In situ investigation of the nature of the active surface of vanadyl pyrophosphate catalysts during *n*-butane oxidation to maleic anhydride

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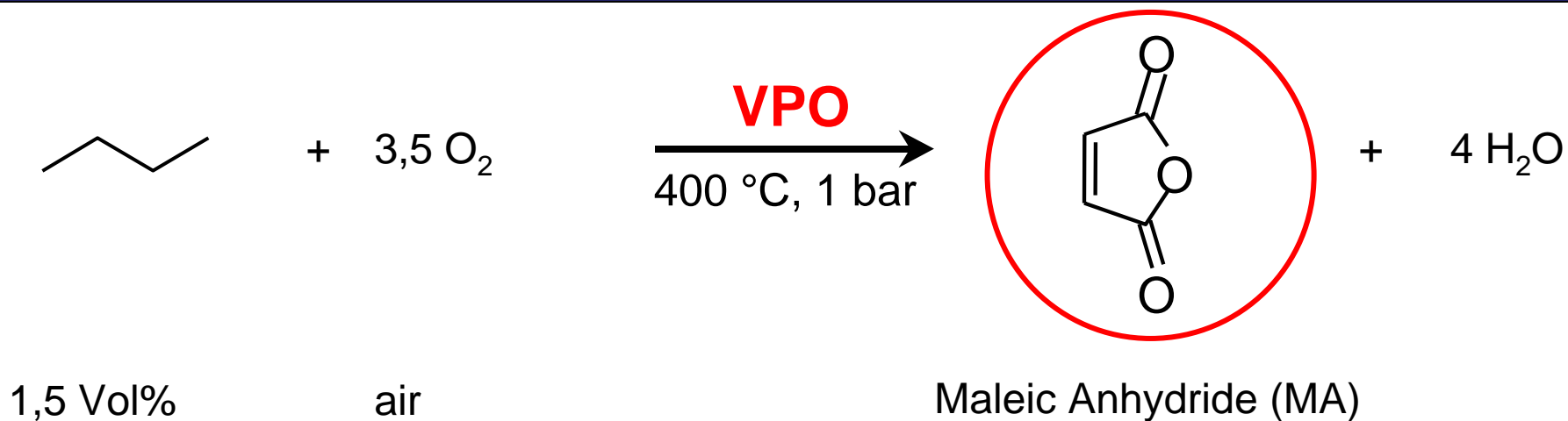
J.A. Lopez-Sanchez, J.K. Bartley, G.J. Hutchings

Department of Chemistry, Cardiff University, Cardiff, United Kingdom

n-Butane Oxidation to MA
by Vanadium Phosphorus Catalysts

$$C_4H_{10} + 3,5\ O_2 \xrightarrow[400\ °C,\ 1\ bar]{VPO} \text{Maleic Anhydride (MA)} + 4\ H_2O$$

1,5 Vol%   air

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

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

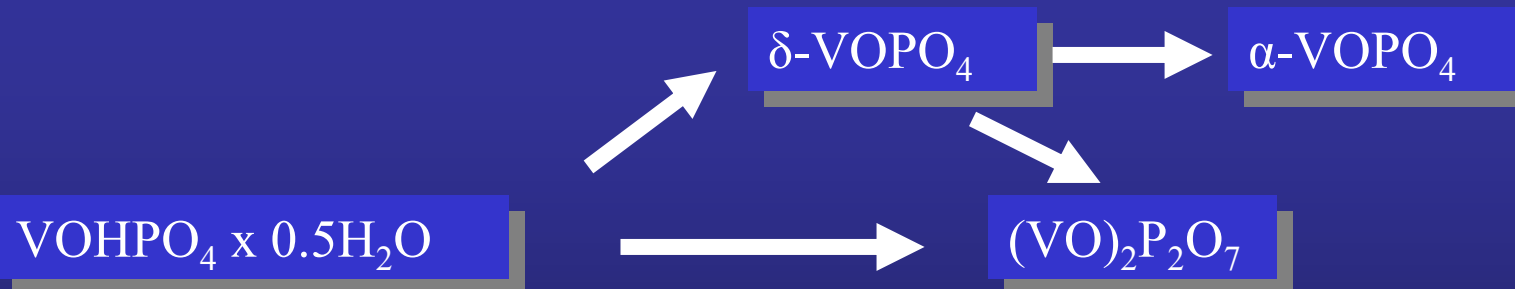M. Hävecker, Electronic Structure, Dept. AC, Fritz-Haber-Institut (MPG), Berlin, Germany

Structural Dynamic

VPO system: capable of easily forming many different phases with similar structures often leading to multiphase system (+ highly disordered phase !)

Activation of the precursor:

$$\delta\text{-VOPO}_4 \longrightarrow \alpha\text{-VOPO}_4$$

$$\text{VOHPO}_4 \text{ x } 0.5\text{H}_2\text{O} \longrightarrow (\text{VO})_2\text{P}_2\text{O}_7$$

M. Abon et al., J. Catal., 156 (1995) 28

Transformation of the chemistry of the material during the catalytic process

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

P/V ratio > 1: not compatible with crystalline $(VO)_2P_2O_7$

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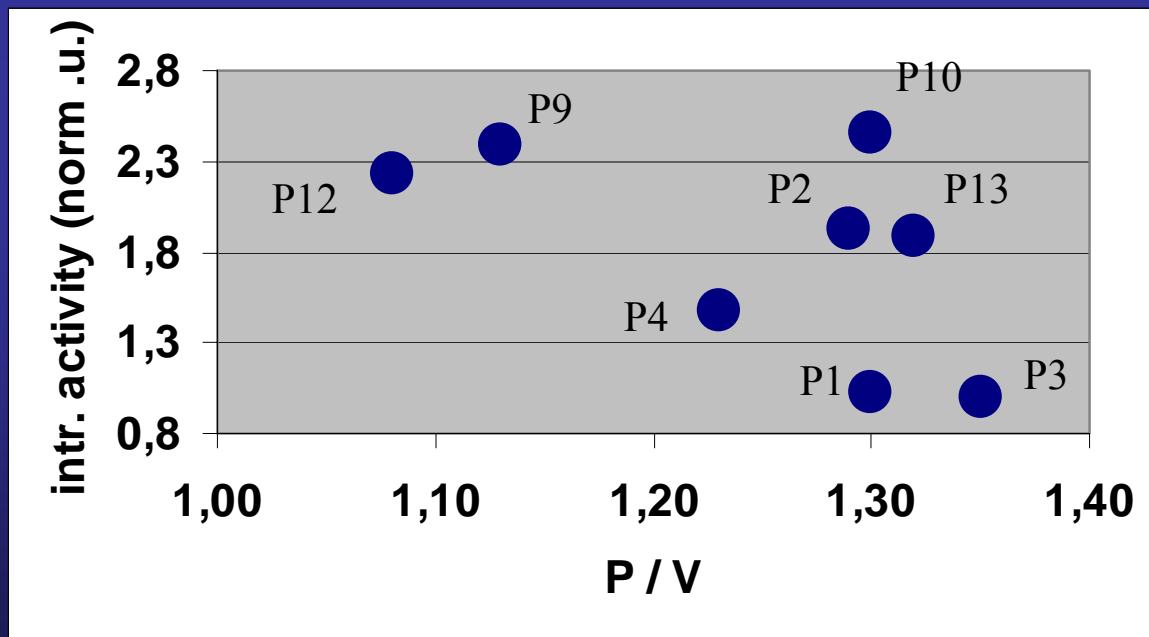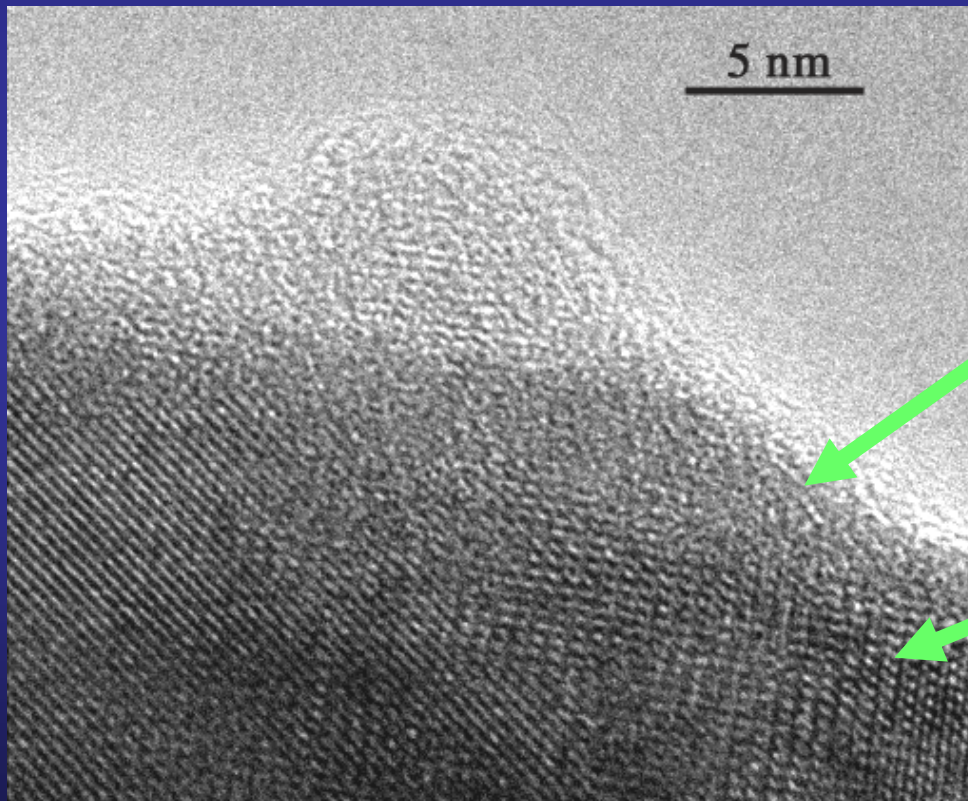P/V ratio > 1: not compatible with crystalline $(VO)_2P_2O_7$

