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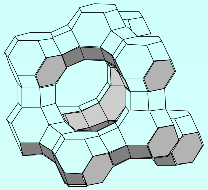

Vanadium phosphates on mesoporous supports: Model catalysts for spectroscopic studies of the selective oxidation of alkanes

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Seminar of SFB 706

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Introduction

**selective oxidation of alkanes
on vanadium-containing
solid catalysts**

**oxidative dehydrogenation
(ODH)**

**alkane alkene
alcohol → aldehyde**

VO$_x$-catalysts

partial oxidation

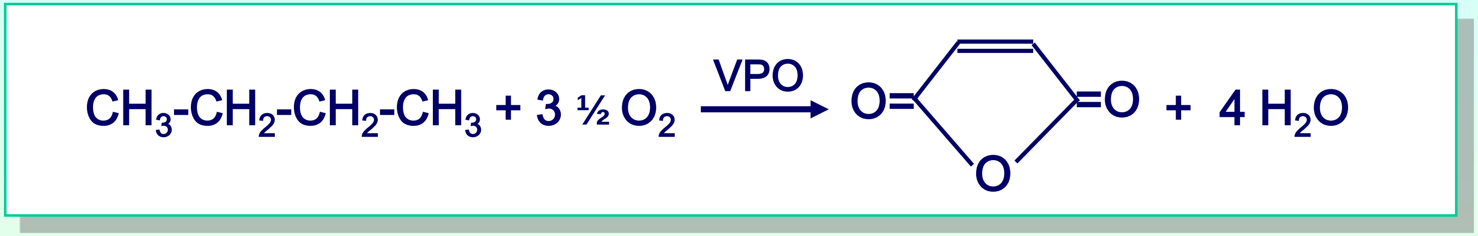
alkane → anhydride

VPO-catalysts

**specific phases and
sites on the catalyst surface**

Selective oxidation of n-butane to maleic anhydride (MA)

- **reaction:**



- possible reaction steps are 1-butene, 1,3-butadiene, dihydrofuran, and furan [1]
- MA is an important intermediate for polyester resin production [1]

- **catalyst:**

- VPO catalysts are prepared by activation of vanadyl hydrogenphosphate hemihydrate $VOHPO_4 \cdot 0.5\ H_2O$ in n-butane/air flow [2]:

reducing atm. → **$(VO)_2P_2O_7$ (vanadyl pyrophosphate)**
oxidizing atm. → **$VOPO_4$ (vanadyl orthophosphate phases)**

- activity increases sharply for P / V ratio reaching > 1

[1] M. Hävecker et al., J. Phys. Chem. B, 107 (2003) 4587.
[2] R.A. van Santen, Handbook of Heterogeneous Catalysis, Springer, 1997, p. 2244.

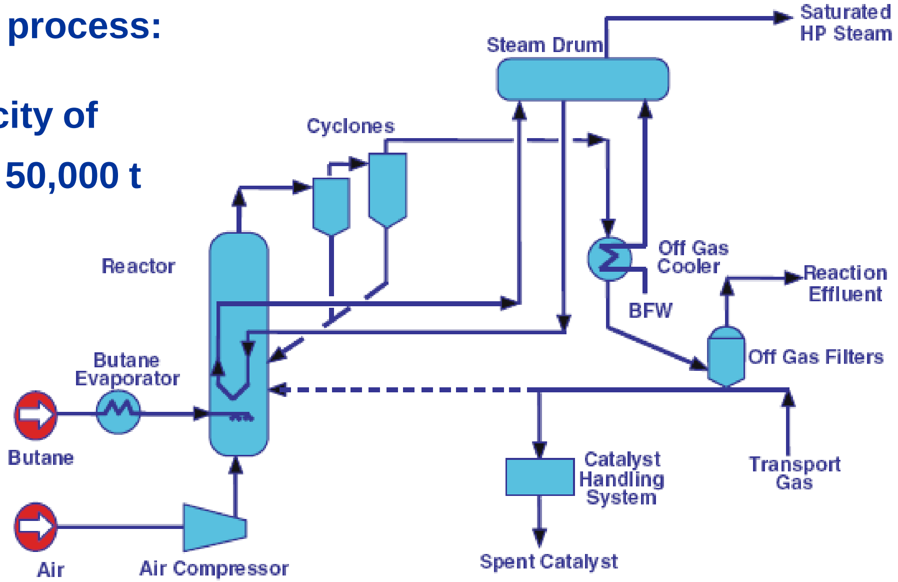
Oxidation of n-butane to maleic anhydride (MA)

- **industrial applications:**
  - **fixed-bed processes by Scientific Design, Huntsman, and BASF**
  - **fluidized-bed processes by Lonza, BP, and Mitsubishi**
  - **transported-bed process by DuPont**

Lonza ALMA process:

annual capacity of

ca. 35.000 to 50,000 t



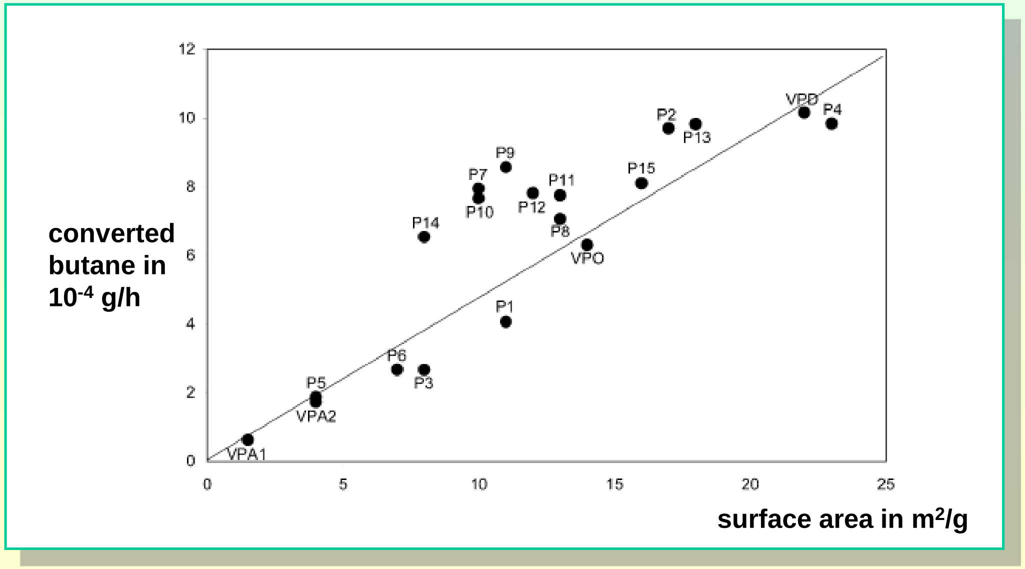
- **process performance:**
  - **53 to 65 % yield to MA with n-butane conversion of maximum 86 %**

N. Ballarina et al., Topics in Catalysis 38 (2006) 147.

Reasons for limited activity

- **local catalyst overheating [1]:**
  - consecutive reactions of combustion (CO, CO_2) decrease the selectivity to MA for conversion over 70-80 %
  - application of thermally conducting supports

- **commercial catalysts have surface areas of 20-30 m^2g^{-1} [2]:**
  - since conversion correlates with surface area, procedures for the preparation of high-area catalysts are required, e.g. on mesoporous supports
  - higher surface areas may allow lower reaction temperatures leading to higher MA selectivities



[1] N. Ballarina et al., Topics in Catalysis 38 (2006) 147; [2] G.J. Hutchings, J. Mater. Chem. 14 (2004) 3385.

