# Vanadium phosphates – preparation, structure and catalysis

Manfred Meisel
Institut für Chemie
Humboldt-Universität zu Berlin

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# Selective oxidation processes of industrial interest

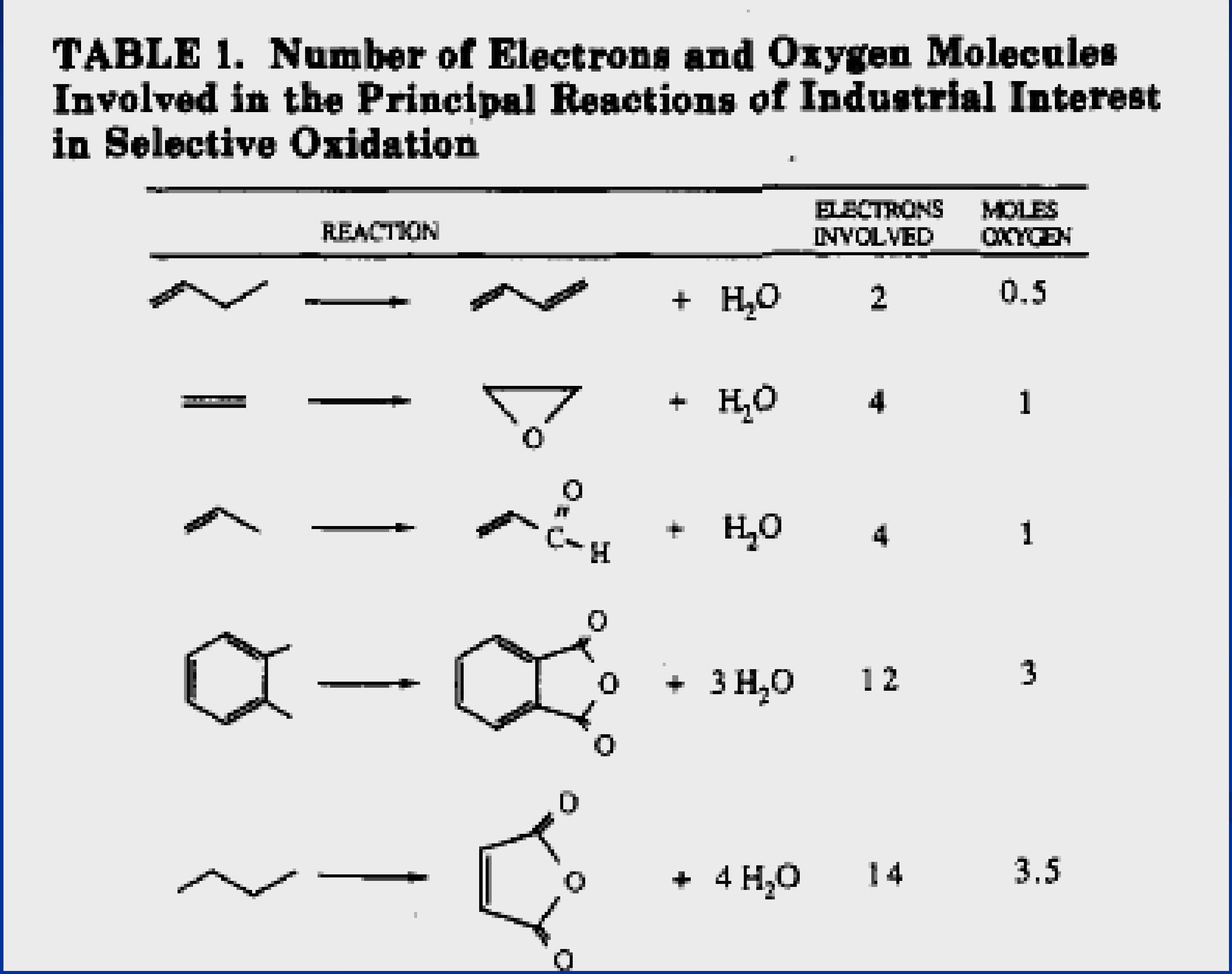


**TABLE 1. Number of Electrons and Oxygen Molecules Involved in the Principal Reactions of Industrial Interest in Selective Oxidation**

| REACTION | ELECTRONS INVOLVED | MOLES OXYGEN |
|---|---|---|
| + $H_2O$ | 2 | 0.5 |
| + $H_2O$ | 4 | 1 |
| + $H_2O$ | 4 | 1 |
| + 3 $H_2O$ | 12 | 3 |
| + 4 $H_2O$ | 14 | 3.5 |