Structural Dynamic

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

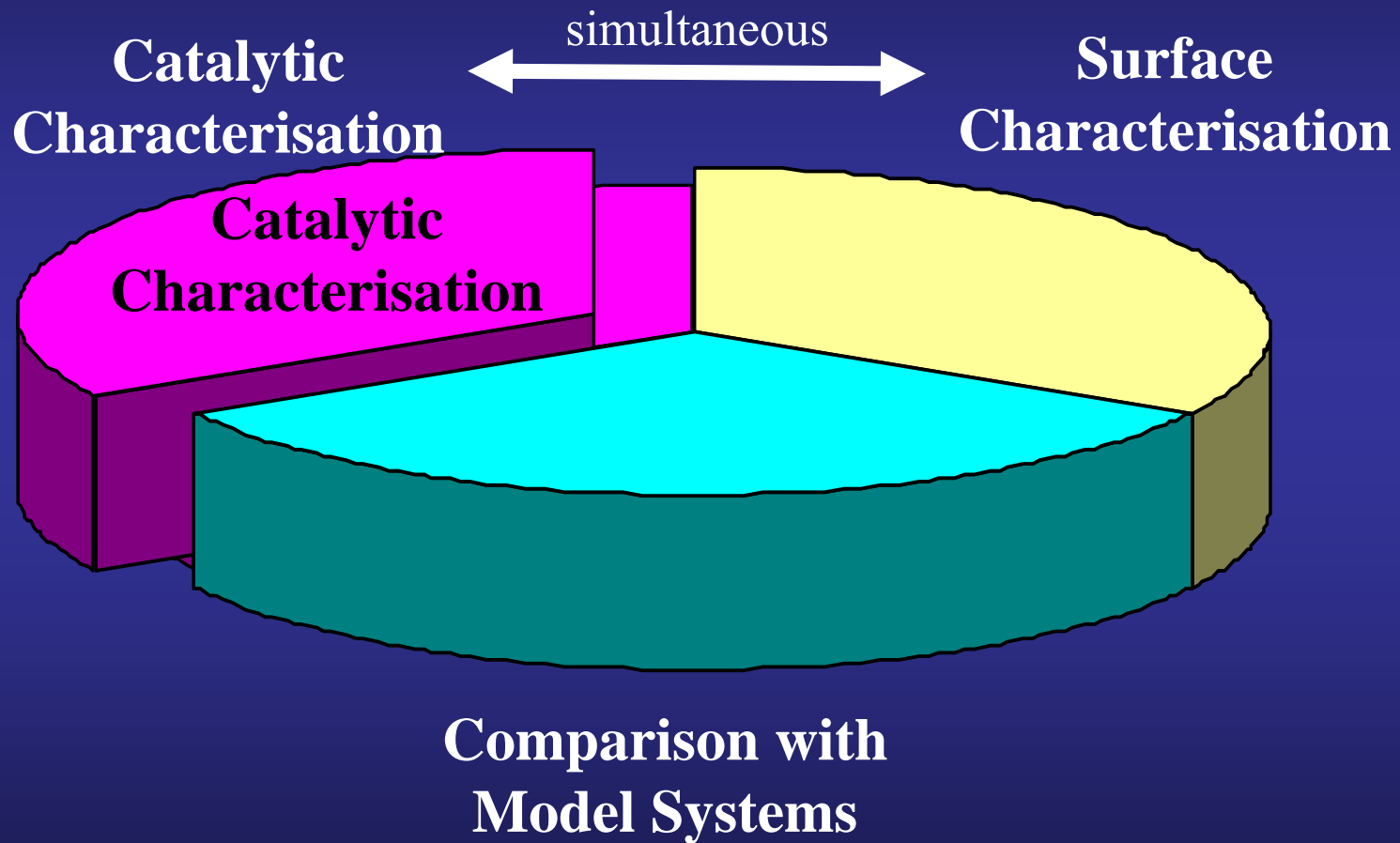P/V ratio > 1: not compatible with crystalline $(VO)_2P_2O_7$

V^{5+} centres involved (G. W. Coulston et al. Science 267 (1997) 191):
not compatible with V^{4+} valence of $(VO)_2P_2O_7$

Completely amorphous material also active
(G. J. Hutchings et al., J. Catal. 208 (2002) 197)

TEM micrograph of catalyst particle:

5 nm

disordered surface adlayer

on well crystallised particles

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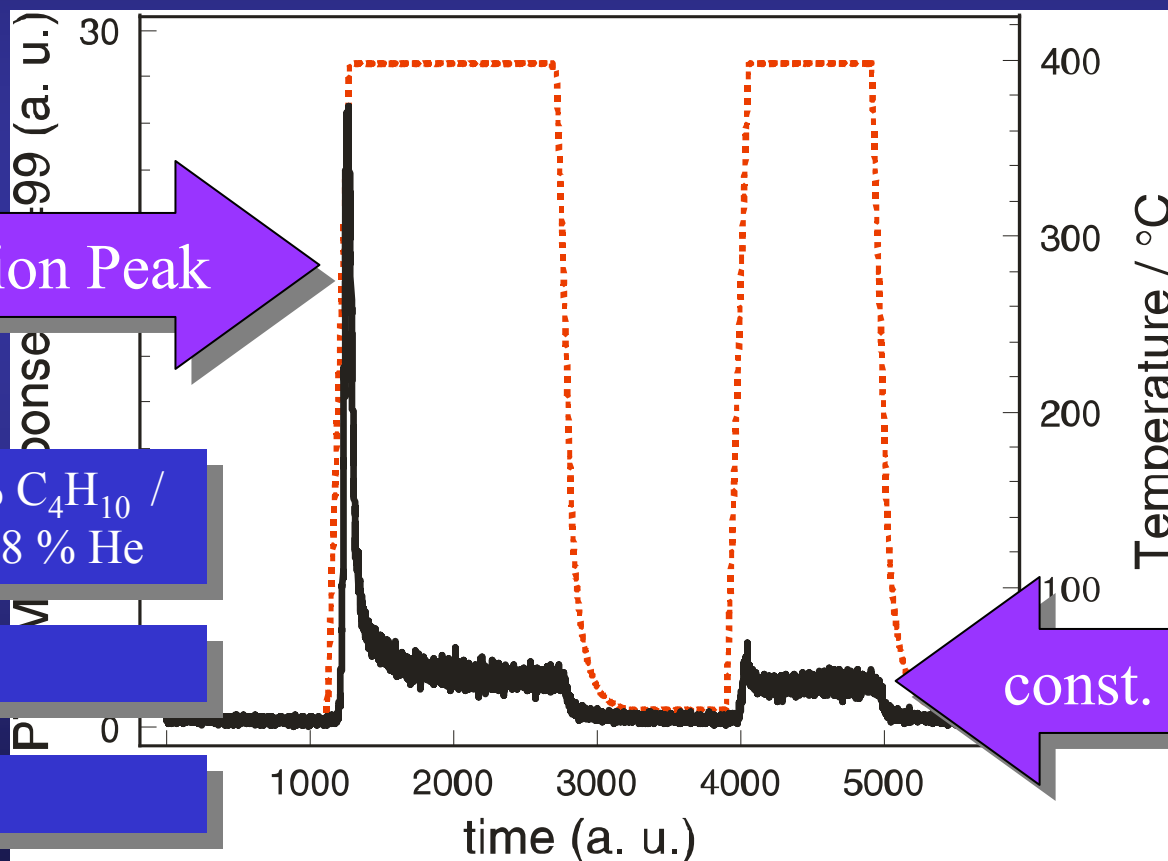(G. J. Hutchings et al., J. Catal. 208 (2002) 197)

How can a stoichiometric compound serve as a source for 7
oxygens per n-C_4H_{10} without collapse of its geometric structure ?