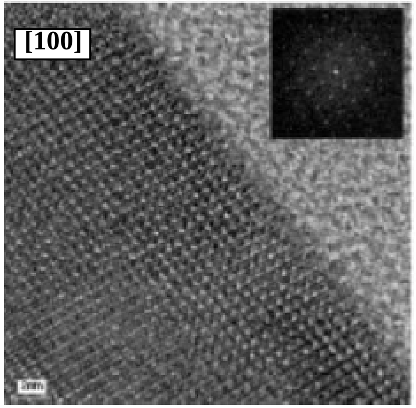
Reasons for limited activity

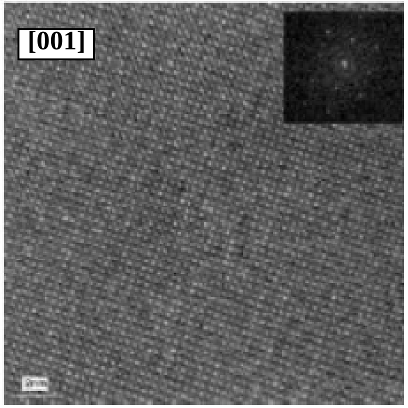
- **considerable controversy concerning the nature of the active component:**

  - **[100] planes of highly crystalline $(VO)_2P_2O_7$ (V^{4+}) [1]**
  - **V^{5+} defect sites and phases in the above-mentioned crystallites [2]**
  - **crystallites with $(VO)_2P_2O_7$ in [100] planes and $VOPO_4$ along [001] planes [2]**

TEM in VPO
sample P10 [2]:

$(VO)_2P_2O_7$ image
along [100] plane





TEM in VPO
sample P10 [2]:

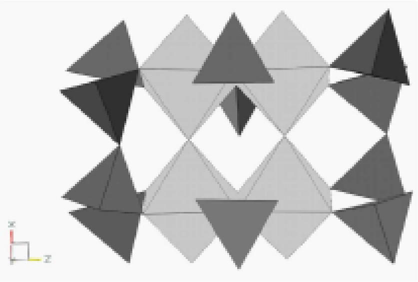
α_{II}-$VOPO_4$ image
along [001] plane

- **MA selectivity depends on concentration of V^{5+} sites [3, 4]**

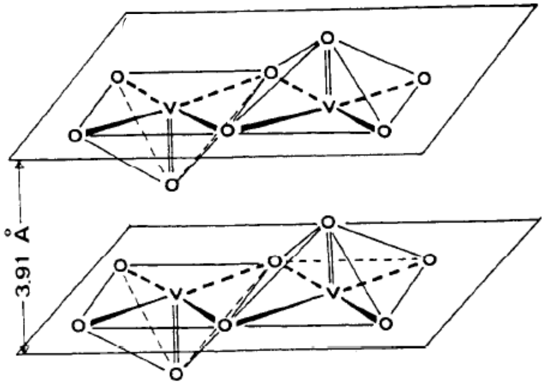
**[1] V.V. Guliants et al., Catal. Today 28 (1996) 275; ([2] G.J. Hutchings, J. Mater. Chem. 14 (2004) 3385;
[3] G.W. Coulston et al., Science 275 (1997) 191; [4] G. Bignardi et al., J. Mol. Catal. A 244 (2006) 244.**

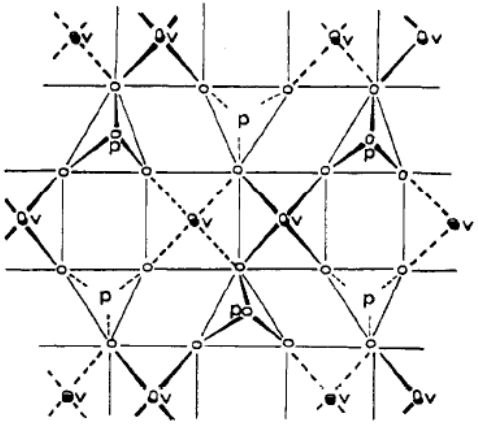
Structure of $(VO)_2P_2O_7$ phases

pairs of edge-sharing octahedra forming chains of alternating short and long V-O bonds



$(VO)_2P_2O_7$



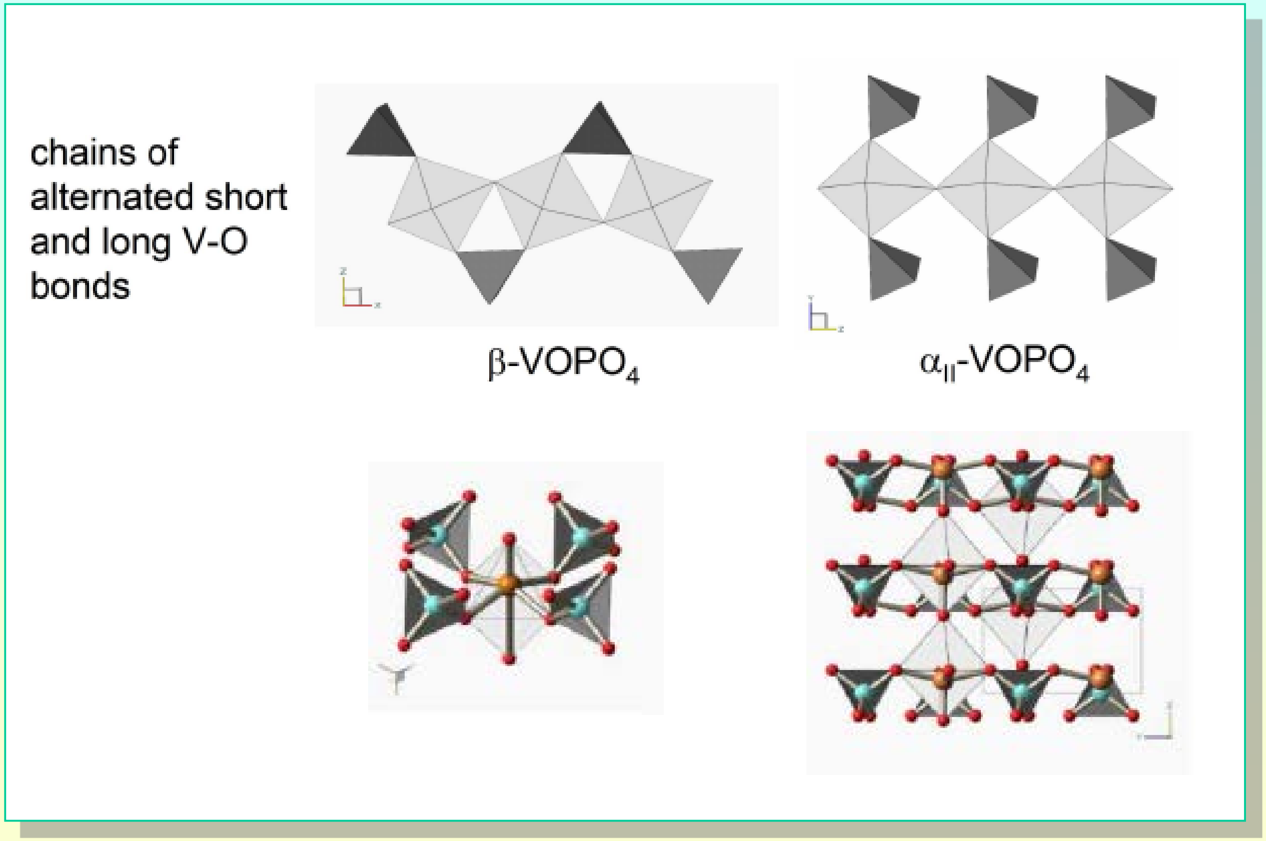


- the V^{4+} phase $(VO)_2P_2O_7$ presents a structure in which VO_6 octahedra are joined by the edges

- pairs of VO_6 octahedra are connected by PO_4 tetrahedra which gives a layer structure in the [100] plane

M.-G. Willinger, PhD Thesis, University of Berlin, 2005
G. Busca et al., J. Phys. Chem. 90 (1986) 1337.