# Vanadium phosphates as catalysts in selective oxidation processes of aliphatic and aromatic hydrocarbons

1. Oxidation of n-Butane to Maleic Anhydride

2. Ammoxidation of Methylaromatics,

   e.g. Toluene to Benzonitrile

# Survey on the known Vanadium(IV) phosphate hydrates

| compound | a in Å | b in Å | c in Å | crystal system | Ref. |
|---|---|---|---|---|---|
| $VOHPO_4$ | 7.440 | 6.401 | 7.088 | orthorhombic | [30] |
| $VOHPO_4 \cdot 0.5H_2O$ | 7.434 | 9.620 | 5.699 | orthorhombic | [28,31] |
| $VOHPO_4 \cdot H_2O$ | 6.546 | 7.37 | 9.44 | monoclinic | [7] |
| $\alpha$ - $VOHPO_4 \cdot 2H_2O$ | 7.613 | 7.431 | 9.482 | monoclinic | [7] |
| $\beta$ - $VOHPO_4 \cdot 2H_2O$ | 5.659 | 7.578 | 12.623 | triclinic | [7] |
| $VOHPO_4 \cdot 3H_2O$ | 7.621 | 7.439 | 9.493 | monoclinic | [7] |
| $VOHPO_4 \cdot 4H_2O$ | 6.379 | 8.921 | 13.462 | triclinic | [28] |
| $(VO)_3(PO_4)_2 \cdot 9H_2O$ | 7.431 | 16.626 | 6.295 | monoclinic | [29] |
| $VO(H_2PO_4)_2$ | 8.959 | 8.956 | 7.967 | orthorhombic | [32] |

