Methanol oxidation on Ru catalysts: Reaction pathways and catalytically active sites

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Russian-German Seminar on Catalysis, Altai Mountains (Siberia), 10/07/2007

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Scientific setting

CH_3OH oxidation: observation of CH_2O production at rather low temperatures (300-400K) on supported RuO_2 [1]

But

temperature programmed desorption shows only partially reduced (Ar^+-ion sputtered) RuO_2 active [2]

CO oxidation: transient surface oxide (TSO) active [3]

TSO characterised by [4,5]:

variable stoichiometry RuO_x ($1<x<2$)

1-4 monolayers of oxygen incorporated within the top few Ru layers

1 H.Liu, E. Iglesias, J. Phys. Chem. B, 2005, 109, 2155
2 H. Madhavaram et al. J. Catal., 2001, 202, 296
3 R. Blume et al. J. Catal., 2006, 239, 354
4 A. Böttcher et al. J. Chem. Phys., 2002, 117, 8104
5 R. Blume et al. J. Phys. Chem. B, 2005, 109, 14052

Experimental

Methanol oxidation on:

Ru(0001) Ru($10\bar{1}0$) Ru(poly) metal or pre-oxidised

CH_3OH/O_2: 0, …., 1, p=0.5mbar, T<=650K

High pressure XPS: in the presence of reactive gas atmosphere

Synchrotron based XPS:
X-ray source: BESSY storage ring, hv=450eV (Ru3d), 650eV (O1s)

Surface sensitive: probing of topmost surface layers
(IMFP: 5Å equal. 1/3 of Mg K-alpha)

Chemical complexity: Reaction Pathways

$CH_3OH \longrightarrow CH_2O + H_2$

$CH_3OH \longrightarrow CO + H_2$

$CH_3OH \longrightarrow C + H_2O + H_2$

$CH_3OH + 1/2\ O_2 \longrightarrow CO + H_2O + H_2$

$CH_3OH + 1/2\ O_2 \longrightarrow CH_2O + H_2O$

$2\ CH_3OH + 1/2\ O_2 \longrightarrow 2\ CH_2O + H_2O + H_2$

$CH_3OH + O_2 \longrightarrow CO + 2\ H_2O$

$CH_3OH + 3/2\ O_2 \longrightarrow CO_2 + 2\ H_2O$

$CH_2O \longrightarrow CO + H_2$

$CO + 1/2\ O_2 \longrightarrow CO_2$

Chemical complexity: surface species

core level	binding energy (eV)	assignment
$Ru3d_{5/2}$	280.1	$Ru(10\bar{1}0)$-bulk
$Ru3d_{5/2}$	279.6, 279.9	$Ru(10\bar{1}0)$-surface
$Ru3d_{5/2}$	280.34, 280.56(weak)	Ru-2O, (1ML O_{ad})
	280.5 -280.6	TSO-RuO_x
$Ru3d_{5/2}$	280.75	RuO_2
$Ru3d_{5/2}$	281.7-283.3	RuO_3 and RuO_4
O1s	530.0	O_{ad} and RuO_x
O1s	530.8-531.9	CO and Ru
O1s	531.0-531.7	OH and Ru
O1s	533.2	H_2O and Ru
O1s	532.8-533.3	CH_3OH_{ad} on metals
O1s	528.7, 529.5	O in RuO_2
O1s	530.4	OH on RuO_2
O1s	531.2	CH_3O on RuO_2
O1s	532.2	CH_2O on RuO_2

Chemical complexity: surface species

Data taken from several sources (literature and own experiments):

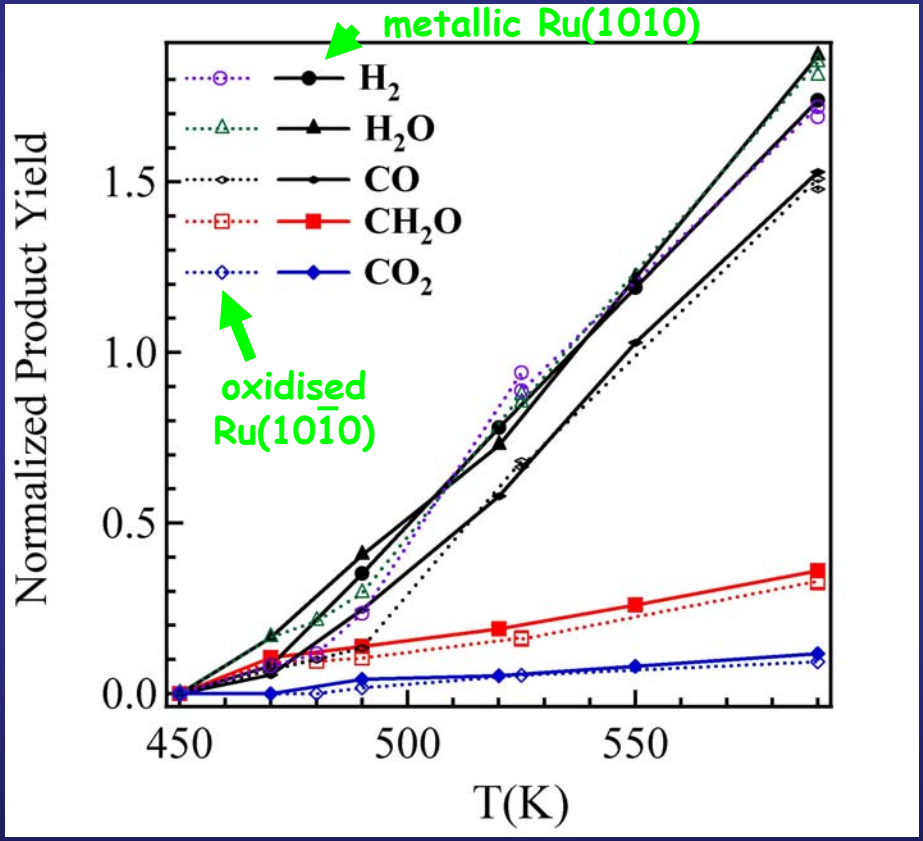
detailed analysis only possible after study of well prepared model surfaces

assignment needs combination of several surface science techniques (mainly XPS/TDS)

by combination of Ru3$d_{5/2}$ and O1s XPS assignment of specific surface species possible

The catalyst at work
$p(CH_3OH)/p(O_2)$: 2.3

Online mass spectrometry



reaction path independent of pre-catalyst state

onset of reaction: 450K

Reaction paths at 590K:

$CH_3OH+1/2O_2 \rightarrow H_2O+H_2+CO$

dominates over:

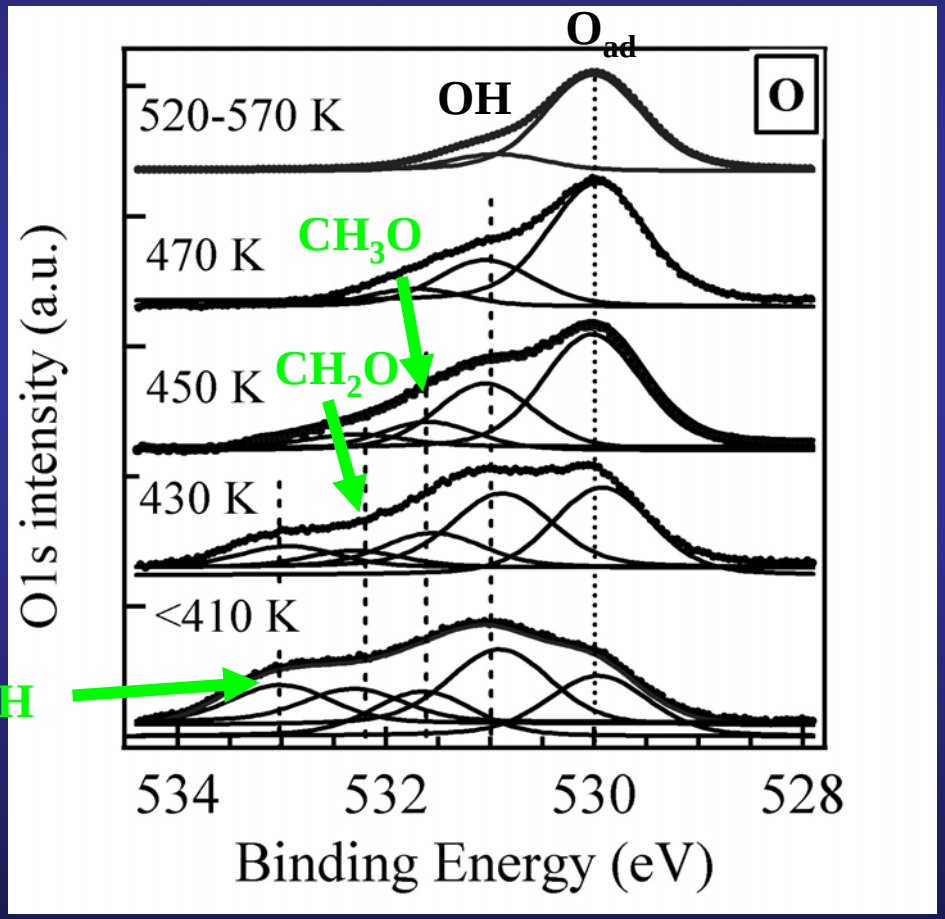
$CH_3OH+1/2O_2 \rightarrow CH_2O+H_2O$

total oxidation to CO_2 negligible

The catalyst at work
$p(CH_3OH)/p(O_2)$: 2.3

O1s core level

pre-catalyst: metallic Ru(10$\bar{1}$0)

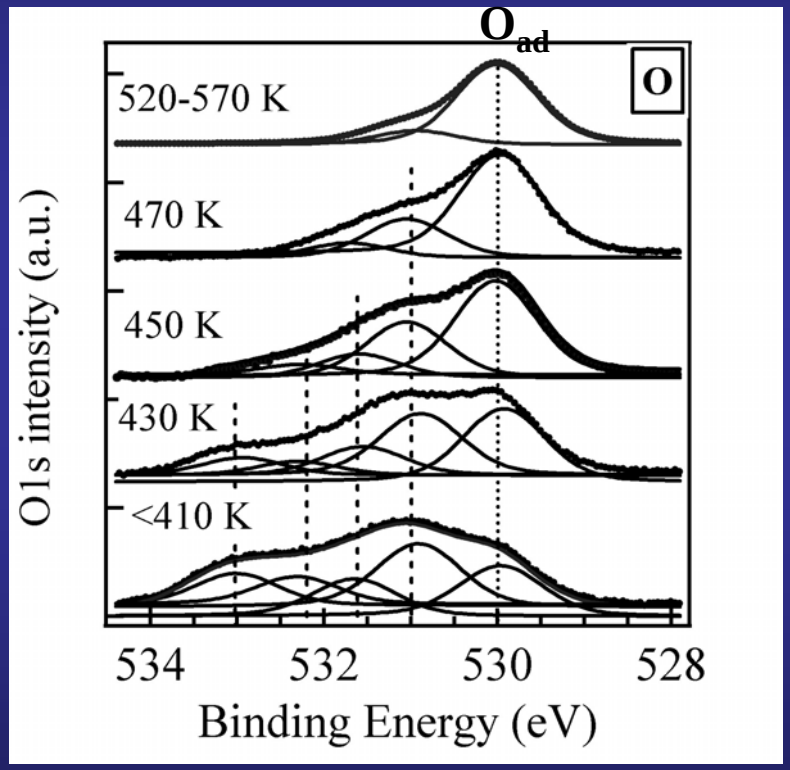


O1s: sequential desorption of CH_3OH derived adspecies

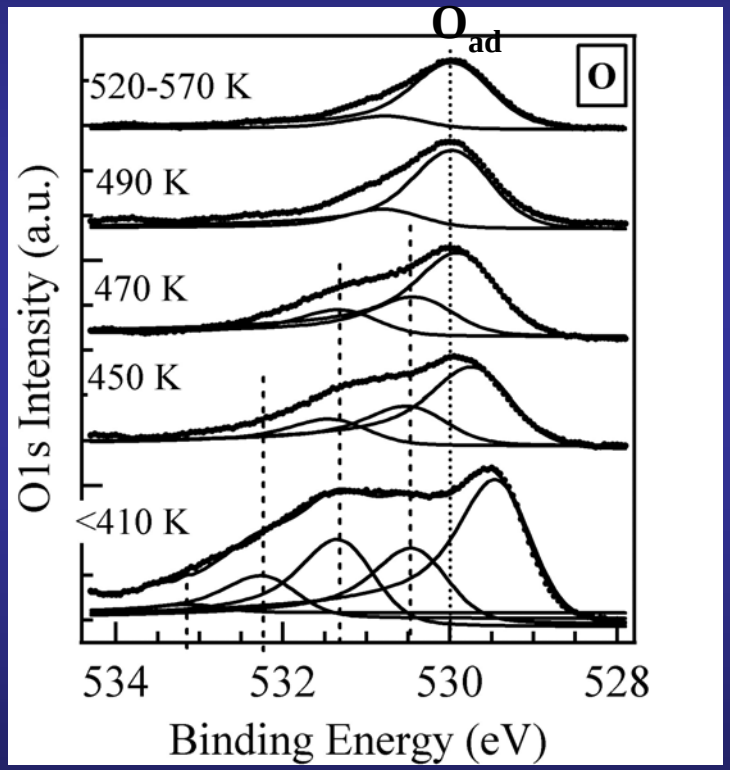
The catalyst at work
$p(CH_3OH)/p(O_2)$: 2.3