Structure of $VOPO_4$ phases



chains of alternated short and long V-O bonds

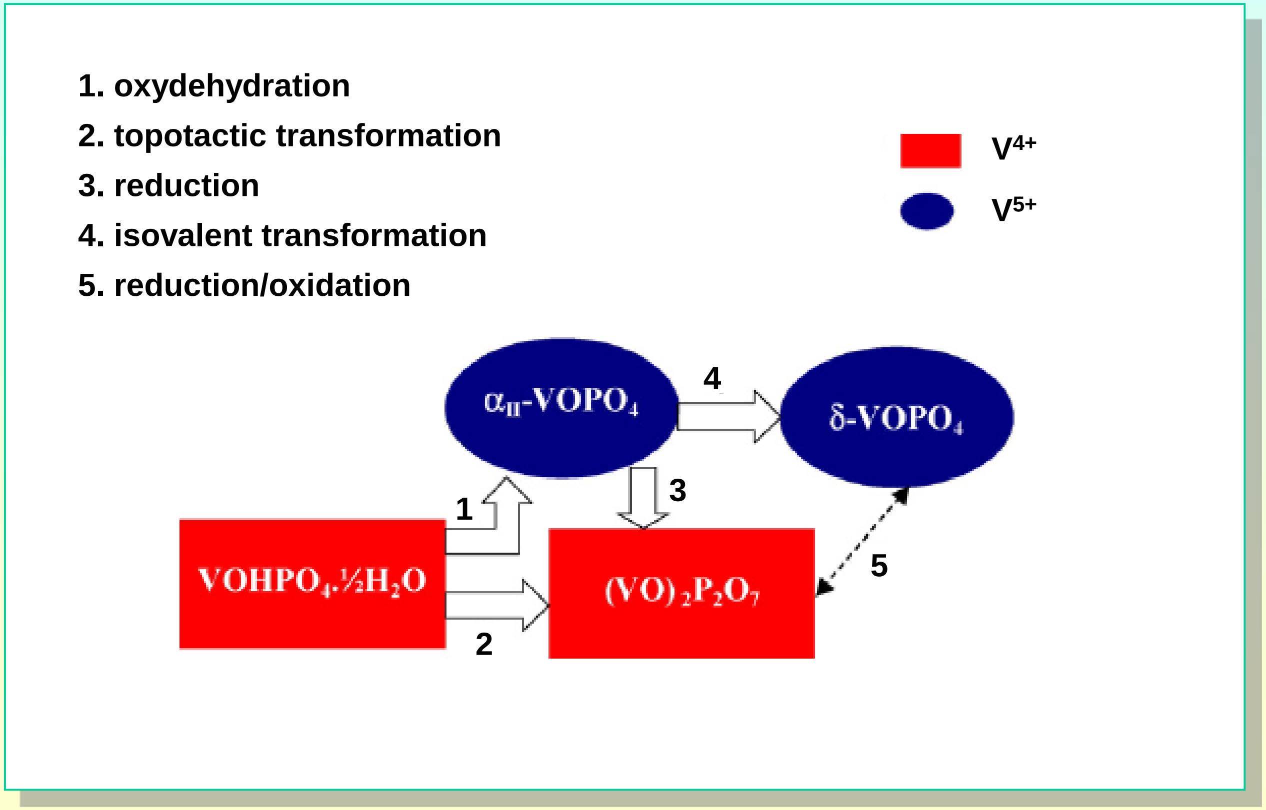
- the V^{5+} phases like vanadyl phosphates $VOPO_4$ are formed by single octahedron linked to the orthophosphate group

- each equatorial oxygen of VO_6 shares a corner of one PO_4

M.-G. Willinger, PhD Thesis, University of Berlin, 2005.

Structural transformations

- suggested transformations of the $VOHPO_4 \cdot 0.5\ H_2O$ precursor during the formation of the final VPO catalyst and the reaction cycle:



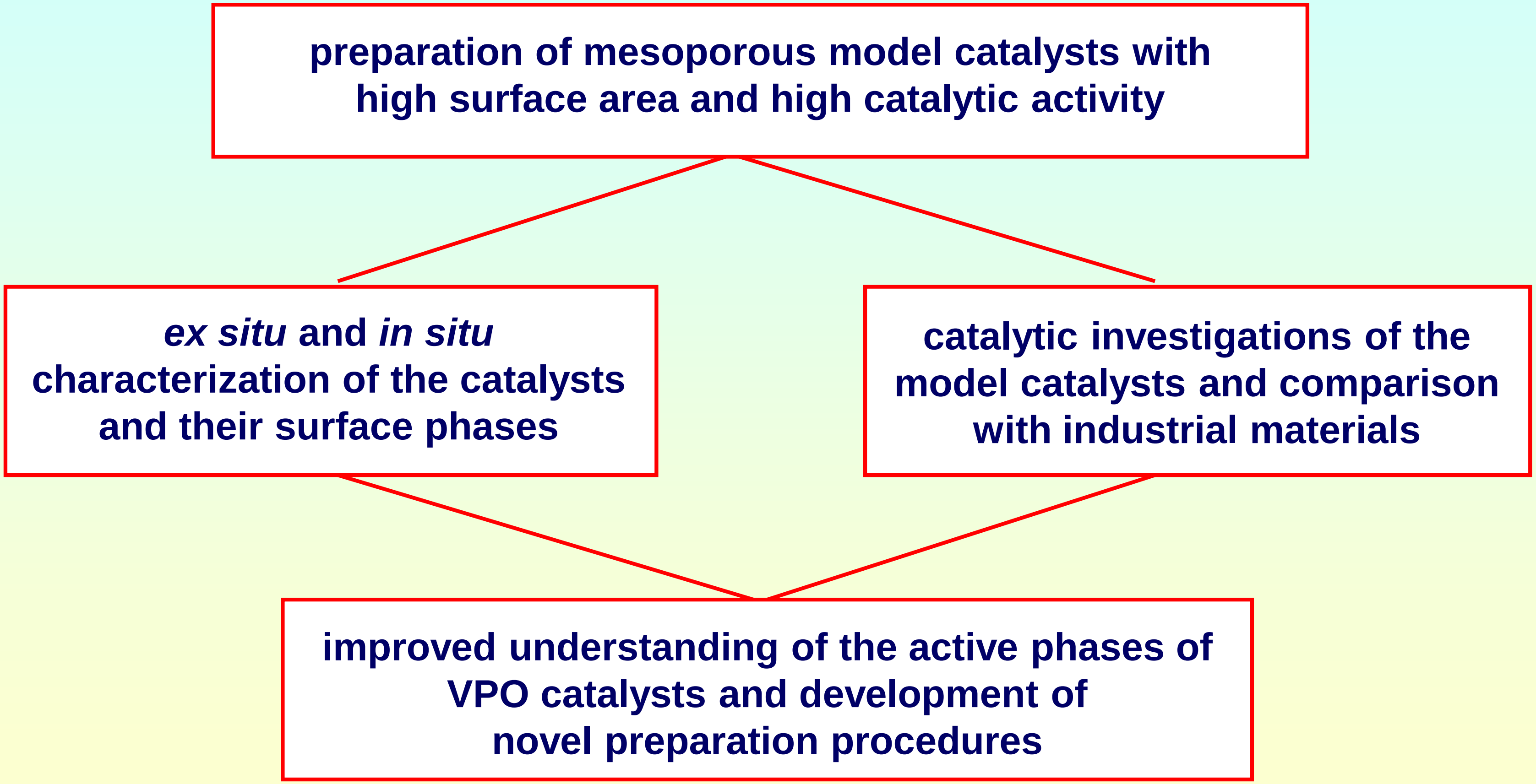
1. oxydehydration
2. topotactic transformation
3. reduction
4. isovalent transformation
5. reduction/oxidation

🟥 V^{4+}

● V^{5+}

C.J. Kiely, G.J. Hutchings, Appl. Catal. A: General 325 (2007) 194.

Aims of the suggested project



preparation of mesoporous model catalysts with high surface area and high catalytic activity

ex situ **and** ***in situ*** **characterization of the catalysts and their surface phases**

catalytic investigations of the model catalysts and comparison with industrial materials

improved understanding of the active phases of VPO catalysts and development of novel preparation procedures

Possible steps of the project I

- development of new procedures for the preparation of supported and compact mesoporous VPO catalysts:
  - mesoporous supports with high surface area (SBA-15, MCM-41 etc.)
  - procedures leading to supported/compact $(VO)_2P_2O_7$ (V^{4+})
  - procedures leading to supported/compact $VOPO_4$ phases (V^{5+})
  - procedures leading to mixtures of V^{4+} and V^{5+} phases
  - preparation of VPO/support systems with different VPO contents

- characterization of the mesoporous supports by REM (TEM), XRD, nitrogen adsorption:
  - morphology of supports and compact mesoporous VPO materials
  - crystalline VPO phases and particle sizes
  - specific surface area before and after loading of the supports with VPO phases

- catalytic studies (n-butane conversion) of the VPO/support systems:
  - comparison of the various VPO/support systems, if possible, also with an industrial catalyst

Possible steps of the project II

- **spectroscopic studies:**
  - effect of the preparation procedure on the nature and contents of different vanadium species
  - VPO/support interactions
  - surface phases involved in the adsorption and conversion of reactants
  - adsorbate complexes formed by reactants on the catalyst surface
  - conversion of n-butane on the most active catalyst systems

- **suggested co-operations with groups of SFB 706:**
  - preparation and characterization of mesoporous supports, Dr. V. Urlacher
  - ESR and Raman spectroscopic studies of vanadium species, Prof. Dr. E. Roduner
  - quantum-chemical studies of surface complexes formed by adsorption of n-butane at the surface sites of supported VPO compounds, PD Dr. G. Rauhut
  - access to TEM equipment (?)