# Some structural aspects of vanadium phosphates

E. Bordes, Catal. Today 3 (1988) 163-174

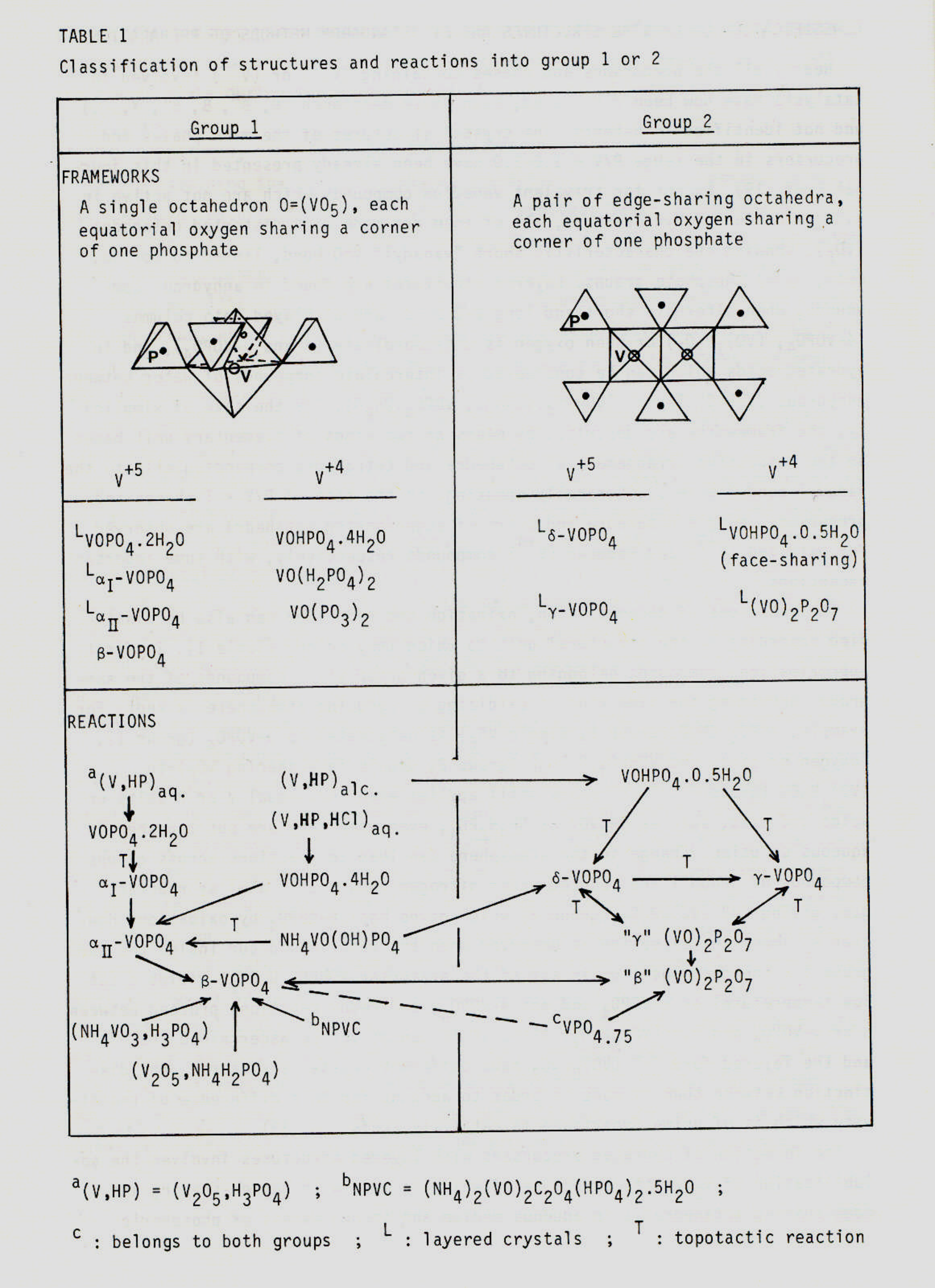


TABLE 1

Classification of structures and reactions into group 1 or 2

| Group 1 | | Group 2 | |
|---|---|---|---|
| FRAMEWORKS<br>A single octahedron O=(VO$_5$), each equatorial oxygen sharing a corner of one phosphate | | A pair of edge-sharing octahedra, each equatorial oxygen sharing a corner of one phosphate | |
| $V^{+5}$ | $V^{+4}$ | $V^{+5}$ | $V^{+4}$ |
| ${}^{L}VOPO_4.2H_2O$ | $VOHPO_4.4H_2O$ | ${}^{L}\delta\text{-}VOPO_4$ | ${}^{L}VOHPO_4.0.5H_2O$<br>(face-sharing) |
| ${}^{L}\alpha_I\text{-}VOPO_4$ | $VO(H_2PO_4)_2$ | | |
| ${}^{L}\alpha_{II}\text{-}VOPO_4$ | $VO(PO_3)_2$ | ${}^{L}\gamma\text{-}VOPO_4$ | ${}^{L}(VO)_2P_2O_7$ |
| $\beta\text{-}VOPO_4$ | | | |