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

Scientific Approach

Catalytic
Characterisation

simultaneous

Surface
Characterisation

Comparison with
Model Systems

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Catalytic Activity

Product Analysis by Online **P**roton **T**ransfer **R**eaction **M**ass **S**pectrometry (PTR-MS)
I(m/e=99) : Maleic Anhydride (MA)

Desorption Peak

const. MA Yield

flow of 1.2 vol % C_4H_{10} / 20 vol % O_2 / 78.8 % He

P_{tot} = 2 mbar

RT to 400 °C

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Catalytic Activity

Relative specific catalytic activity (MA) at different total pressure: 1bar $\Leftrightarrow$ 2 mbar

In situ XAS

2 mbar

1 bar

specific activity:
Y(MA)/m(cat)

test reactor
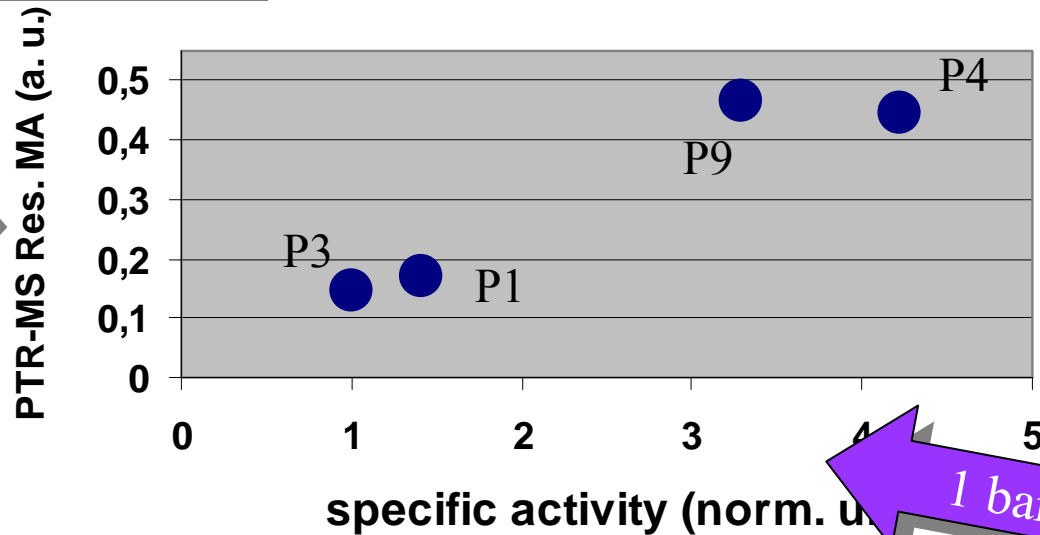
	Spec. activity	Intrinsic activity	steady_norm	Surface area
P3	=! 1.00	=! 1.00	=!1.00	=!1.00
P1	1.41	1.02	1.17	1.38
P4	4.22	1.47	3.06	2.89
P9	3.29	2.39	3.21	1.38
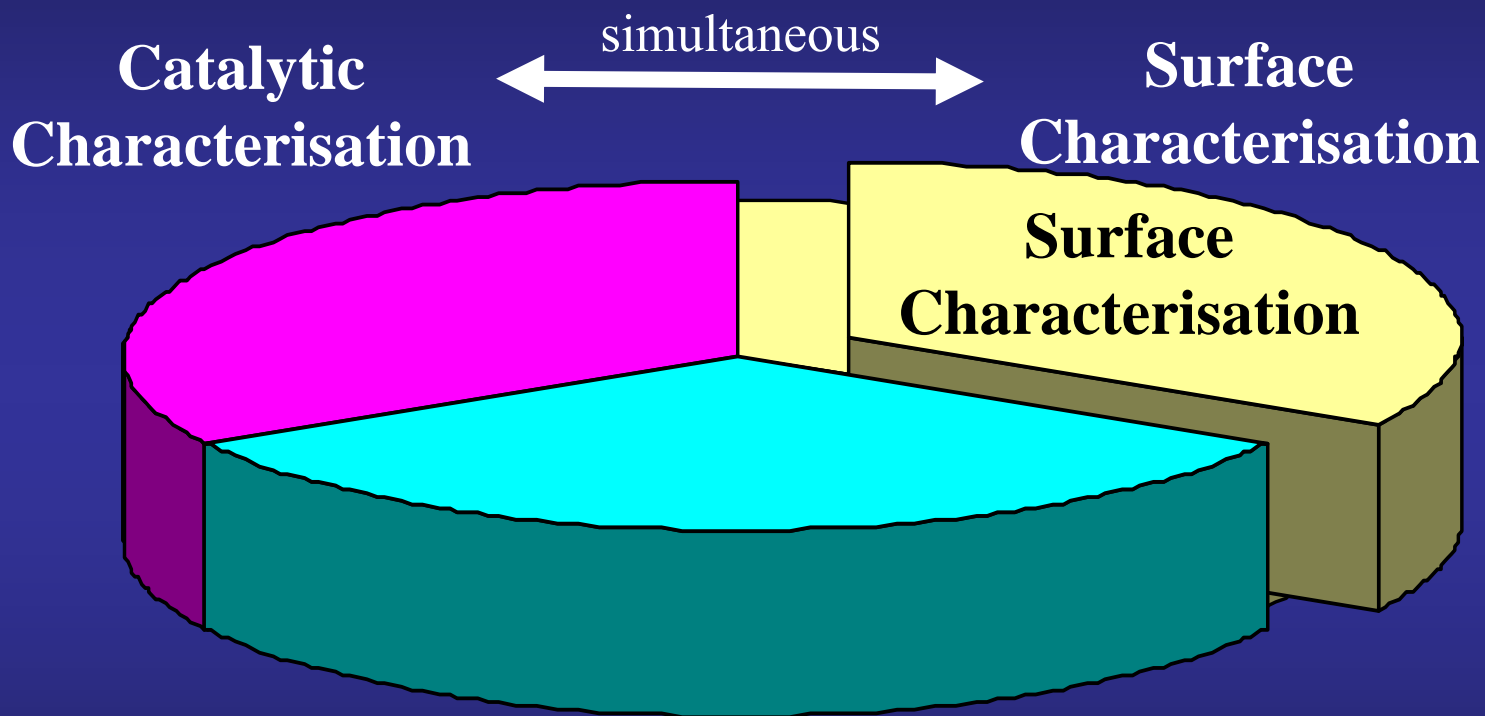
M. Hävecker, Electronic Structure, Dept. AC, Fritz-Haber-Institut (MPG), Berlin, Germany

Spectroscopy

X-ray absorption spectroscopy

Near
Edge
X-ray
Absorption
Fine
Structure

X-ray photoelectron spectroscopy

Why X-ray absorption spectroscopy in the soft energy range ?