Contribution of NMR spectroscopy

- **NMR methods:**

  - **^{1}H and ^{29}Si MAS NMR investigations of the surface OH groups and support material and solid-state ^{13}C NMR studies of reactants**

  - **^{51}V MAS NMR investigations of V^{5+} species: Isotropic chemical shift δ_{iso}, shift anisotropy $\Delta\delta$, quadrupole coupling constant C_{QCC}, and asymmetry parameter η**

Material	δ_{iso}	$\Delta\delta$	η_δ	C_{QCC}	η_Q	References
α_I-$VOPO_4$	-691 ppm	880 ppm	0.00	1.55 MHz	0.55	[1]
α_{II}-$VOPO_4$	-755 ppm	992 ppm	0.08	0.63 MHz	0.09	[2]
β-$VOPO_4$	-735 ppm	818 ppm	0.05	1.45 MHz	0.44	[2]
γ-$VOPO_4$/1	-755 ppm	955 ppm	0.15	0.55 MHz	0.68	[2]
γ-$VOPO_4$/2	-739 ppm	942 ppm	0.07	1.32 MHz	0.55	[2]

  - **$\Delta\delta$ values of 900 to 1300 ppm indicate distorted VO_6 octahedra**

[1] O.B. Lapina et al., J. Mol. Catal. A: Chem. 162 (2000) 381.
[2] R. Siegel et al., Magn. Reson. Chem. 42 (2004) 1022.

Contribution of NMR spectroscopy

- NMR methods:

  - ^{31}P spin-echo NMR studies of phosphorous atoms at vanadium V^{5+}, V^{4+}, and V^{5+} species existing upon different preparation steps and before and after application of VPO catalysts:

^{31}P spin-echo NMR signals	Phosphorous species and phases	References
-20 to 5 ppm	P at V^{5+} in $VOPO_4$ phases	[1]
200-1500 ppm	P at V^{4+}/V^{5+} dimers in poorly crystalline $(VO)_2P_2O_7$	[1]
1625 ppm	P at V^{4+} in $VOHPO_4 \cdot 0.5\ H_2O$	[2]
2300 ppm	P at V^{4+} in $VO(H_2PO_4)_2$	[2]
2400 ppm	P at V^{4+} in poorly crystalline $(VO)_2P_2O_7$	[1]
2600 ppm	P at V^{4+} in crystalline $(VO)_2P_2O_7$	[2]
4650 ppm	P at V^{3+} in VPO_4	[2]

Contribution of NMR spectroscopy

- ^{31}P MAS NMR studies of phosphorous atoms at vanadium V^{5+} species in $VOPO_4$ phases:

^{31}P MAS NMR signals	V^{5+} phases	References
-20.5 ppm	α_{II}-$VOPO_4$	[3]
-11.5 ppm	β-$VOPO_4$	[3]
-21.2 ppm, -17.3 ppm (ca. 1:1) -14.9 ppm (very weak shoulder)	γ-$VOPO_4$	[3]
-17.6 ppm, -8.4 ppm (ca. 1:1) -6.5 ppm (very weak shoulder)	δ-$VOPO_4$	[3]
2.7 to 3.6 ppm	α_I-$VOPO_4$	[4, 5, 6]
3.9 ppm	$VOPO_4 \cdot n\ H_2O$	[4]

[1] M.T. Sananes-Schulz et al., J. Catal. 166 (1997) 388.
[2] M.T. Sananes, A. Tuel, Solid State Nuclear Magn. Reson., 6 (1996) 157.
[3] F. Ben Abdelouahab et al., J. Catal. 134 (1992) 151.
[4] S.A. Ennaciri et al., Eur. J. Solid State Inorg. Chem. 30 (1993) 227.
[5] K.E. Birkeland et al., J. Phys. Chem. B 101 (1997) 6895.
[6] K. Ait-Lachgar et al., J. Catal. 177 (1998) 224.

First investigations of supported VPO catalysts

- **preparation of VPO/SBA-15 catalysts according to Ref. [1]:**

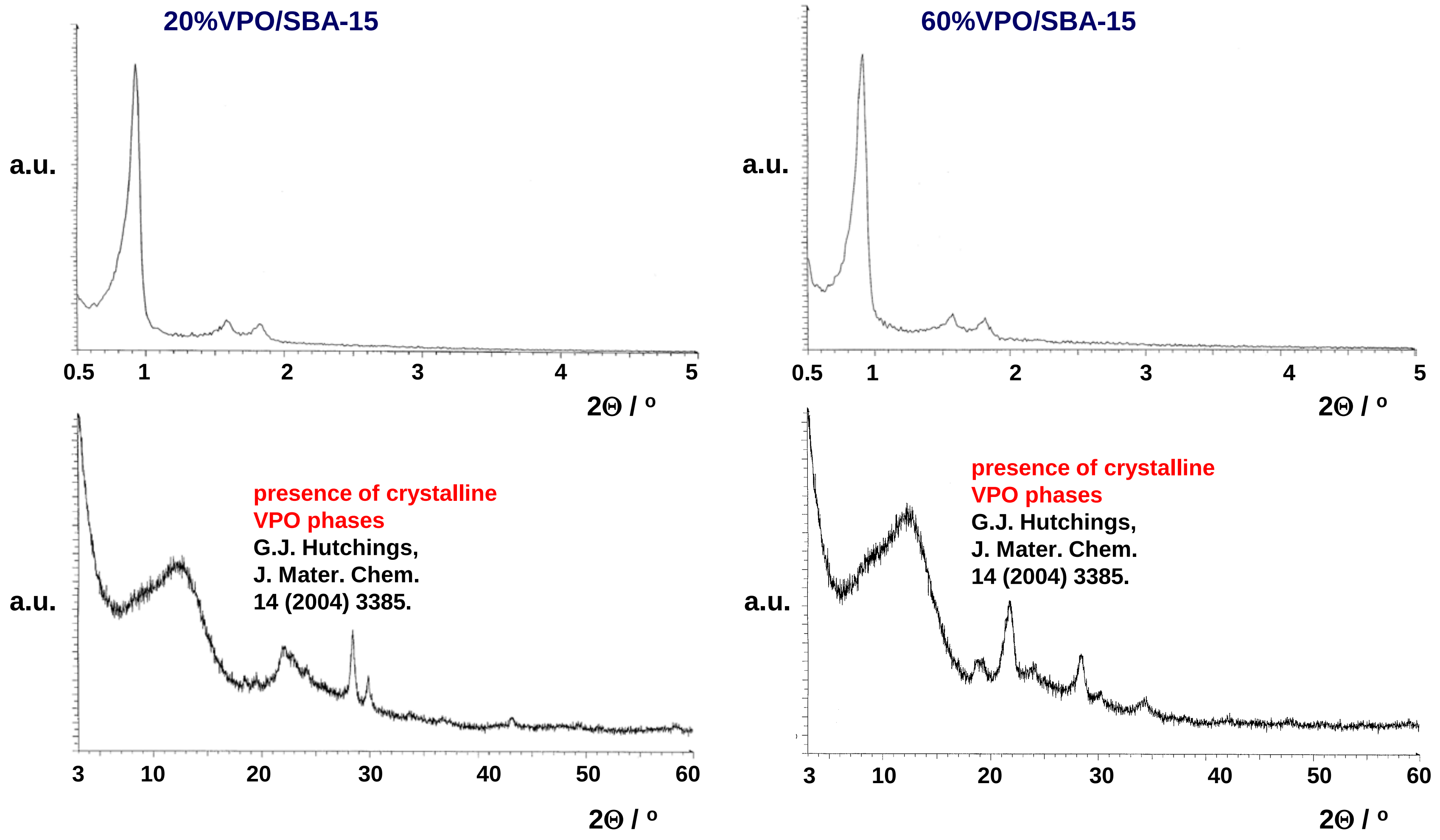
  - **siliceous SBA-15 is added to isobutyl/benzyl alcohols (1 : 1) with V_2O_5, PEG 6.000 and H_3PO_4**
  - **VPO loadings of 20 to 60 wt.%**
  - **activation in a flow of 1.5 % n-butane, 17.5 % O_2 and balance N_2 (100 ml/min) at 673 K for 15 h**

- **ICP-AES and nitrogen adsorption:**

Samples	P / V	BET surface m^2 / g	Pore volume cm^3 / g
SBA-15	-	1164	1.25
20%VPO/SBA-15	1.09	662	0.80
60%VPO/SBA-15	1.04	456	0.54

[1] X.-K. Li et al., J. Catal. 238 (2006) 232.