REACTIONS

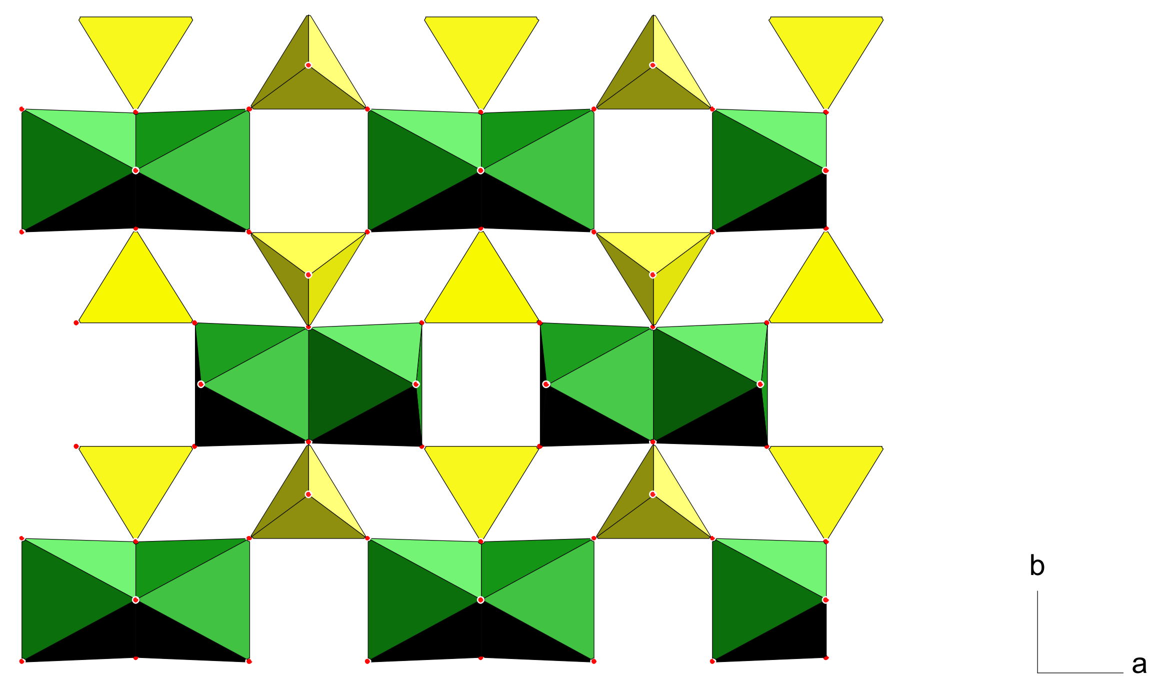
$$\begin{tikzcd}
{}^{a}(V,HP)_{aq.} \arrow[d] & & (V,HP)_{alc.} \arrow[rrr] & & & VOHPO_4.0.5H_2O \arrow[ddl, "T"'] \arrow[ddr, "T"] & \\
VOPO_4.2H_2O \arrow[d, "T"'] & & (V,HP,HCl)_{aq.} \arrow[d] & & & & \\
\alpha_I\text{-}VOPO_4 \arrow[d] & & VOHPO_4.4H_2O \arrow[dll] & & \delta\text{-}VOPO_4 \arrow[rr, "T"] \arrow[dr, leftrightarrow, "T"'] & & \gamma\text{-}VOPO_4 \arrow[dl, leftrightarrow, "T"] \\
\alpha_{II}\text{-}VOPO_4 \arrow[dr] & & NH_4VO(OH)PO_4 \arrow[ll, "T"'] \arrow[urr] & & & \text{"}\gamma\text{"}\ (VO)_2P_2O_7 \arrow[d] & \\
& \beta\text{-}VOPO_4 \arrow[rrrr, leftrightarrow] \arrow[drrr, dash, dashed] & & & & \text{"}\beta\text{"}\ (VO)_2P_2O_7 & \\
(NH_4VO_3,H_3PO_4) \arrow[ur] & & {}^{b}NPVC \arrow[ul] & & {}^{c}VPO_{4.75} \arrow[ur] & & \\
& (V_2O_5,NH_4H_2PO_4) \arrow[uu] & & & & &
\end{tikzcd}$$

${}^{a}(V,HP) = (V_2O_5,H_3PO_4)$ ; ${}^{b}NPVC = (NH_4)_2(VO)_2C_2O_4(HPO_4)_2.5H_2O$ ;

${}^{c}$ : belongs to both groups ; ${}^{L}$ : layered crystals ; ${}^{T}$ : topotactic reaction

# Vanadium phosphates as catalysts in selective oxidation processes of aliphatic and aromatic hydrocarbons

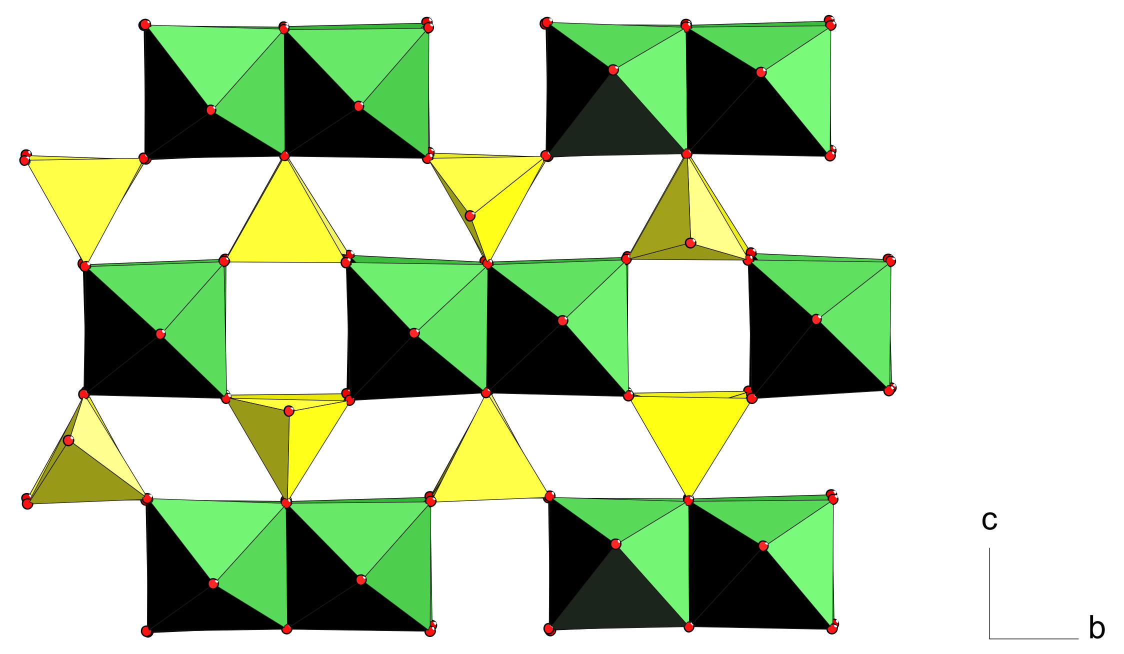
## Structure of the hemihydrate (precursor)