O1s core level

pre-catalyst: metallic Ru(10$\bar{1}$0)



pre-catalyst: oxidized Ru(10$\bar{1}$0)

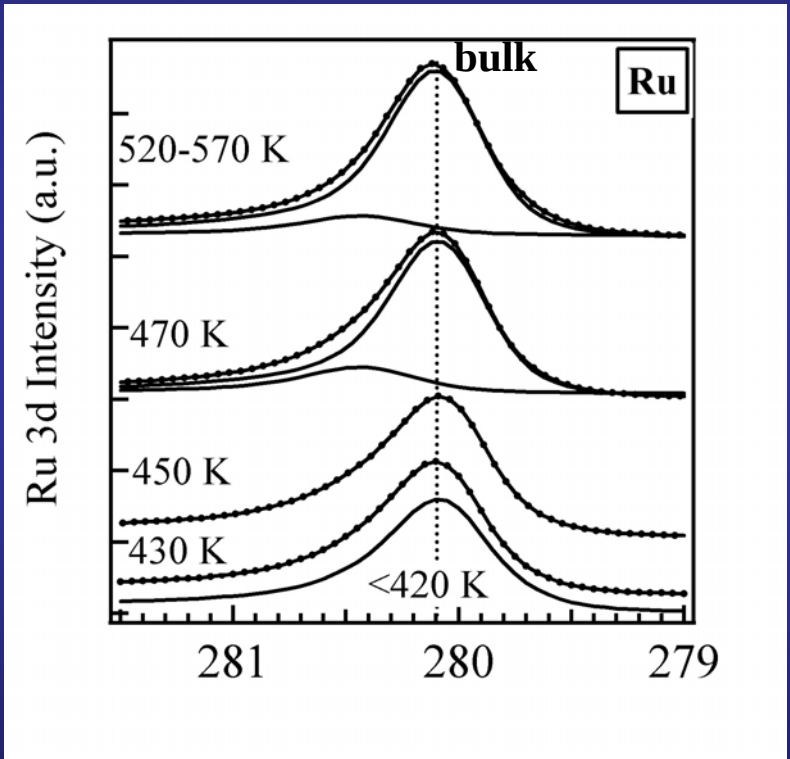


O1s: O_{ad} dominant species for both pre-catalyst at reaction conditions

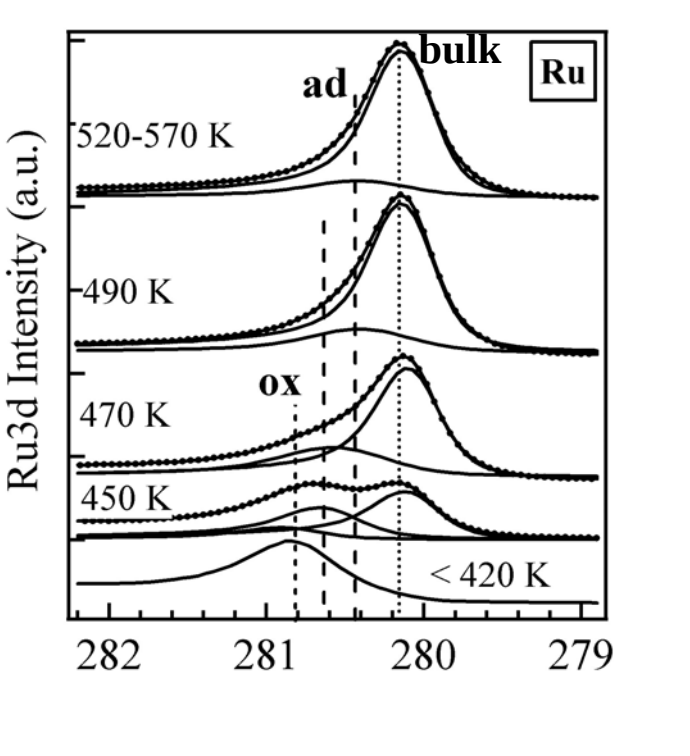
The catalyst at work
$p(CH_3OH)/p(O_2)$: 2.3

$Ru3d_{5/2}$ core level

pre-catalyst: metallic Ru(10$\bar{1}$0)



pre-catalyst: oxidized Ru(10$\bar{1}$0)

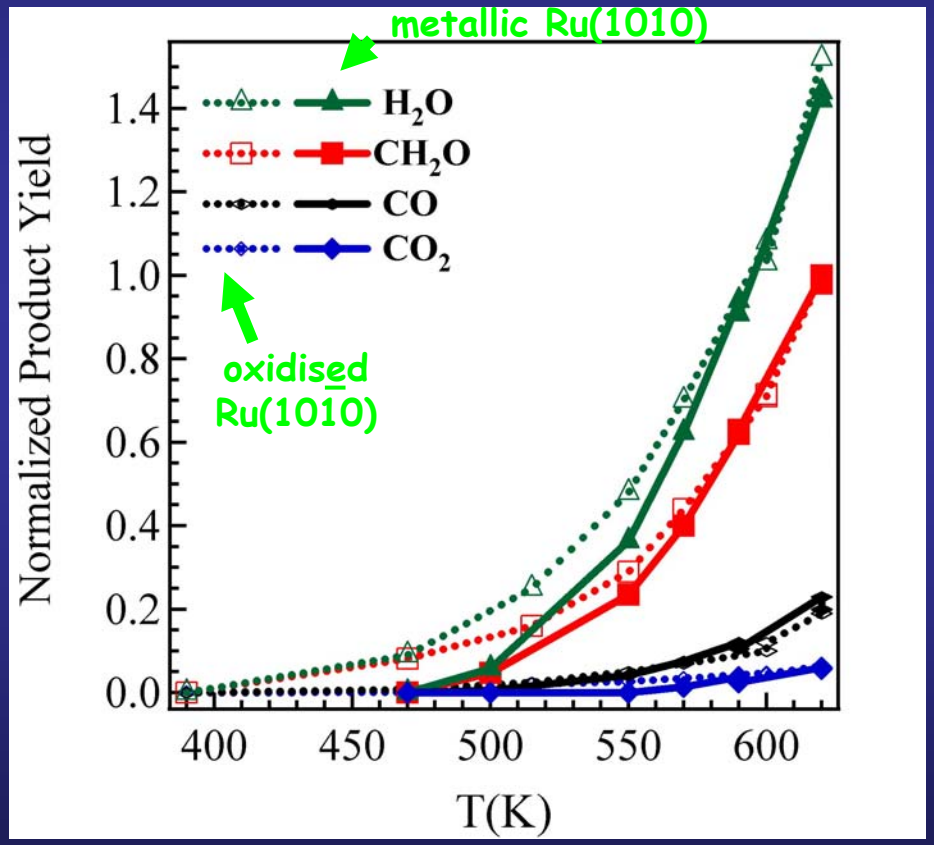


Ru3d: metallic for both pre-catalysts at reaction conditions

minor amount of adsorbed species

The catalyst at work
$p(CH_3OH)/p(O_2)$: 1.5

Online mass spectrometry



reaction path independent of pre-catalyst state

onset of reaction: +30K for metallic pre-catalyst

Reaction paths at 550K-620K:

$$CH_3OH + 1/2O_2 \rightarrow CH_2O + H_2O$$

at higher temperatures:

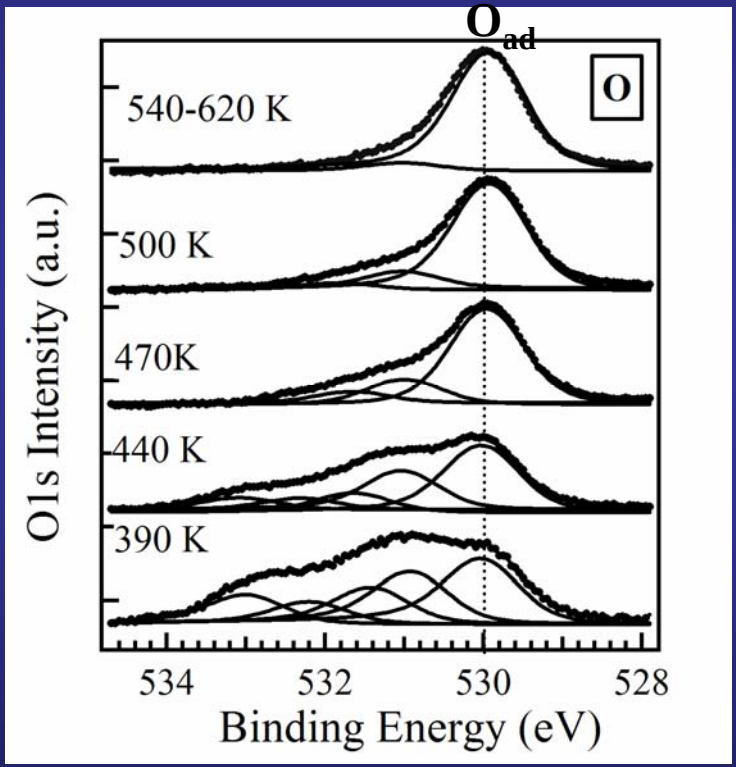
$$CH_3OH + O_2 \rightarrow CO + 2\,H_2O$$

traces of CO_2 (total oxidation)

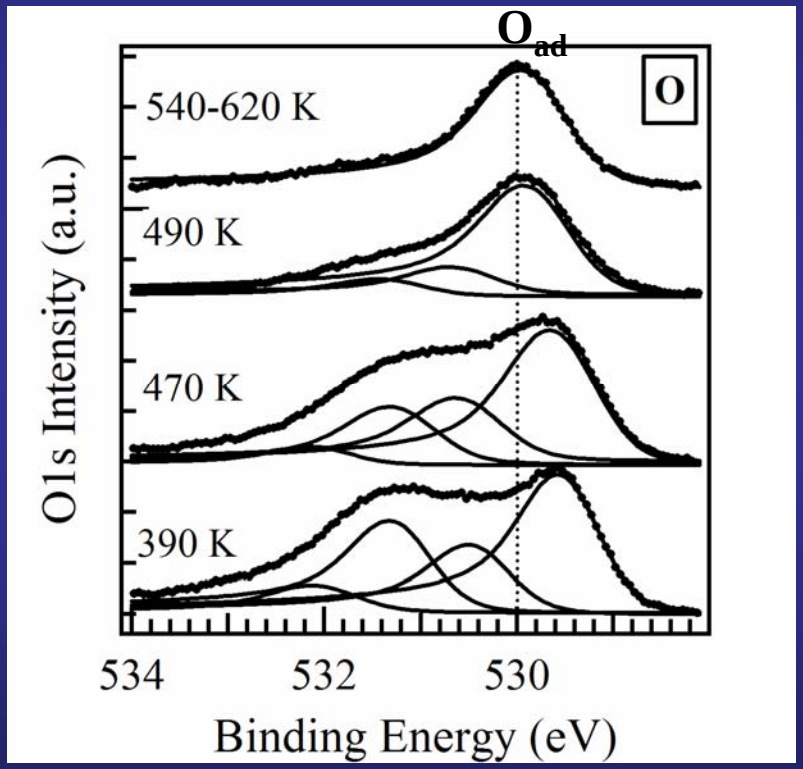
The catalyst at work
$p(CH_3OH)/p(O_2)$: 1.5

O1s core level

pre-catalyst: metallic Ru(10$\bar{1}$0)



pre-catalyst: oxidized Ru(10$\bar{1}$0)