XRD studies of VPO/SBA-15



20%VPO/SBA-15

60%VPO/SBA-15

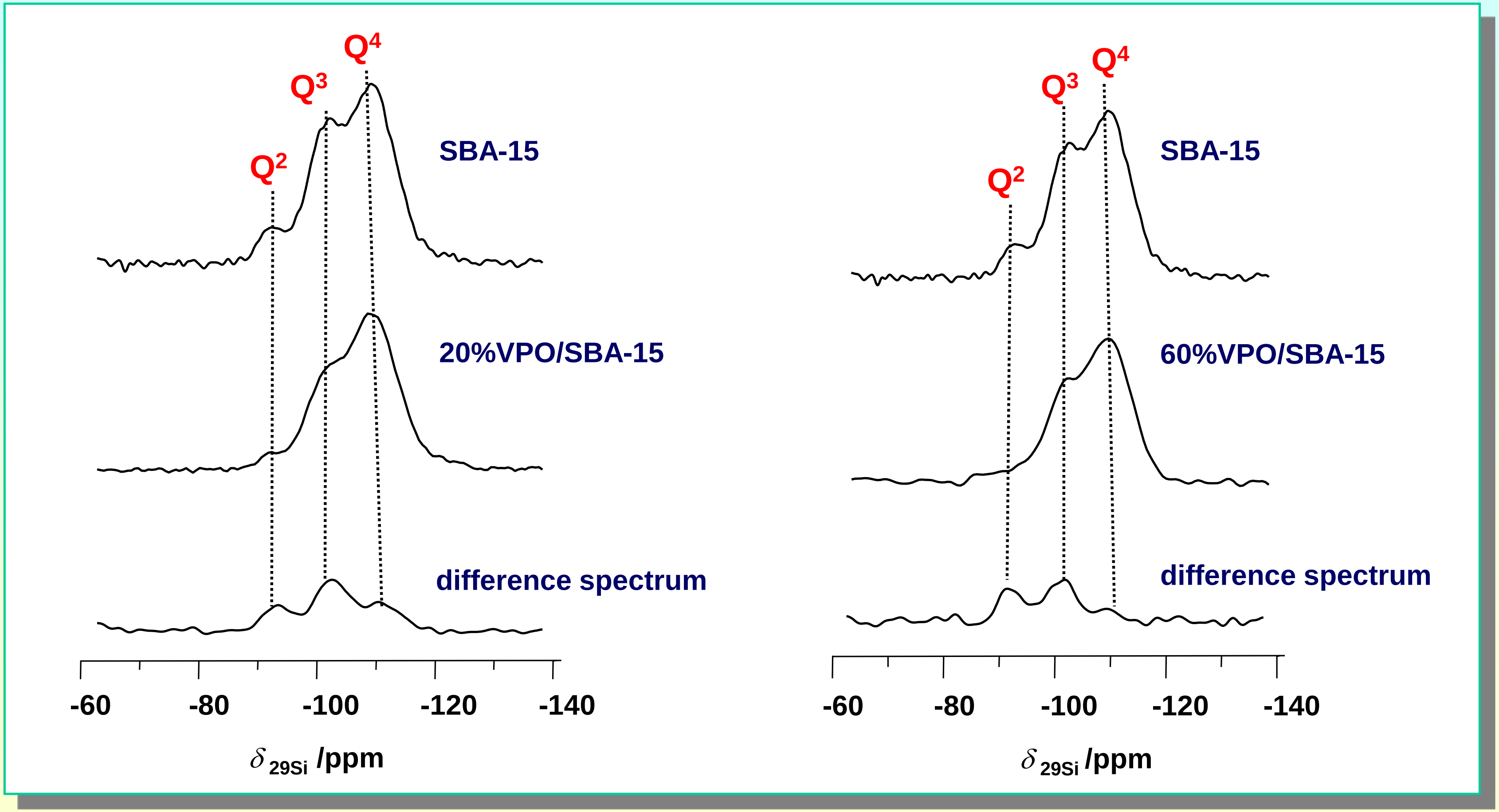
presence of crystalline VPO phases

G.J. Hutchings, J. Mater. Chem. 14 (2004) 3385.

presence of crystalline VPO phases

G.J. Hutchings, J. Mater. Chem. 14 (2004) 3385.