Scheme of cross linking of polyhedra in $VOHPO_4$* 0.5 $H_2O$

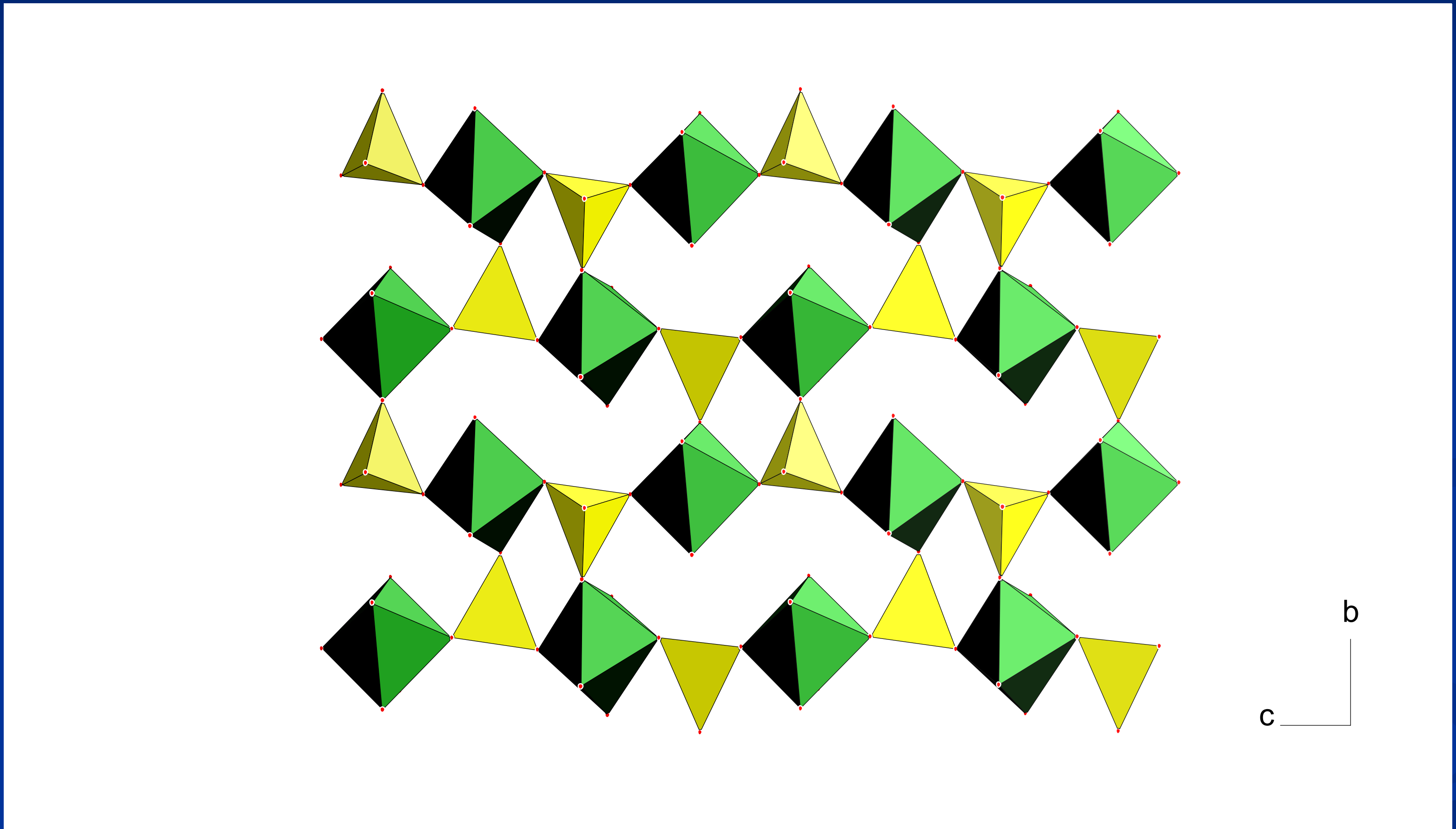
# Vanadium phosphates as catalysts in selective oxidation processes of aliphatic and aromatic hydrocarbons