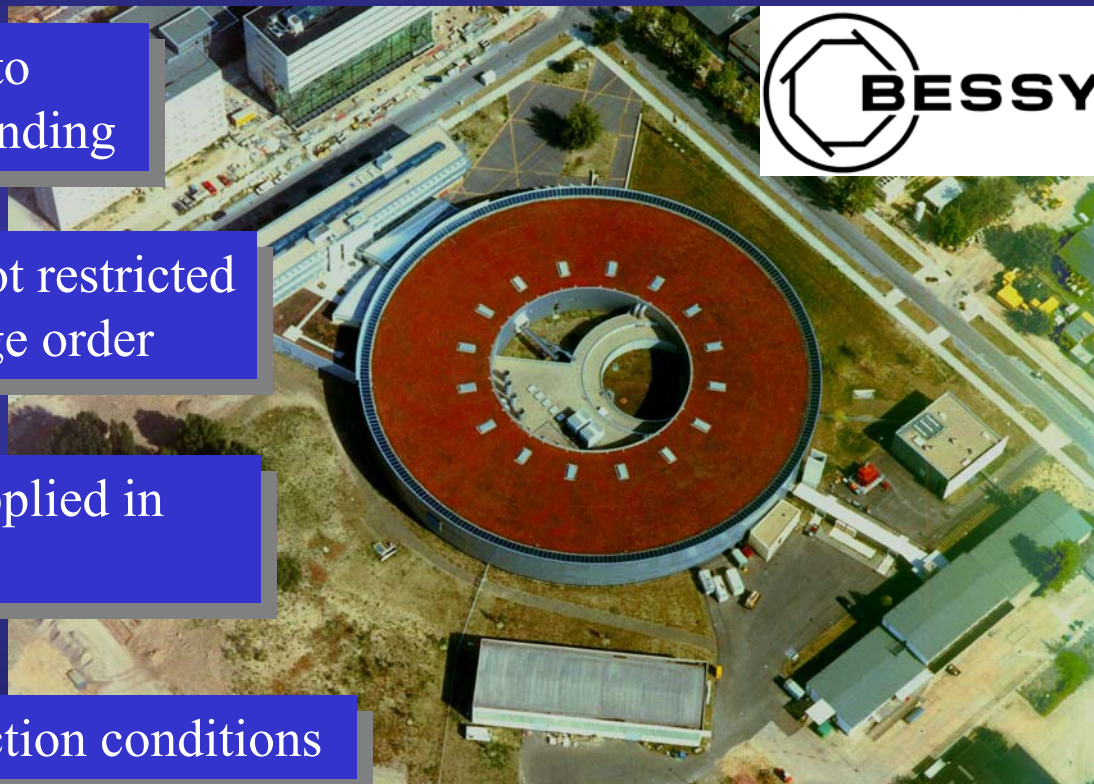➡ V L$_3$-edge very sensitive to details of the chemical bonding

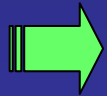➡ XAS as a local process not restricted to material with long range order

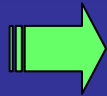➡ Surface sensitive when applied in the electron yield mode

➡ Can be applied under reaction conditions

BESSY

(Photographs: Luftbild u. Pressefoto R.Grahn)

A. Knop-Gericke et al., Nucl. Instr. Meth. A 406 (1998) 311
M. Hävecker et al., Angew. Chem. 110 (1998) 2049; Int. Ed. 37 (1998) 206

Why X-ray photoelectron spectroscopy at a synchrotron ?
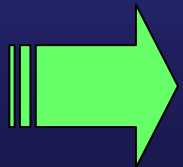
➡ High photon flux and brilliance

➡ Tuneable monochromatic X-ray source:

high spectral resolution
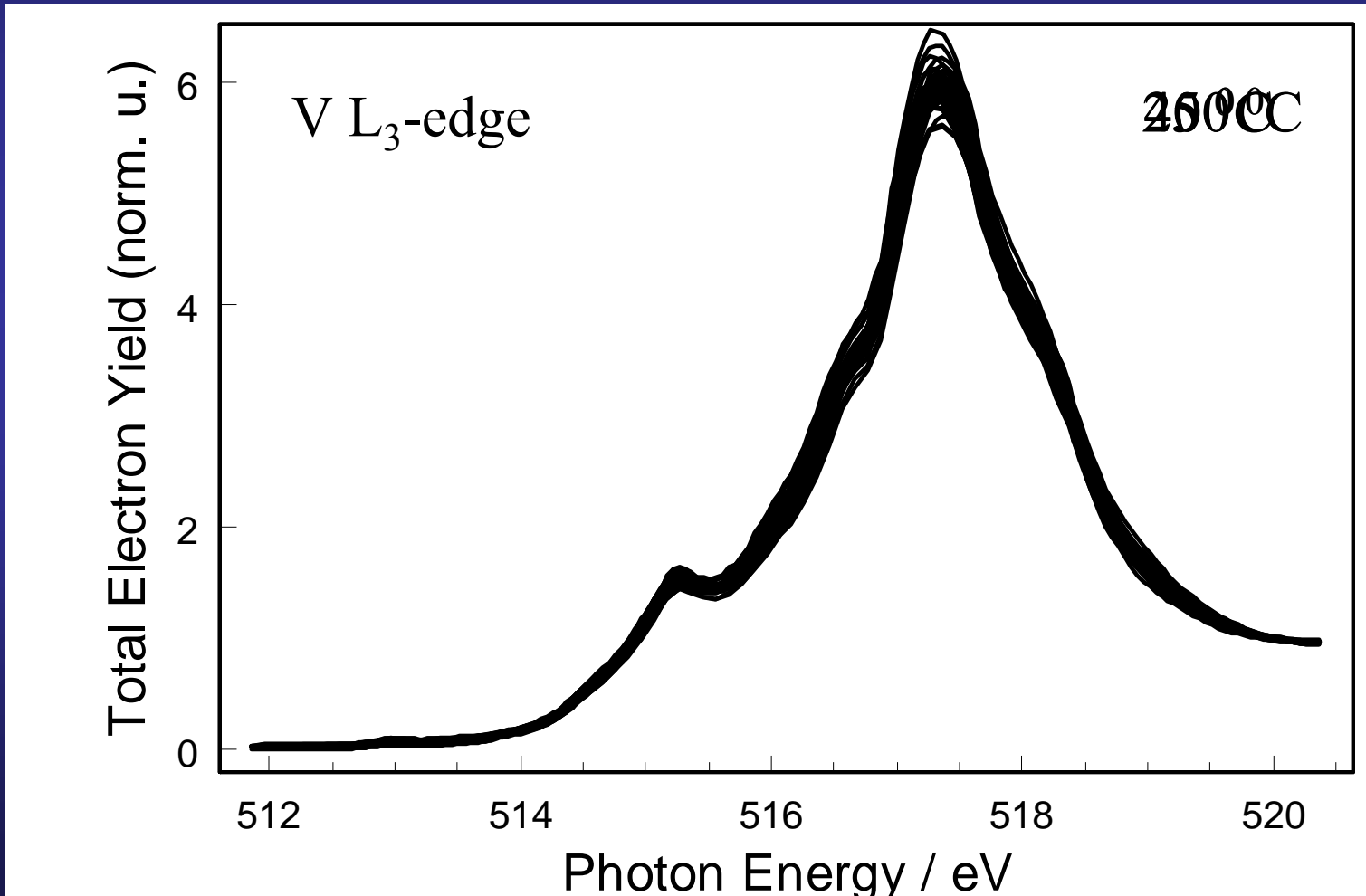
variation of photon energy allows depth profiling

➡ **P81 / P134**

(Photographs: Luftbild u. Pressefoto R.Grahn)

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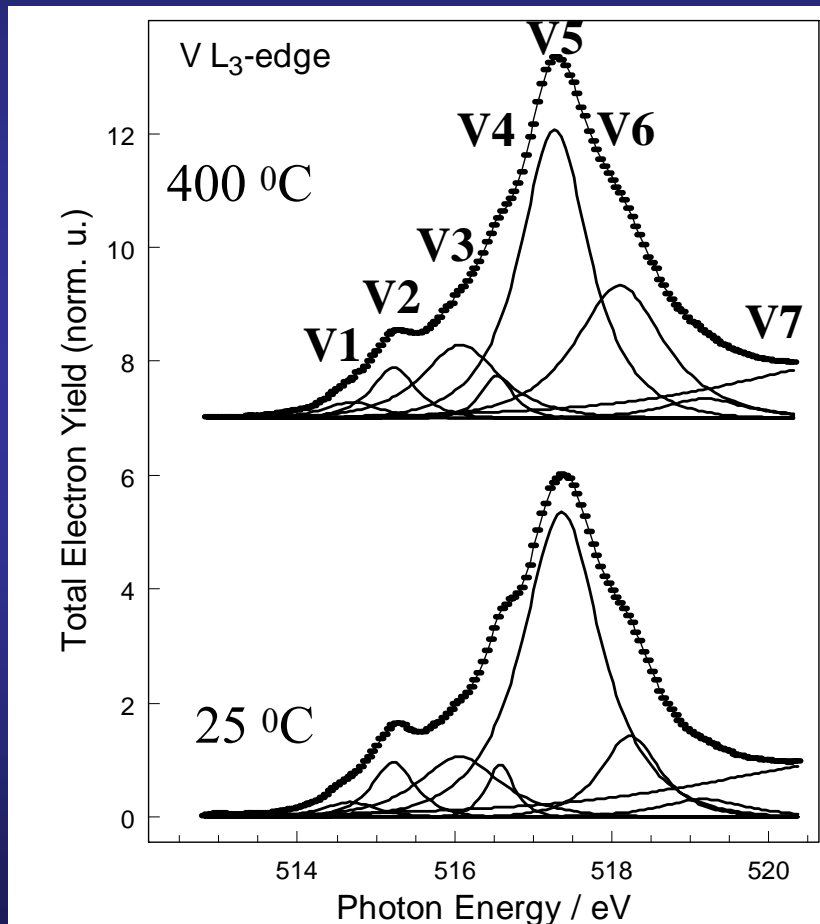heating / cooling cycles in n-C_4H_{10}/O_2/He atmosphere at a total pressure of 2 mbar