^{29}Si MAS NMR of VPO/SBA-15

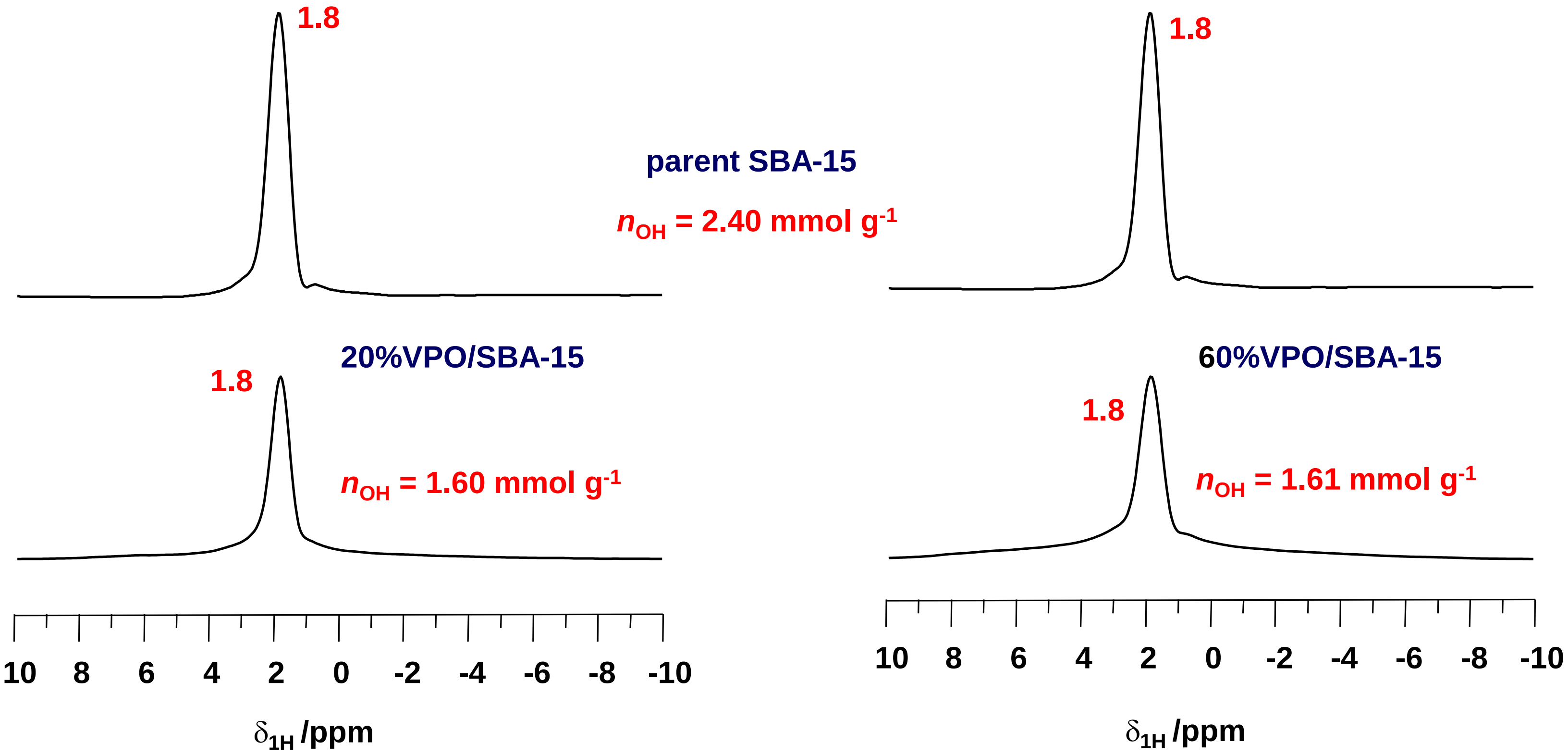


→ **VPO compounds cover the mesoporous support and are not separate phases**

^1H MAS NMR of VPO/SBA-15

VPO/SBA-15 materials were dehydrated at 723 K for 12 h

ν_0 = 400.31 MHz, D0 = 10 s, NS = 250



parent SBA-15

n_{OH} = 2.40 mmol g^{-1}

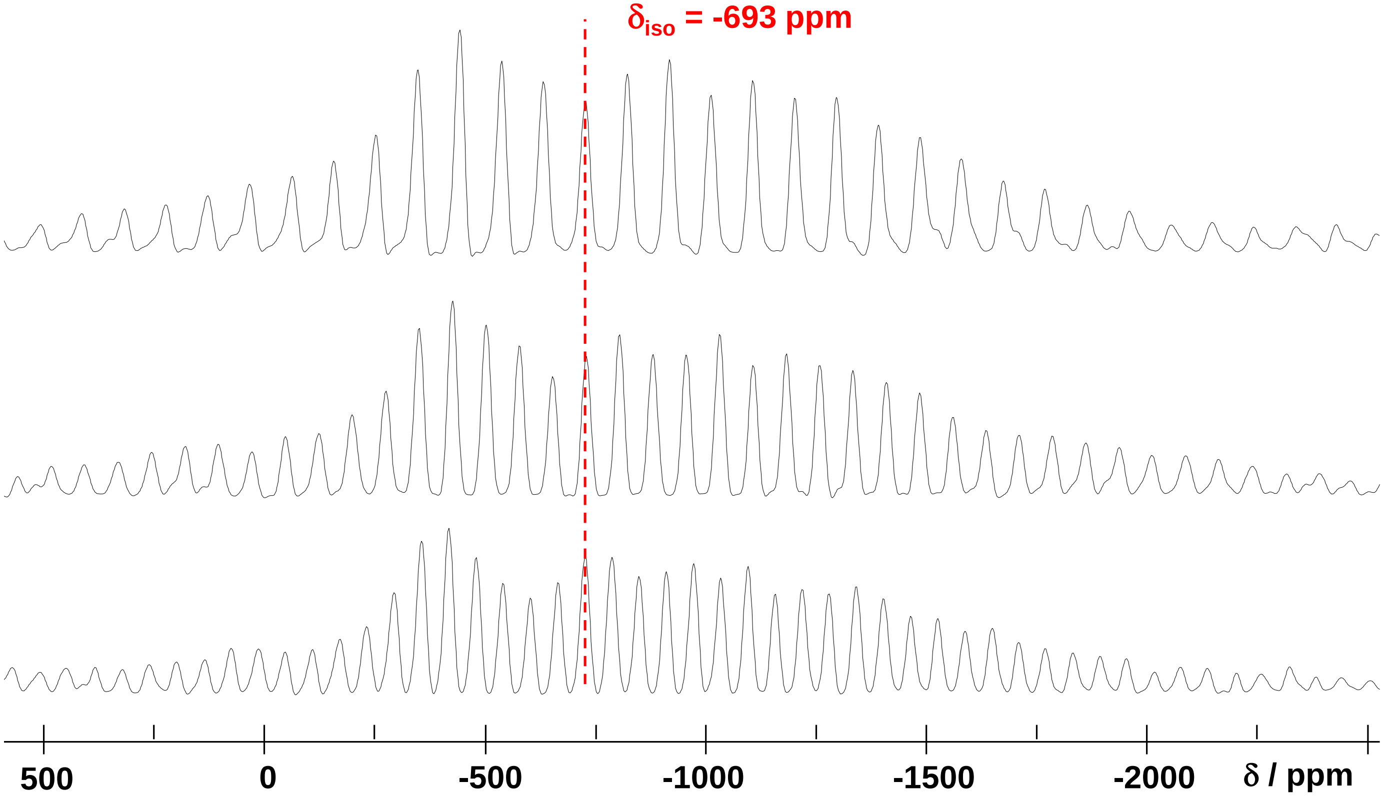
20%VPO/SBA-15

n_{OH} = 1.60 mmol g^{-1}

60%VPO/SBA-15

n_{OH} = 1.61 mmol g^{-1}

^{51}V MAS NMR of 20%VPO/SBA-15

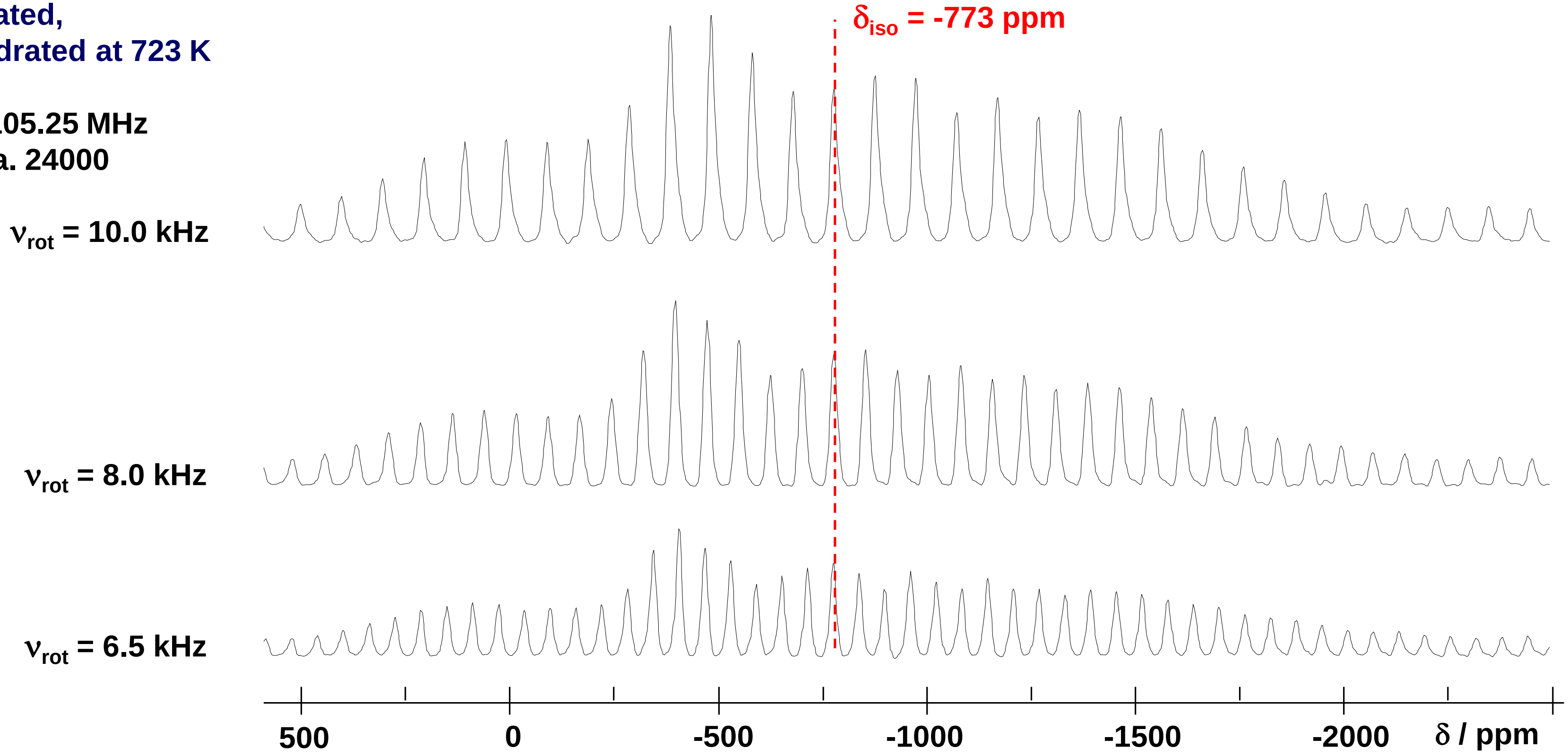


Material	δ_{iso}	$\Delta\delta$	η_δ	C_{QCC}	η_Q
20%VPO/SBA-15	-693 ppm	-830 ppm	0.07	1.99 MHz	0.71

^{51}V MAS NMR of 60%VPO/SBA-15

activated,
dehydrated at 723 K

ν_0 = 105.25 MHz
NS ca. 24000

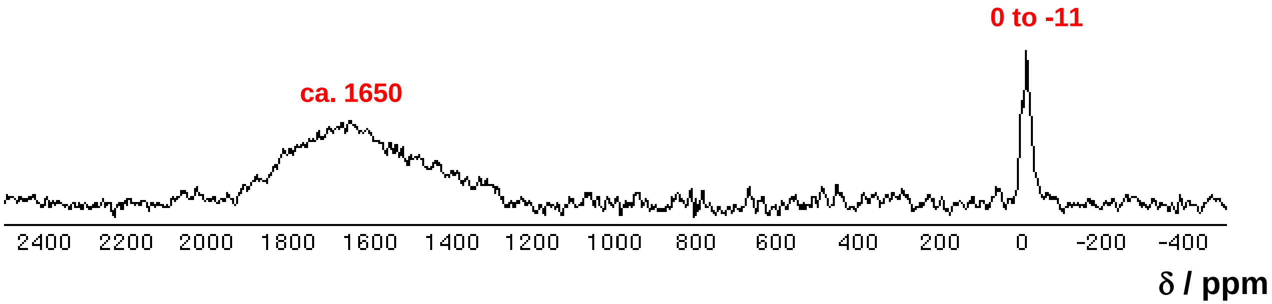


Material	δ_{iso}	$\Delta\delta$	η_δ	C_{QCC}	η_Q
60%VPO/SBA-15	-773 ppm	-900 ppm	0.10	1.99 MHz	0.59

