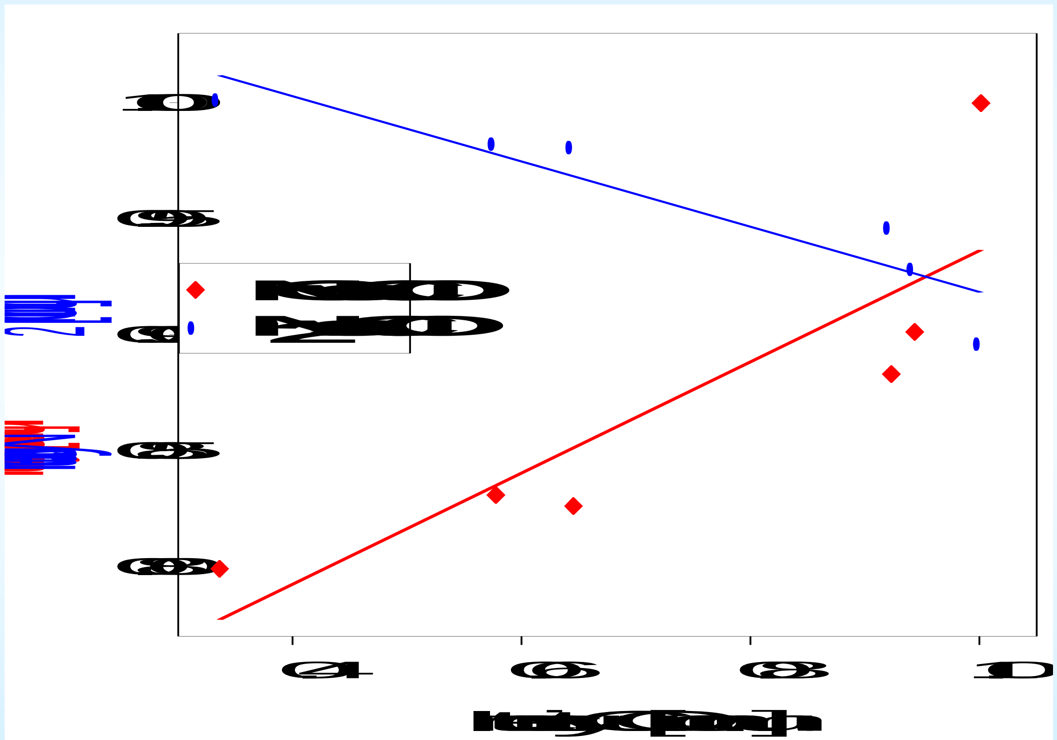
Correlation of NO and N_2 with CuO

- @ <u>1.2mbar</u>, 670K und $NH_3:O_2=1:12$



- trend visible: higher NO concentration in product gas with increasing CuO content; oppositional for N_2

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Summary

➢ <u>methanol oxidation over copper</u>

- ⦿ partial oxidation of methanol to formaldehyde is correlated to a suboxide
- ⦿ suboxide is detectable only under reaction conditions
- ⦿ total oxidation is catalysed by oxidic species

➢ ammonia oxidation over copper

- ⦿ deactivation of the catalyst for $p \leq 0.4$ mbar by the formation of Cu_3N
- ⦿ no deactivation for $p \geq 1.2$ mbar
- ⦿ correlation of NO and N_2 production with copper oxides