The VPO V L₃-NEXAFS

Analysis of spectral shape by unconstrained least squares fit

V valence

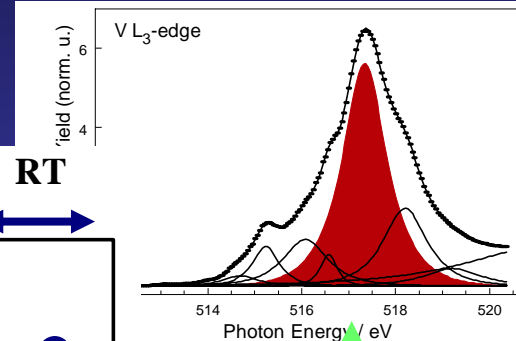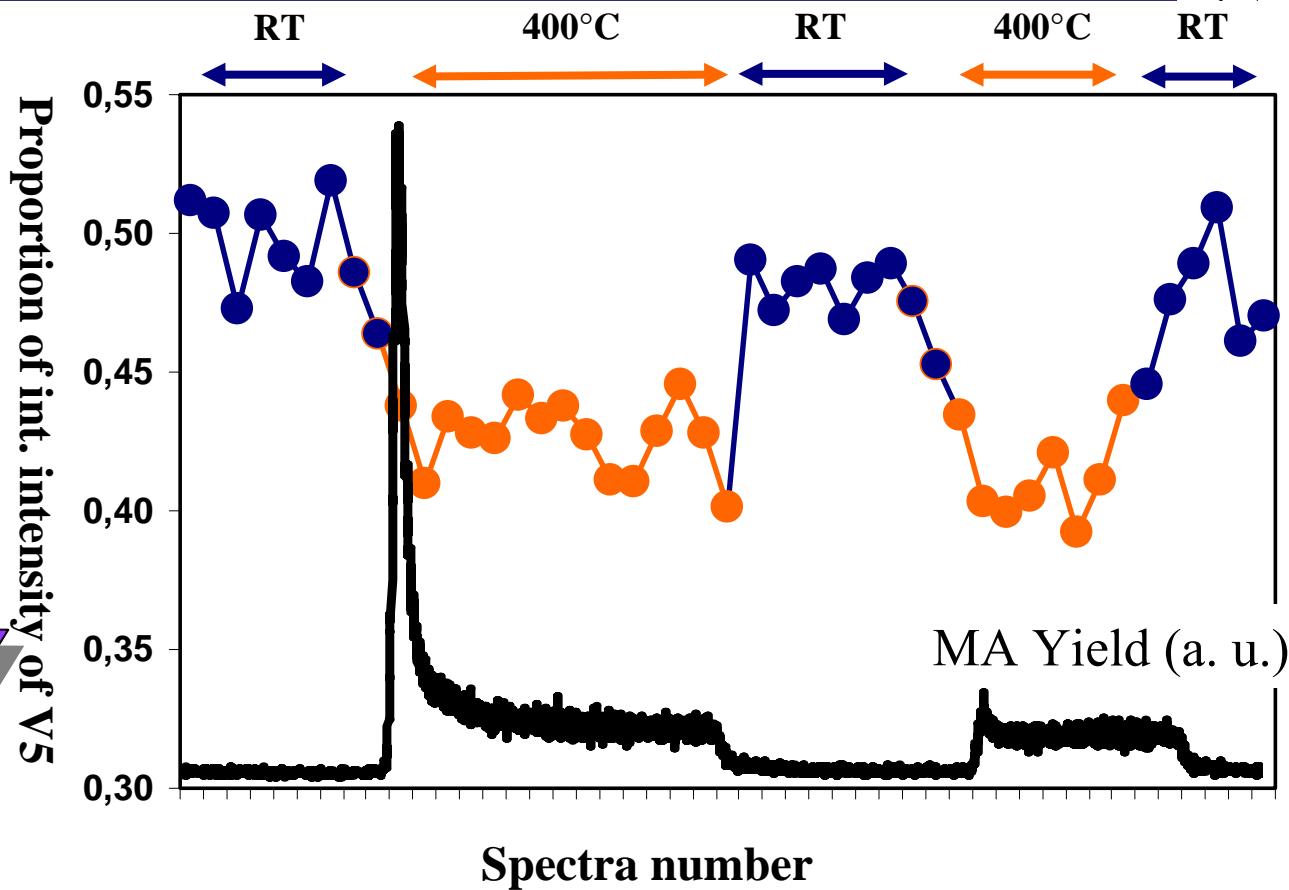Details of the local chemical bonding

Local geometric structure

M. Abbate et al., J. Electron Spectrosc. Rel. Phenom., 62 (1993) 185
M. Hävecker et al., J. Electron Spectrosc. Rel. Phenom., 125 (2002) 79

Changes of NEXAFS while heating

Relative spectral intensity of V_5 at V L_3-edge
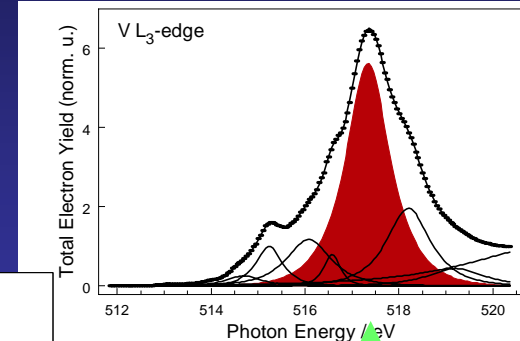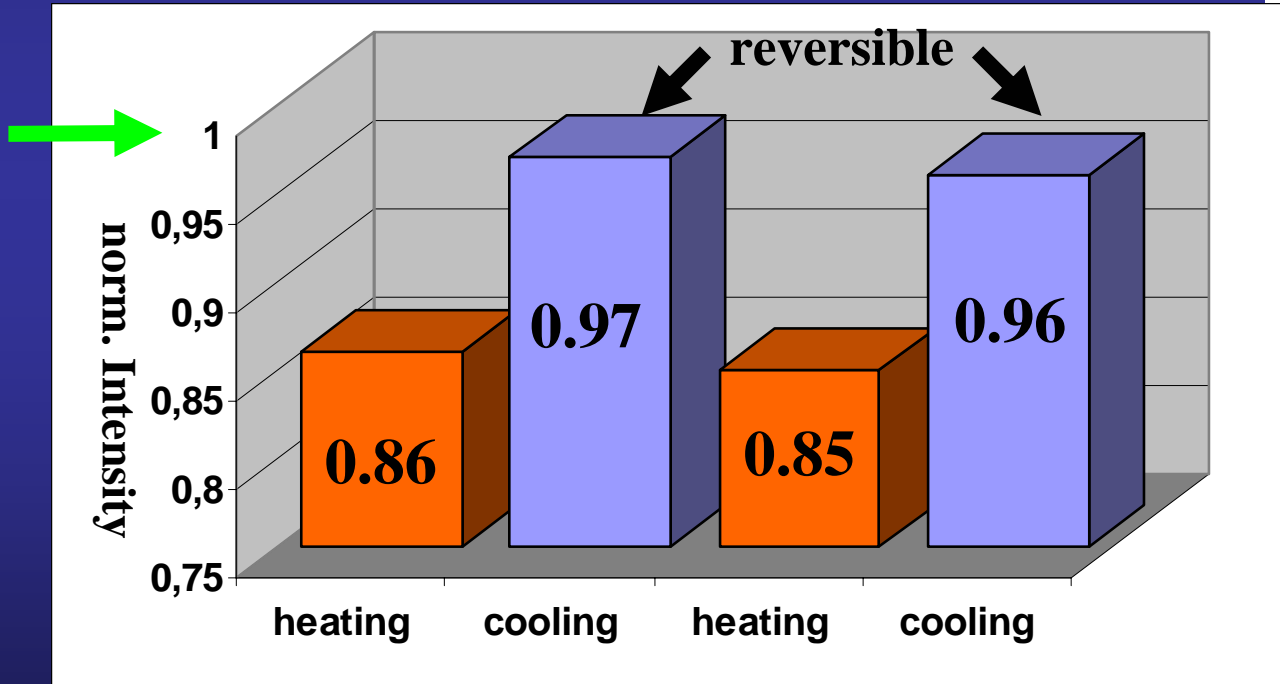
Decrease while active

V L_3-edge

Photon Energy / eV

V_5

RT   400°C   RT   400°C   RT

Proportion of int. intensity of V5

MA Yield (a. u.)