^{31}P MAS NMR of 60%VPO/SBA-15

non-activated precursor

ν_0 = 161.98 MHz
ν_{rot} = 10 kHz
NS ca. 1000

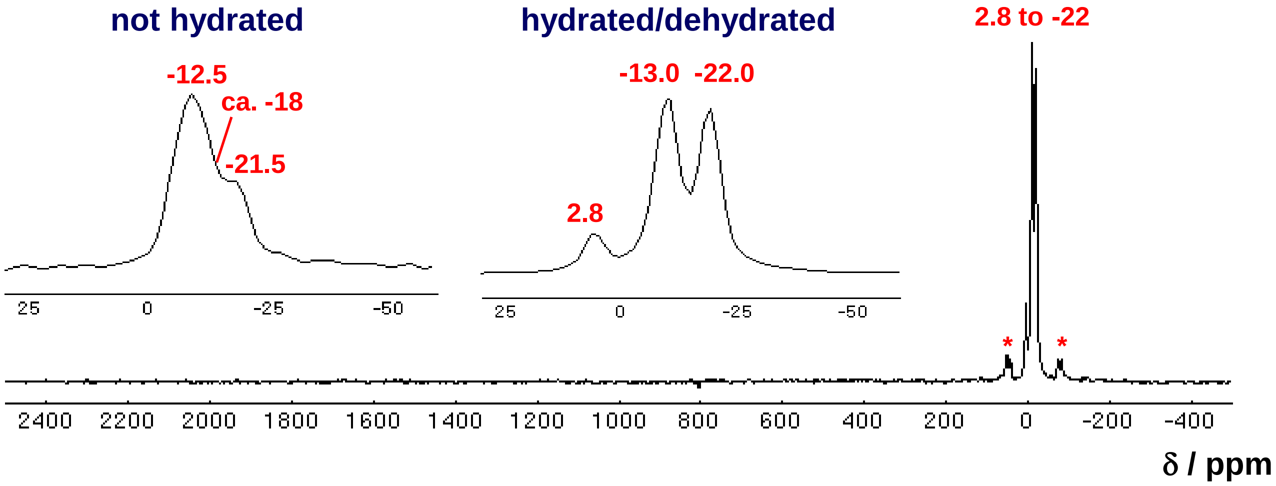


P at V^{4+} in $VOHPO_4$ 0.5 H_2O

P at V^{5+} in $VOPO_4$

activated at 673 K for 15 h

ν_0 = 161.98 MHz
ν_{rot} = 10 kHz
NS ca. 1000


not hydrated

hydrated/dehydrated

P at V^{5+} in α_I-$VOPO_4$ (2.8 ppm), β-$VOPO_4$ (-13 ppm), δ-$VOPO_4$ (ca. -18 ppm) and α_{II}-$VOPO_4$ (-22 ppm)