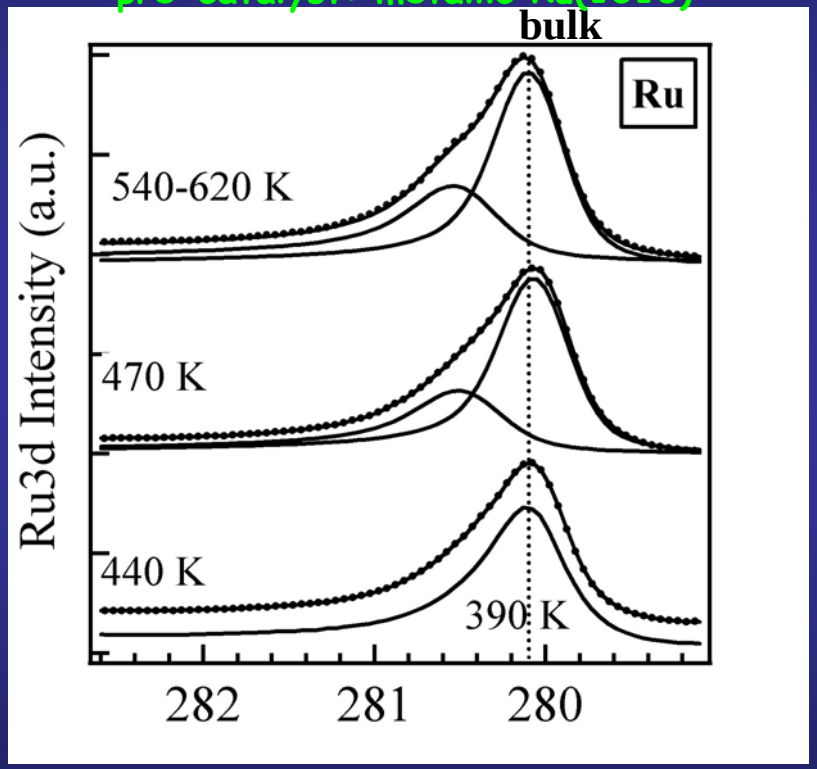


O1s: O_{ad} dominant species for both pre-catalyst at reaction conditions

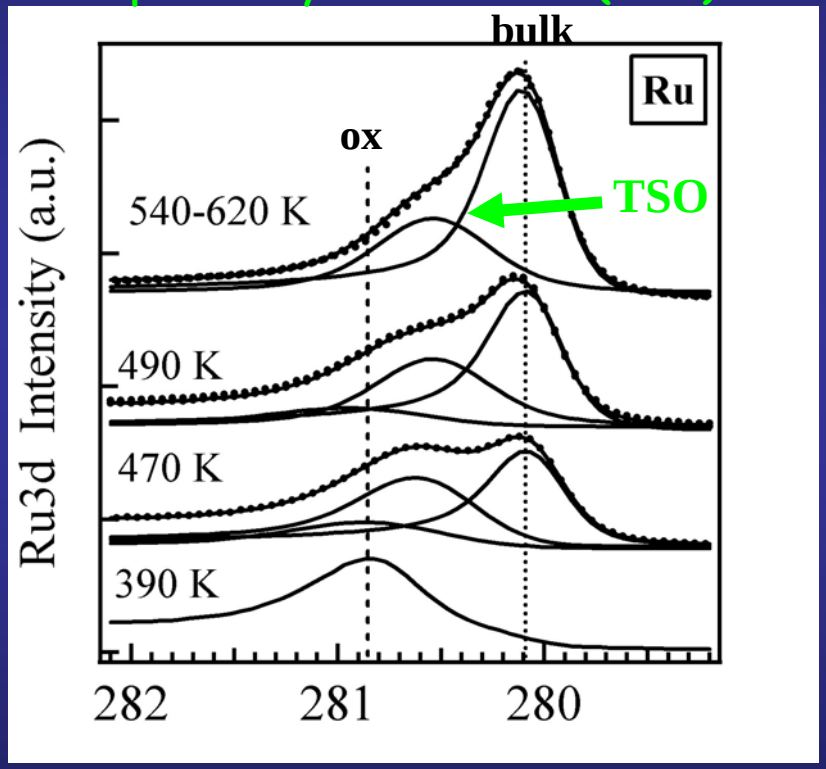
The catalyst at work
$p(CH_3OH)/p(O_2)$: 1.5

$Ru3d_{5/2}$ core level

pre-catalyst: metallic $Ru(10\bar{1}0)$



pre-catalyst: oxidized $Ru(10\bar{1}0)$

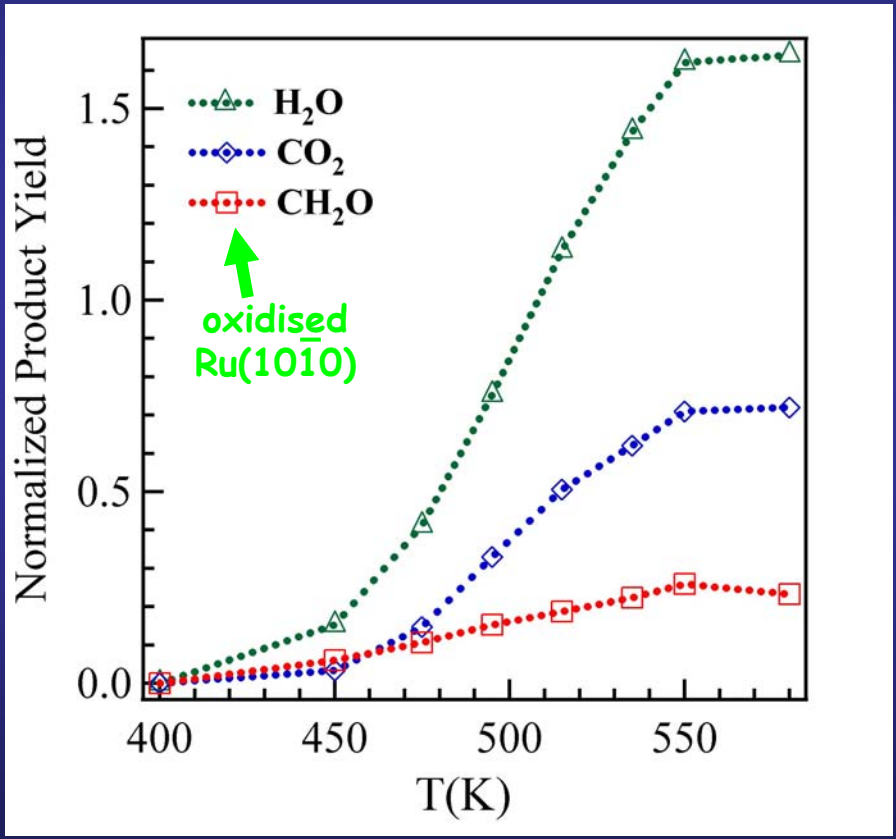


Ru3d: metallic for both pre-catalyst at reaction conditions

+ RuO_x (transient surface oxide state (TSO), BE=280.6eV)

The catalyst at work
$p(CH_3OH)/p(O_2)$: 0.75

Online mass spectrometry



pre-catalyst: oxidized

Reaction paths at 550K-600K:

$CH_3OH + 3/2 O_2 \rightarrow CO_2 + 2\ H_2O$

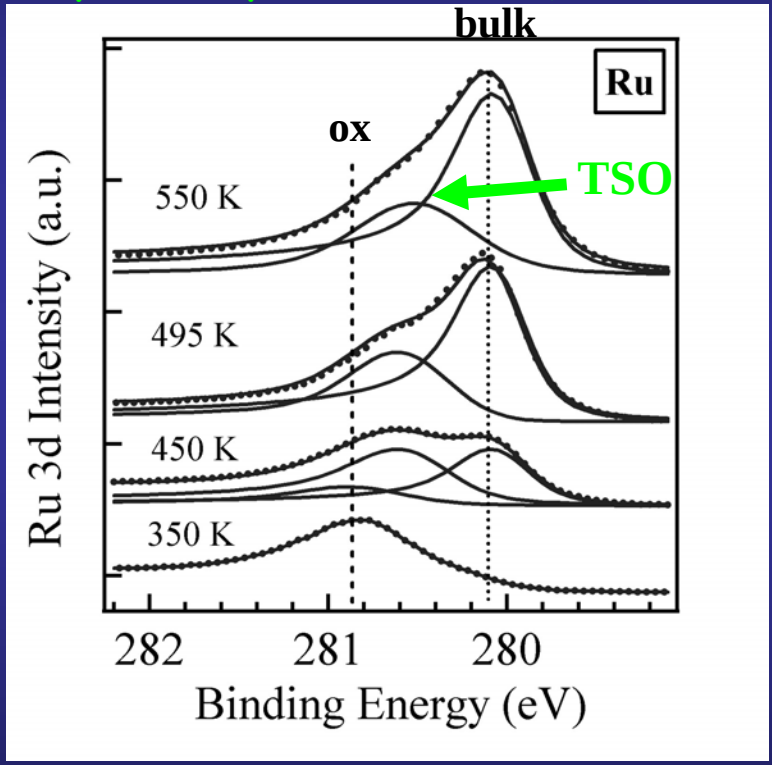
dominates over:

$CH_3OH + 1/2 O_2 \rightarrow CH_2O + H_2O$

The catalyst at work
$p(CH_3OH)/p(O_2)$: 0.75

$Ru3d_{5/2}$ core level

pre-catalyst: oxidized Ru(10$\bar{1}$0)



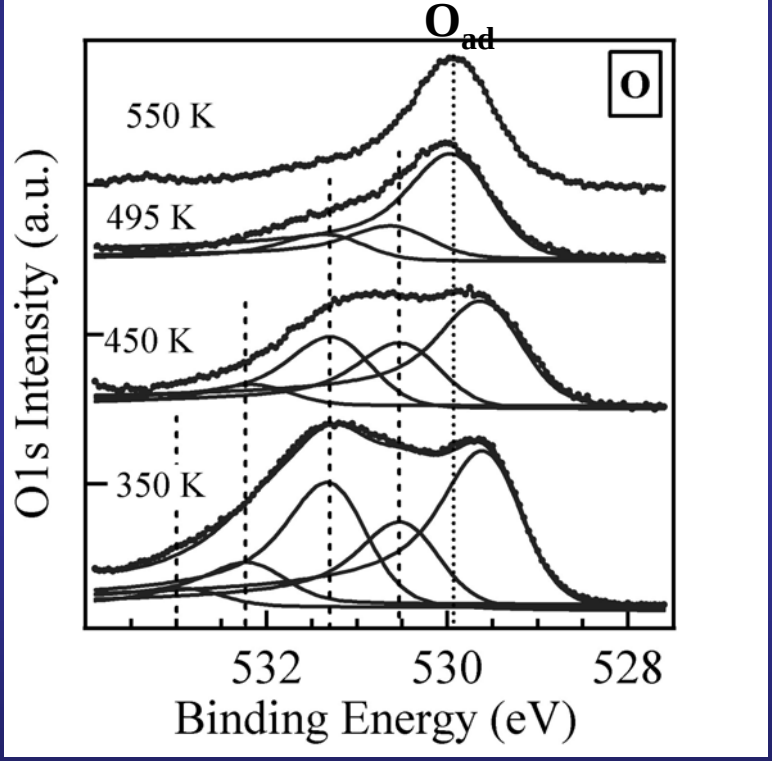
Ru3d: metallic for both pre-catalyst at reaction conditions

+ RuO_x (transient surface oxide state (TSO), BE=280.6eV)

The catalyst at work
$p(CH_3OH)/p(O_2)$: 0.75

O1s core level

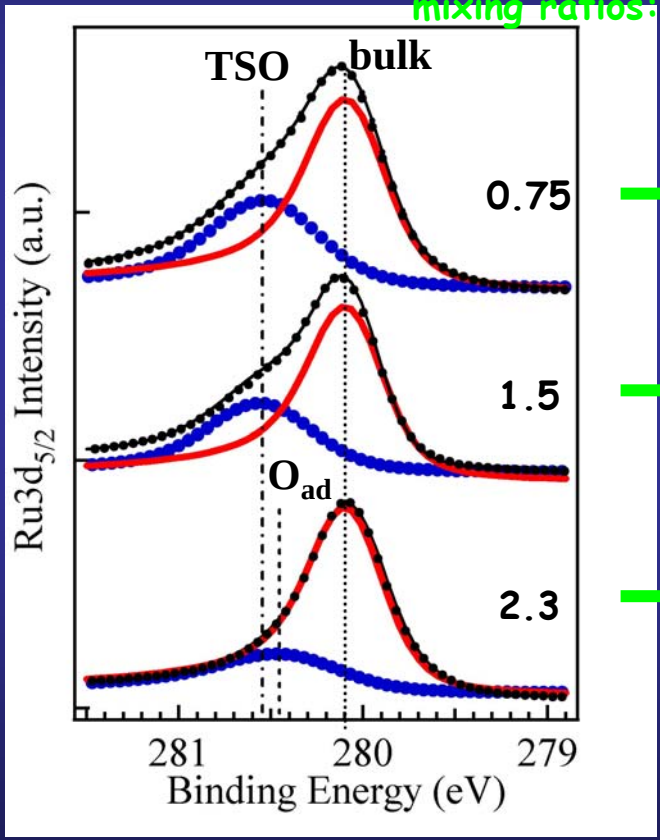
pre-catalyst: oxidized Ru(10$\bar{1}$0)



O1s: O_{ad} dominant species at reaction conditions

The catalyst at work
Summary

$Ru3d_{5/2}$ core level



dominant reaction pathway:

$CH_3OH + 3/2 O_2 \rightarrow CO_2 + 2\ H_2O$

$CH_3OH + 1/2 O_2 \rightarrow CH_2O + H_2O$

$CH_3OH + 1/2 O_2 \rightarrow H_2O + H_2 + CO$

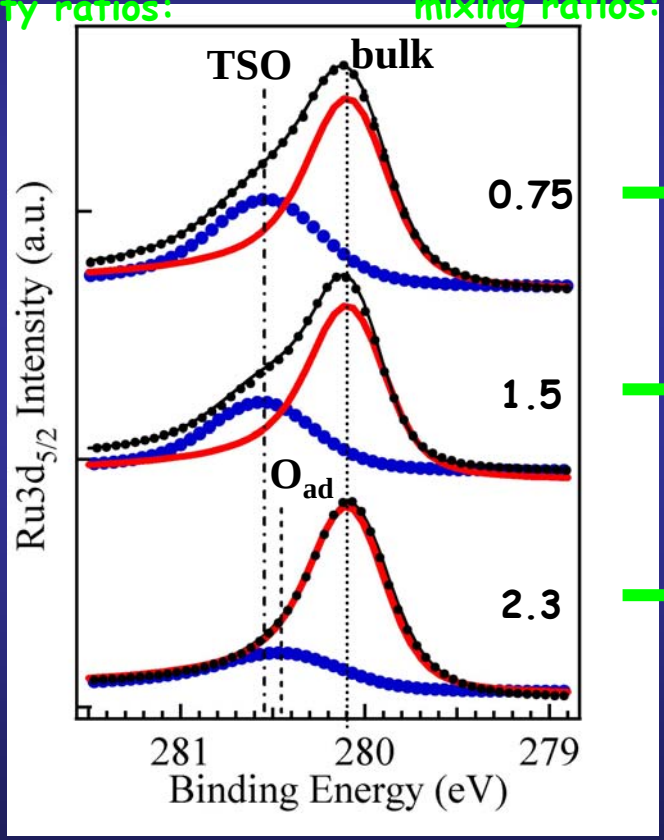
transition from oxygen adsorption to TSO