## Structure of the pyrophosphate (catalyst)



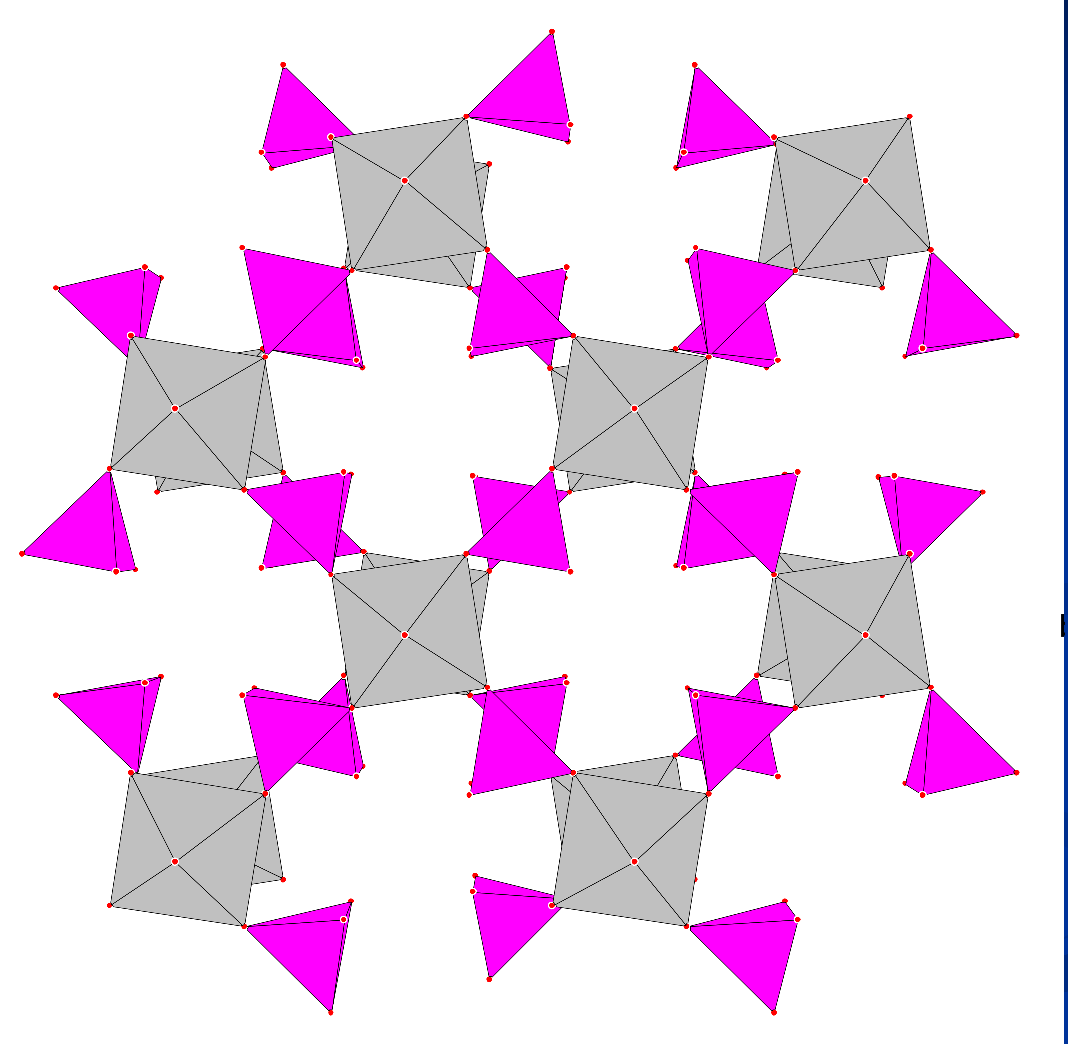
Scheme of cross linking of polyhedra in $(VO)_2P_2O_7$