^{13}C MAS NMR of n-butane on 60%VPO/SBA-15

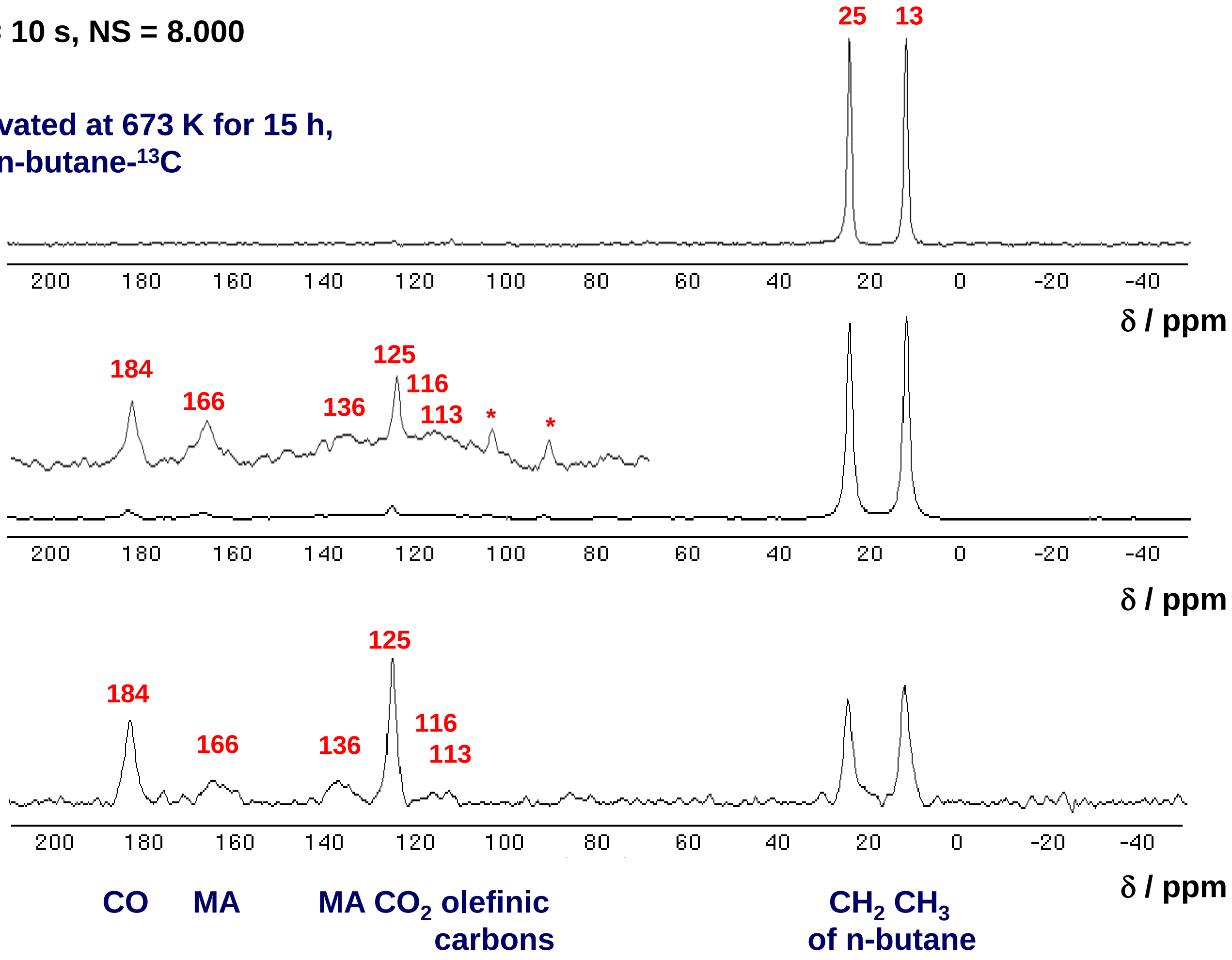
ν_0 = 100.61 MHz, D0 = 10 s, NS = 8.000

60%VPO/SBA-15 activated at 673 K for 15 h, loaded with 60 mbar n-butane-^{13}C

no heating

heated at 523 K for 20 min

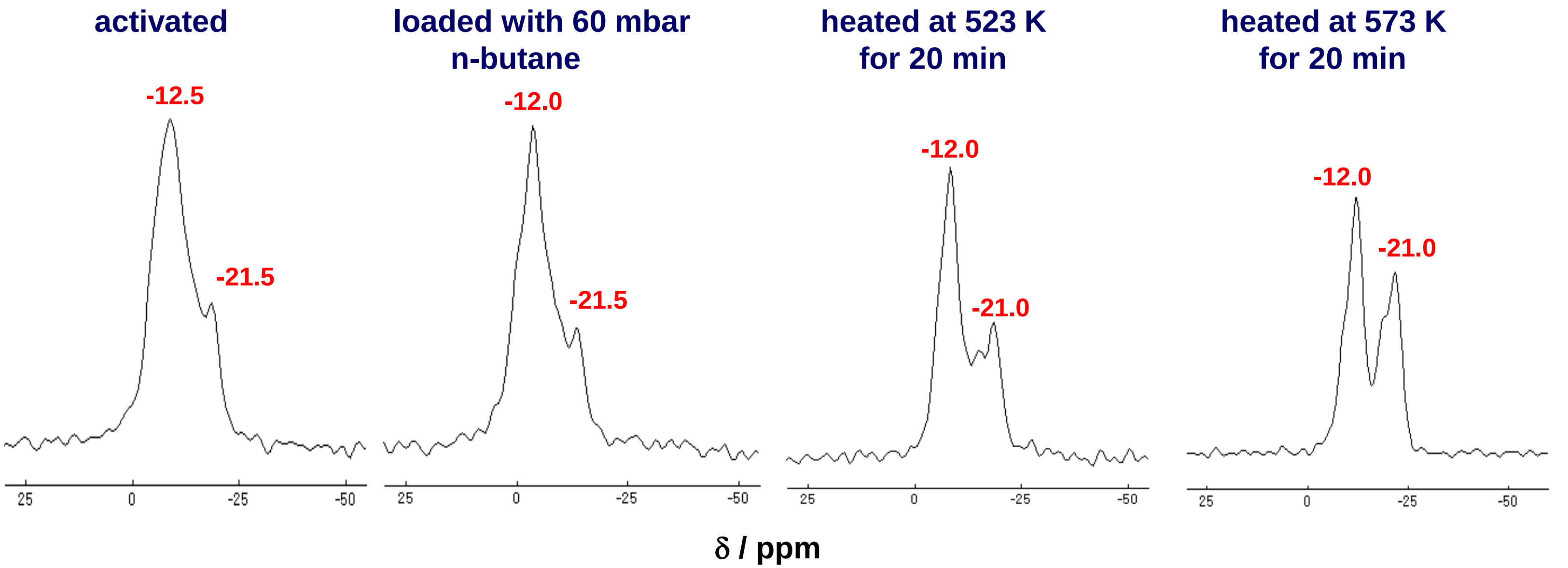
heated at 573 K for 20 min



^{31}P MAS NMR of 60%VPO/SBA-15

60%VPO/SBA-15 activated at 673 for 15 h

ν_0 = 161.98 MHz, ν_{rot} = 10 kHz, NS = 200



activated | **loaded with 60 mbar n-butane** | **heated at 523 K for 20 min** | **heated at 573 K for 20 min**

-21.5 to -21.0 ppm: P at V^{5+} in α_{II}- and γ-$VOPO_4$

-8 and -18 ppm: P at V^{5+} in δ-$VOPO_4$ → decrease upon conversion of n-butane

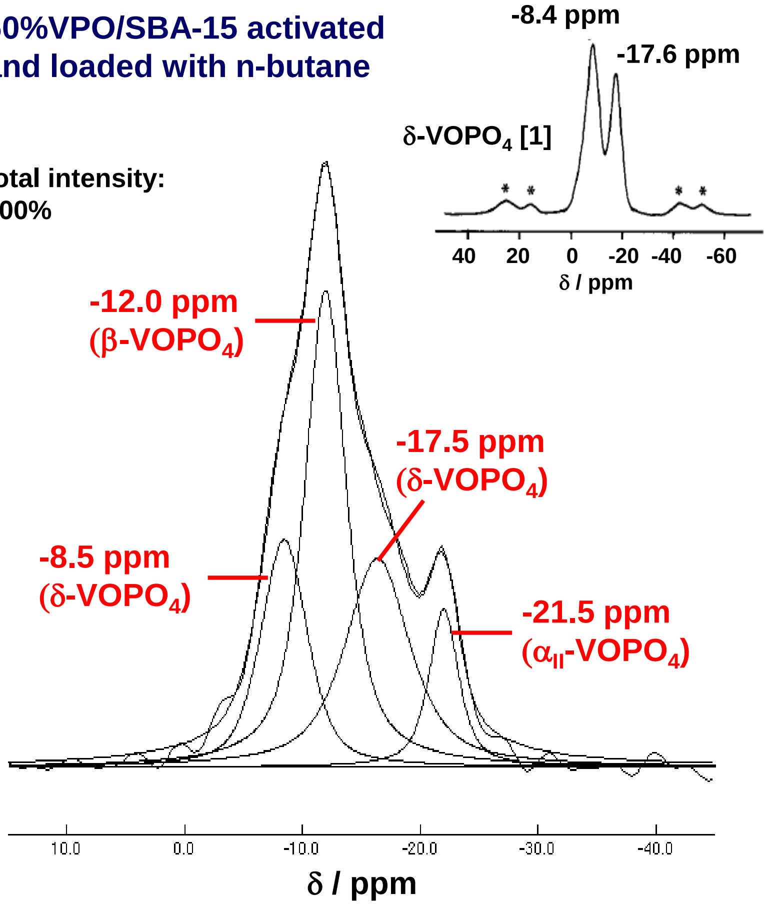
-11.5 to -12.5 ppm: P at V^{5+} in β-$VOPO_4$

(β-$VOPO_4$ is not moisture sensitive, C.J. Kiely et al., J. Catal. 162 (1996) 31)

Simulation of ^{31}P MAS NMR spectra

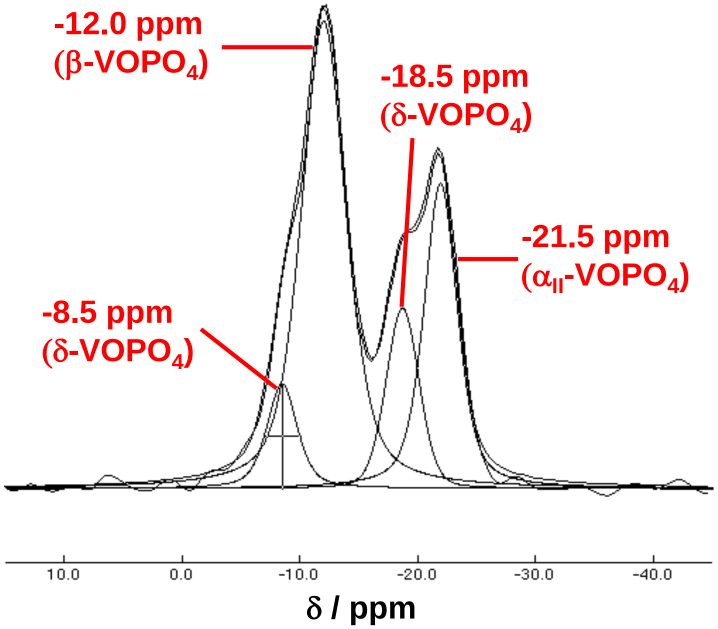
60%VPO/SBA-15 activated and loaded with n-butane

total intensity:
100%



60%VPO/SBA-15 activated,
loaded with n-butane,
and heated at 573 K

total intensity:
94%



[1] F. Ben Abdelouahab et al., J. Catal. 134 (1992) 151.

Summary

- conversion of n-butane to maleic anhydride on VPO catalysts is an important industrial process, however, with limited n-butane conversion and MA yield

- improvement of VPO catalysts requires deeper insight into the nature of active sites and surface phases and the development of novel preparation procedures for the catalyst material

- solid-state NMR spectroscopy is a suitable method for studying VPO materials upon different preparation and activation steps and after catalytic application

- double resonance techniques of NMR spectroscopy allow specific investigations of surface phases containing the adsorption sites of reactant molecules

- combination of NMR (V^{5+}), ESR (V^{4+}) and UV/Vis (V^{3+}) spectroscopy are complementary tools to gain complete insight into the oxidation states of vanadium in VPO catalysts

- quantum-chemical investigations could be very useful for supporting the interpretation of experimental results and for improving our understanding of the reactant activation on the catalyst surface

Acknowledgements

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VPO materials

Bejoy Thomas
NMR studies

Jörg Frey
catalytic studies
novel VPO materials

Deutsche Forschungsgemeinschaft

Alexander von Humboldt foundation

Fonds der Chemischen Industrie

NMR group of the ITC

co-workers:

- **4 PhD students, 1 technician,**

experimental equipment:

- **solid-state NMR spectrometer Bruker MSL-400,**
- **modified probes for *in situ* MAS NMR-UV/Vis spectroscopy under flow conditions,**
- **equipment for catalytic studies (on-line GC, in connection with *in situ* NMR),**
- **equipment for preparation of solid-state NMR samples under well-defined conditions (vacuum lines, glove box).**