Spectra number

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Changes in NEXAFS: Relative spectral Intensity

rel. Intensity of V_5 before first heating cycle =! 1

reversible

norm. Intensity

0.86   0.97   0.85   0.96

heating   cooling   heating   cooling

V_5

V L_3-edge

heating: RT $\rightarrow$ 400°C
cooling: 400°C $\rightarrow$ RT

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rel. Intensity of V_6 before first heating cycle =! 1

V L$_3$-edge

not reversible, related to attached surface molecules ?

V_6

heating: RT → 400°C
cooling: 400°C → RT

norm. Intensity

1.61   1.28   1.77   1.31

heating   cooling   heating   cooling

Comparison: Catalysts of different performance

Investigation of 3 catalysts of different <u>intrinsic</u> (Y(MA)/surf. area) catalytic activity

$$Y_{MA}(P1) \overset{x\,1.6}{>} Y_{MA}(P2) \overset{x\,1.5}{>} Y_{MA}(P3)$$

(J. A. Lopez-Sanchez et al., to be published)

V_5
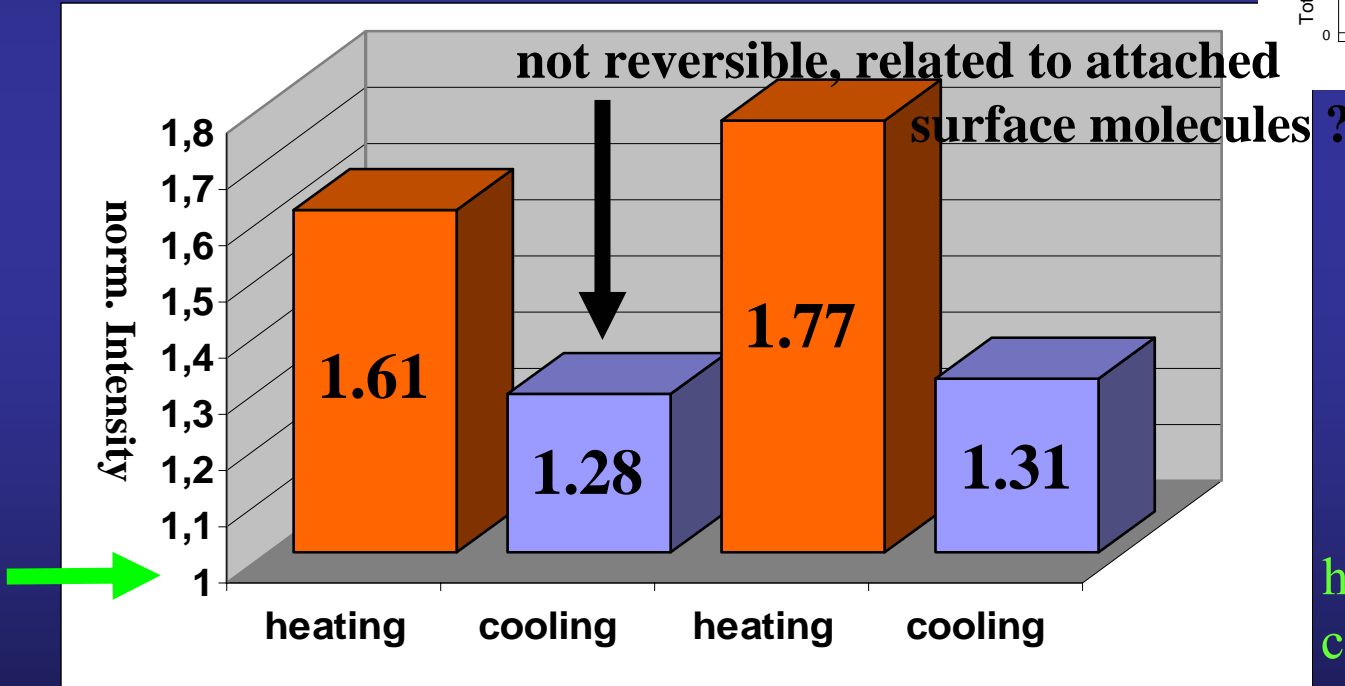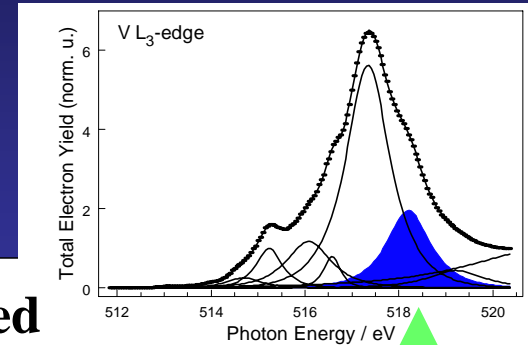
heat.: RT $\rightarrow$ 400°C