# Structures of Vanadium(IV) hydrogenphosphate hydrates



Scheme of cross linking of the polyhedra in β-$VOHPO_4 * 2\ H_2O$

# Structures of Vanadium(IV) hydrogenphosphate hydrates



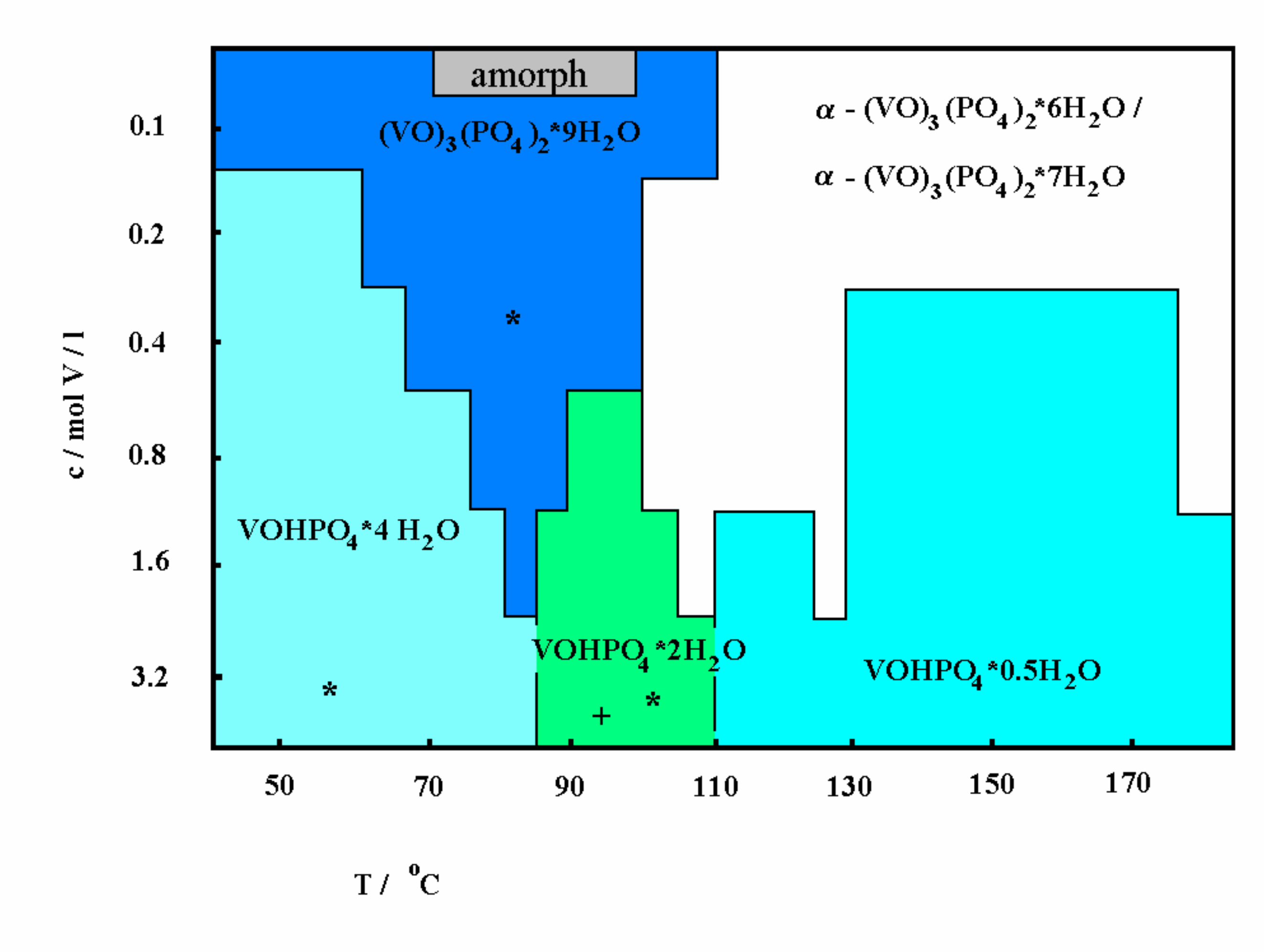
Scheme of cross linking of the polyhedra in $VO(H_2PO_4)_2$