The catalyst at work
Summary

$Ru3d_{5/2}$ core level

$TSO+O_{ad}$/Ru(bulk) intensity ratios:

$CH_3OH:O_2$ mixing ratios:



0.56

0.46

0.15

dominant reaction pathway:

$CH_3OH+3/2O_2 \rightarrow CO_2 + 2\,H_2O$

$CH_3OH+1/2O_2 \rightarrow CH_2O + H_2O$

$CH_3OH+1/2O_2 \rightarrow H_2O + H_2 + CO$

different catalyst states facilitate different reaction pathways and activity

transition from oxygen adsorption to TSO

The catalyst at work
Summary

catalyst surface species:		dominant reaction pathway:
Ru(bulk) + Ru(TSO+O_{ad})	→	$CH_3OH+3/2O_2 \rightarrow CO_2 + 2\ H_2O$
increasing amount of accumulated oxygen	↑	
Ru(bulk) + Ru(TSO+O_{ad})	→	$CH_3OH+1/2O_2 \rightarrow CH_2O + H_2O$
Ru(bulk) + O_{ad} (submono)	→	$CH_3OH+1/2O_2 \rightarrow H_2O + H_2 + CO$

Summary

Key findings:

different pre-catalysts surfaces evolve into the same catalytically active state

reaction pathways are identical on the polycrystalline, close packed and open single crystal Ru catalyst (→ long range order not important)

RuO_2 is not the active state for the different oxidation regimes investigated in the study, instead partially reduced surface (RuO_x, TSO)

chemical potential of the reactants determine dynamics of the active state on the catalyst surface

Acknowledgement

AvH foundation

BESSY staff

Financial support by NANO2 (NMP3-CT-2003-505670)

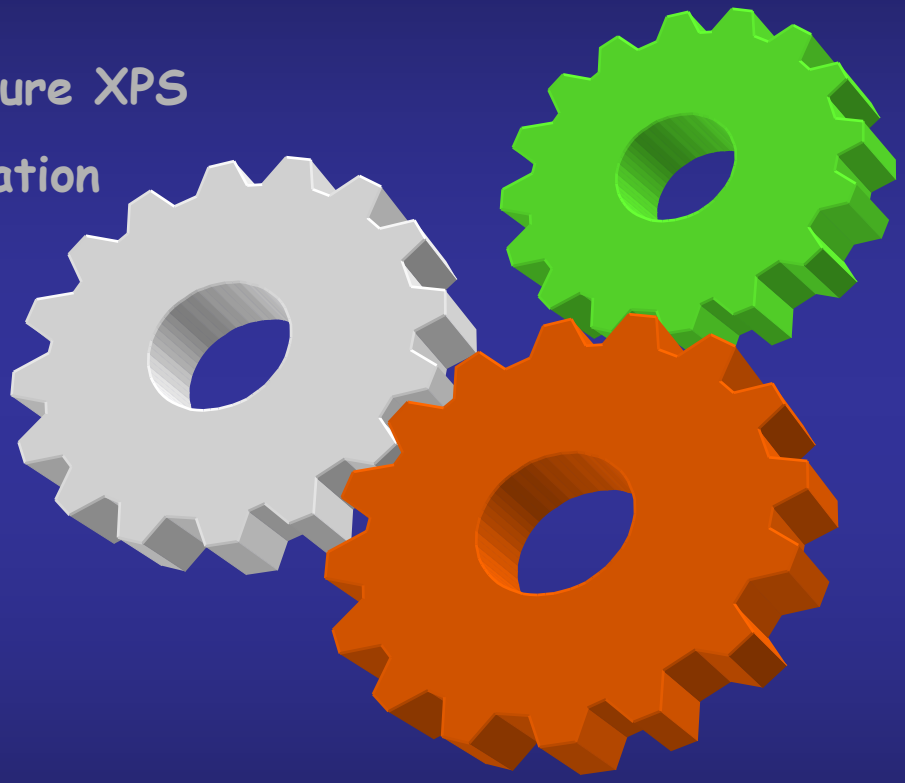

MAX-PLANCK-GESELLSCHAFT


AC
FHI

Concept of ISISS at BESSY

Infrastructure for experiments with chemical background

High pressure XPS end station



State of the art soft X-ray beamline

M. Hävecker, Surface Analysis, Dept. AC, Fritz-Haber-Institut (MPG), Berlin, Germany

Outlook: In situ XPS / XAS
The future at BESSY

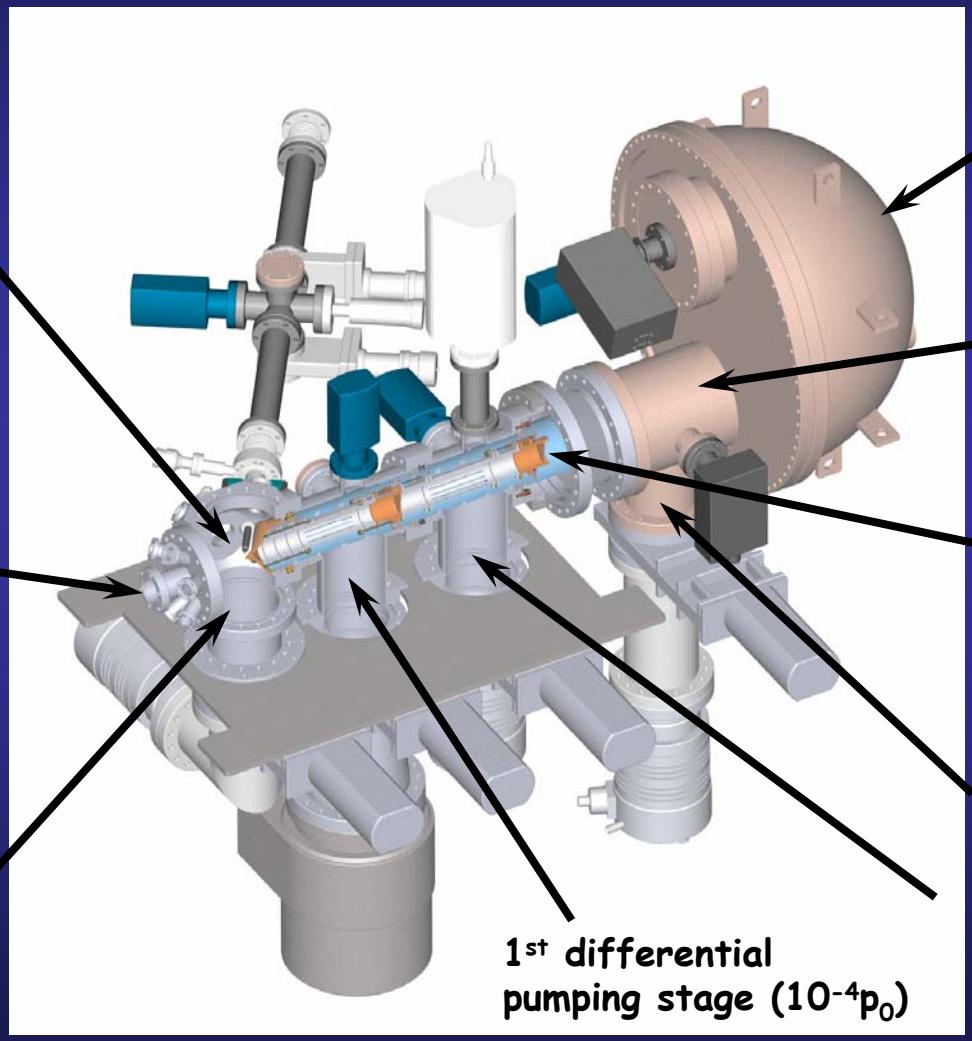
ISISS:

Innovative Station for In Situ Spectroscopy

A project of BESSY and the Dep. Inorganic Chemistry, Fritz-Haber-Institut

- Installation of a beamline exclusively used for in situ spectroscopy in the soft X-ray range
- Installation of infrastructure optimized for these kind of experiments on site (e.g. chemical lab, gas supply, gas analytics)
- Later, further implementation of other in situ spectroscopy techniques: multi wavelength Raman, UV-Vis, fluorescence yield
- Start of user operation of the beamline: 2007

The high pressure XPS / XAS apparatus



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

mass spectrometer and additional pumping

Experimental cell supplied by gas lines (p_0)

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

Analyzer input lens

Focal point of analyzer input lens

3rd differential pumping stage ($10^{-8}p_0$)

2nd differential pumping stage ($10^{-6}p_0$)

1st differential pumping stage ($10^{-4}p_0$)

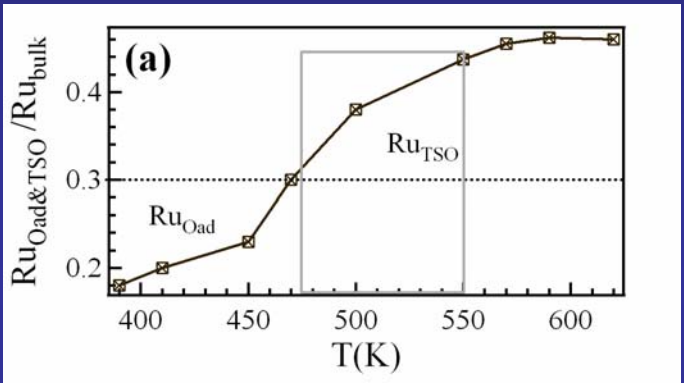
The X-ray Source: Synchrotron Radiation

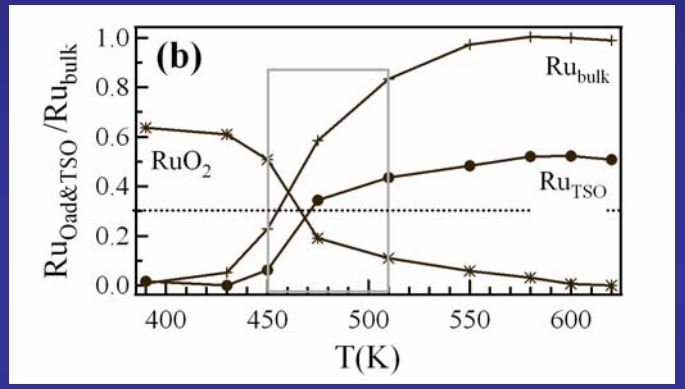
Berliner**E**lektronen**s**peicherring**g**esell-schaft für **Sy**nchrotronstrahlung

Experiments done at undulator 49/2 at BESSY

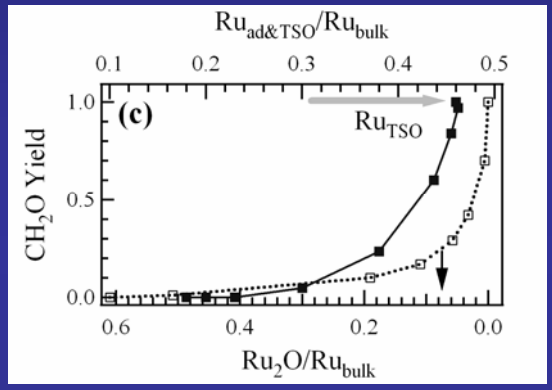
- tuneable X-ray source
- high intensity (10^{12} photons / s / 100 mA)
- high resolution (150 meV)
- small spot size

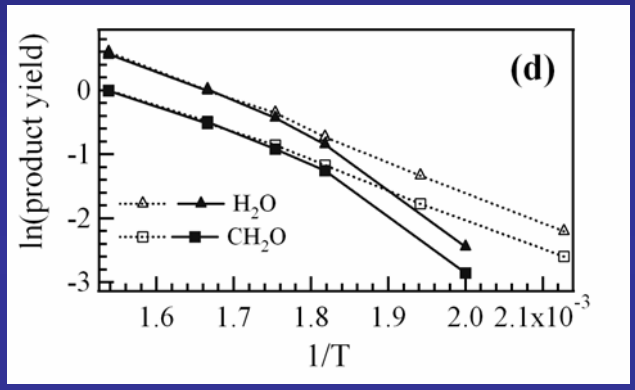
M. Hävecker, Electronic Structure, Dept. AC, Fritz-Haber-Institut (MPG), Berlin, Germany


(a)
$Ru_{Oad&TSO}/Ru_{bulk}$
0.2
0.3
0.4
Ru_{Oad}
Ru_{TSO}
400
450
500
550
600
T(K)


(b)
$Ru_{Oad&TSO}/Ru_{bulk}$
0.0
0.2
0.4
0.6
0.8
1.0
RuO_2
Ru_{bulk}
Ru_{TSO}
400
450
500
550
600
T(K)

Cu3p


Ru_ad&TSO/Ru_bulk
0.1
0.2
0.3
0.4
0.5
(c)
Ru_TSO
CH2O Yield
1.0
0.5
0.0
0.6
0.4
0.2
0.0
Ru2O/Ru_bulk


(d)
ln(product yield)
0
-1
-2
-3
H2O
CH2O
1.6
1.7
1.8
1.9
2.0
2.1x10^-3
1/T

Zn3p

Cu3p