cool.: 400°C $\rightarrow$ RT

Comparison: VPO and V_2O_5

Catalytic Characterisation

← simultaneous →

Surface Characterisation

Comparison with Model Systems

Comparison with Model Systems

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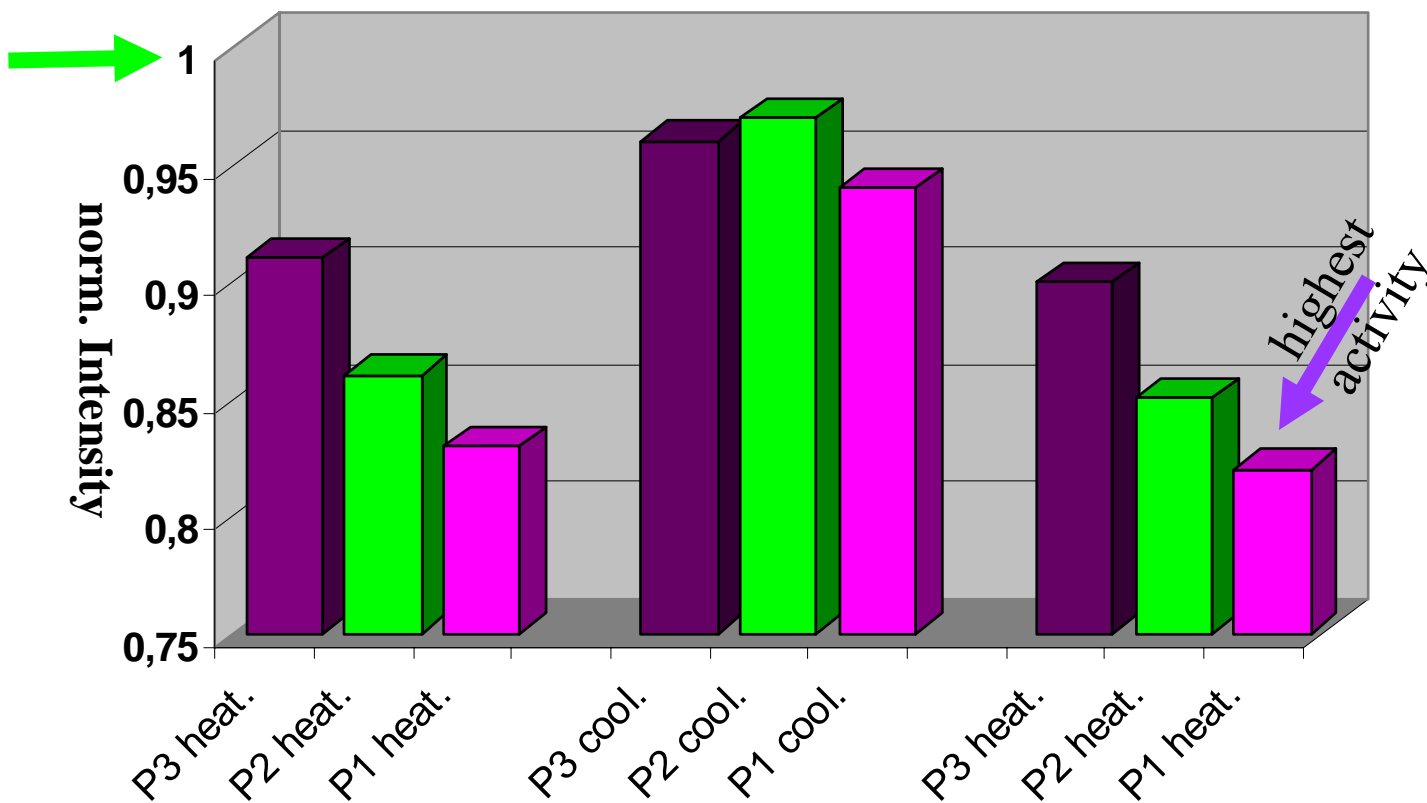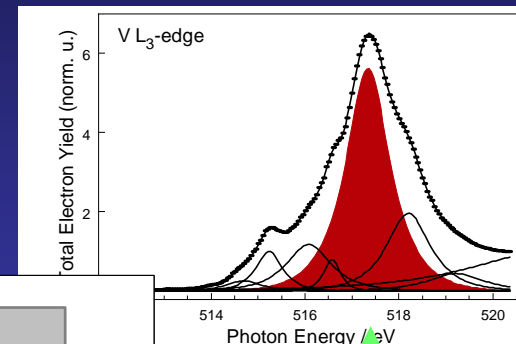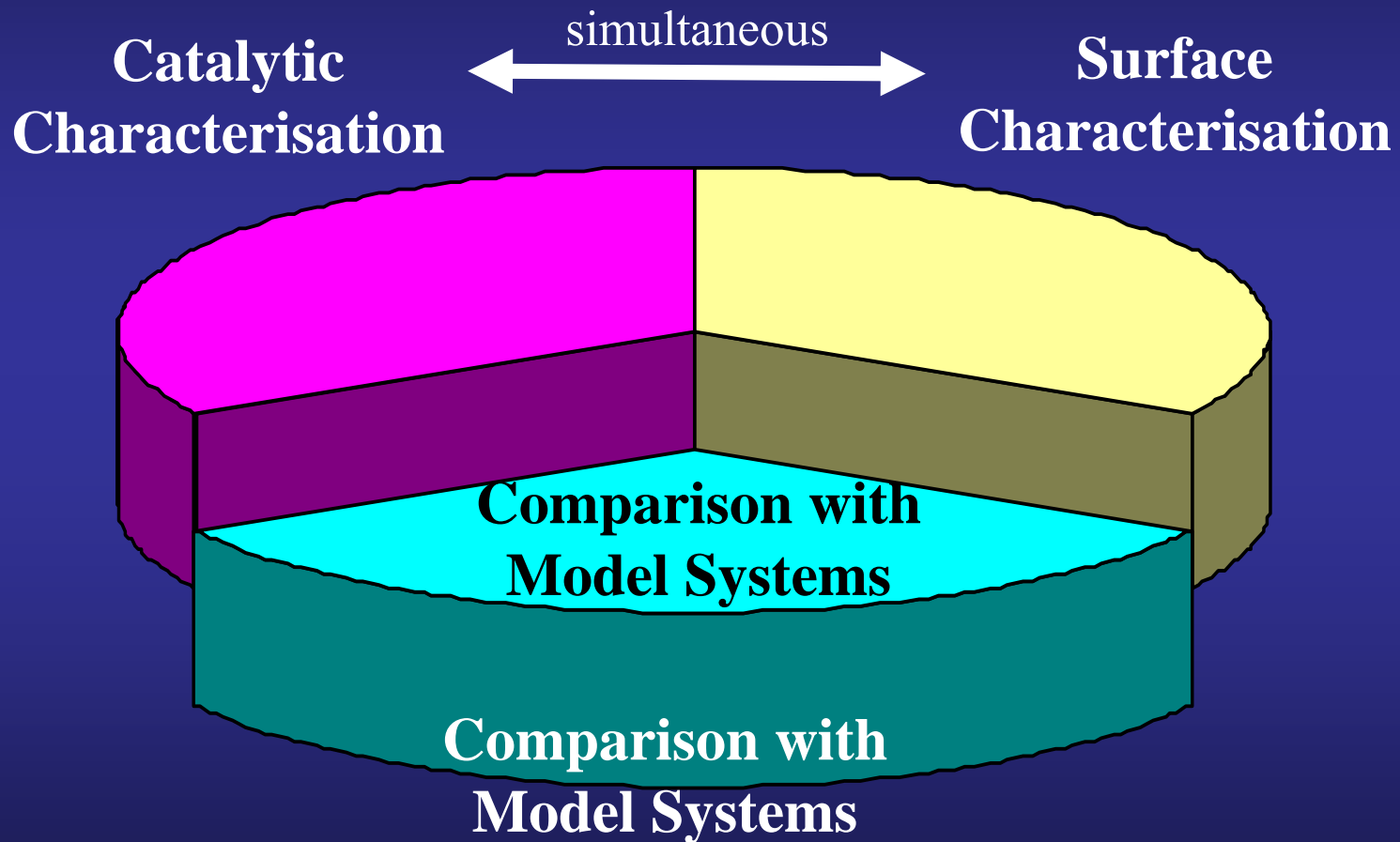
Interpretation of V L$_3$ NEXAFS

Redistribution of spectral weight in NEXAFS
(+ slight shift of resonance position)
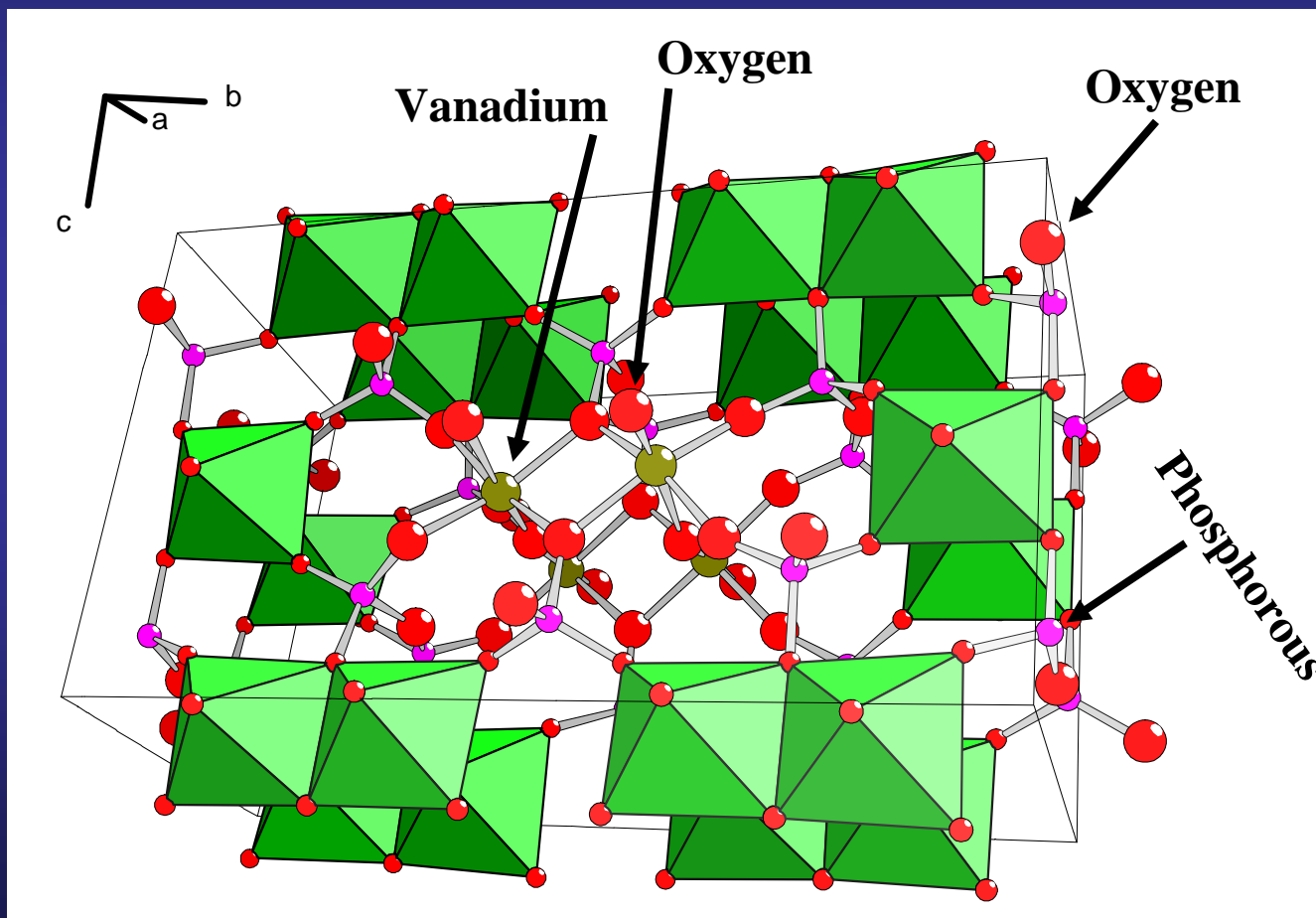
Change of the d-electron density

Change of the local electronic structure

Assignment of certain regions in NEXAFS (resonances (V5, V6))
to specific V-O bonds :
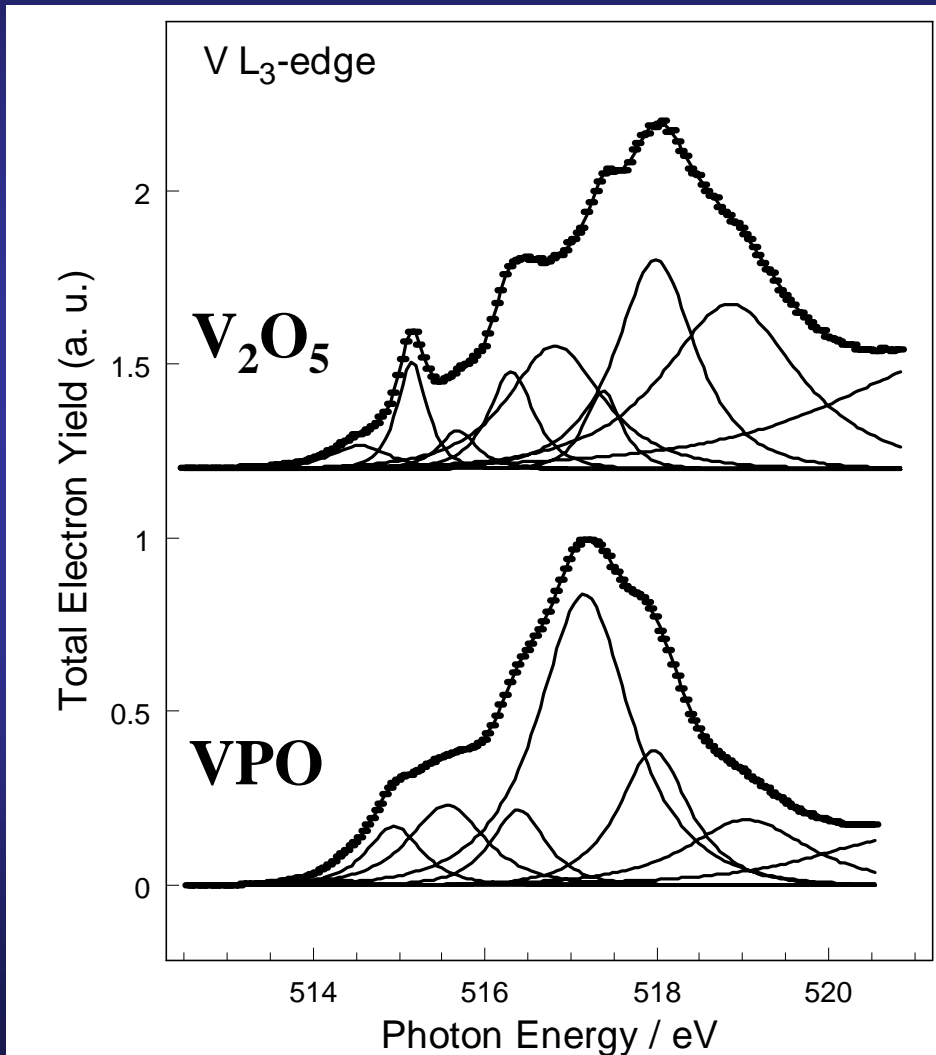
V_2O_5 as model system for VPO

Vanadyl Pyrophosphate Structure

NEXAFS of VPO and V_2O_5

M. Hävecker, Electronic Structure, Dept. AC, Fritz-Haber-Institut (MPG), Berlin, Germany
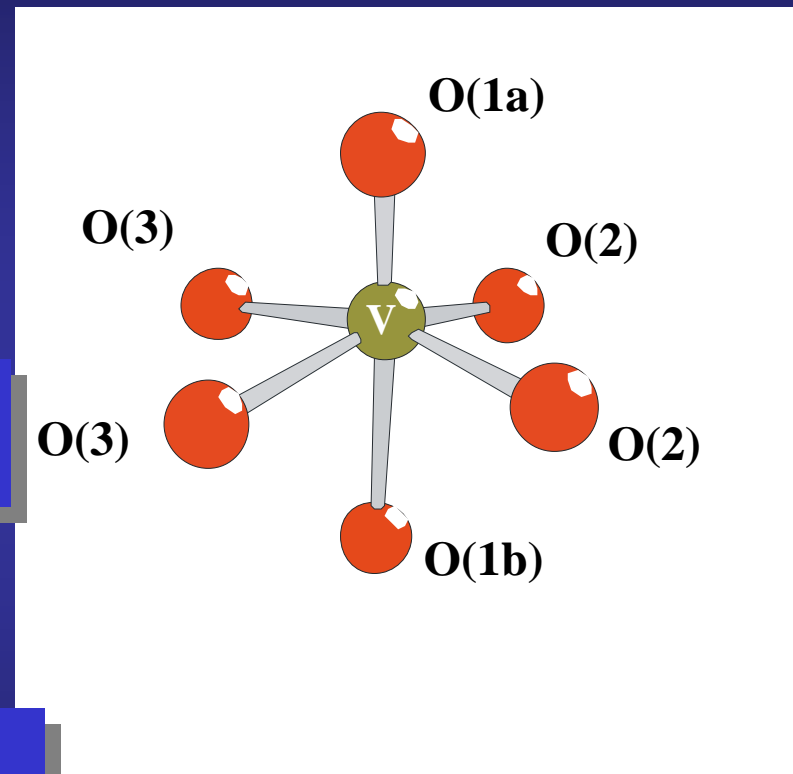
Identification of resonances (V5, V6):

V$_2$O$_5$ as model substance for VPO

DFT calculation of DOS (V$_2$O$_5$!)*:

V$_2$O$_5$: Close relationship between geometric and electronic structure at V L$_3$-absorption edge

$\Rightarrow$ main contributions to NEXAFS resonances appear in a sequence of V-O bond length

$\Rightarrow$ V6: O(1a)
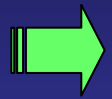$\Rightarrow$ V5: ?
(similar to O(2))

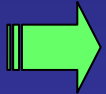M. Hävecker et al., J. Electron Spectrosc. Rel. Phenom., 125 (2002) 79

*Eyert et al., Phys. Rev. B 57 (1998) 12727

Summary

➡️ **NEXAFS changes partially reversible under n-butane oxidation conditions (resonance intensity, resonance position)**
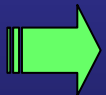
➡️ **Observation of dynamic rearrangements (electronic and/or geometric structure) of VPO catalyst under n-butane oxidation conditions** (M. Hävecker et al., J. Phys. Chem., accepted)

in line with: N.-Y. Topsøe et al., Cat. Lett. 76 (2001) 11 (vanadia DeNOx catalysts)
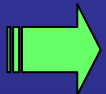
➡️ **Structural flexibility influences the catalytic activity**

➡️ **Unlikely that a stoichiometric bulk phase like $(VO)_2P_2O_7$ facilitates this reversible structural changes**

➡️ **Support for dynamic surface concept** (J.- C. Volta., Catal. Today, 32 (1996) 29)

Thanks !

BESSY staff

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Alexey Pestryakov

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