# Systematic studies on the crystallization of vanadium phosphates

- autoclave reaction
- investigation of the crystallization in dependence on temperature and concentration
- Starting from a stock solution of the composition:

36 ml 85% $H_3PO_4$, 90 ml water, 45,3 g oxalic acid dihydrate were heated to 80°C; under stirring 43,5 g $V_2O_5$ were added in portions; for 12 h heated nearly to boiling; final weight of the stock solution by adding of water ⇨ 220g

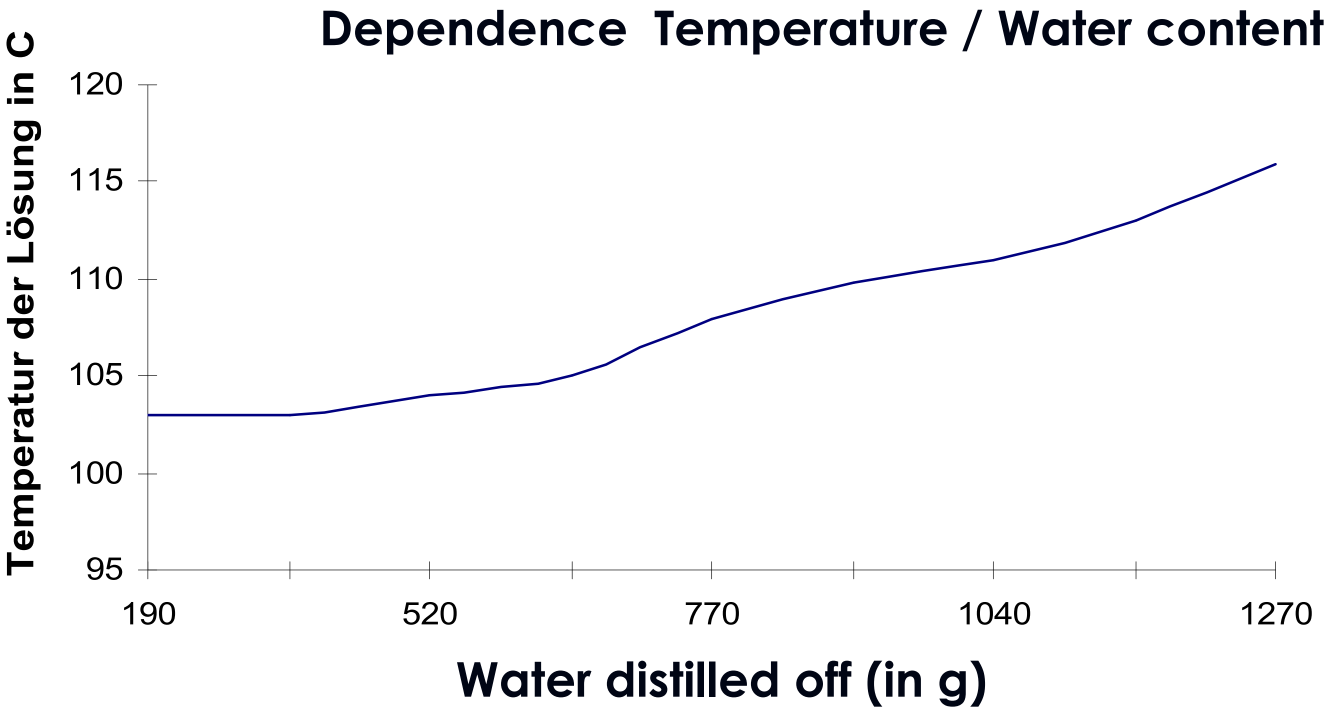
# Schematic phase formation diagram of vanadyl hydrogenphosphate hydrates and vanadyl phosphate hydrates



- * single crystals + single crystals of $\gamma$ - $VOHPO_4 \cdot 2 H_2O$

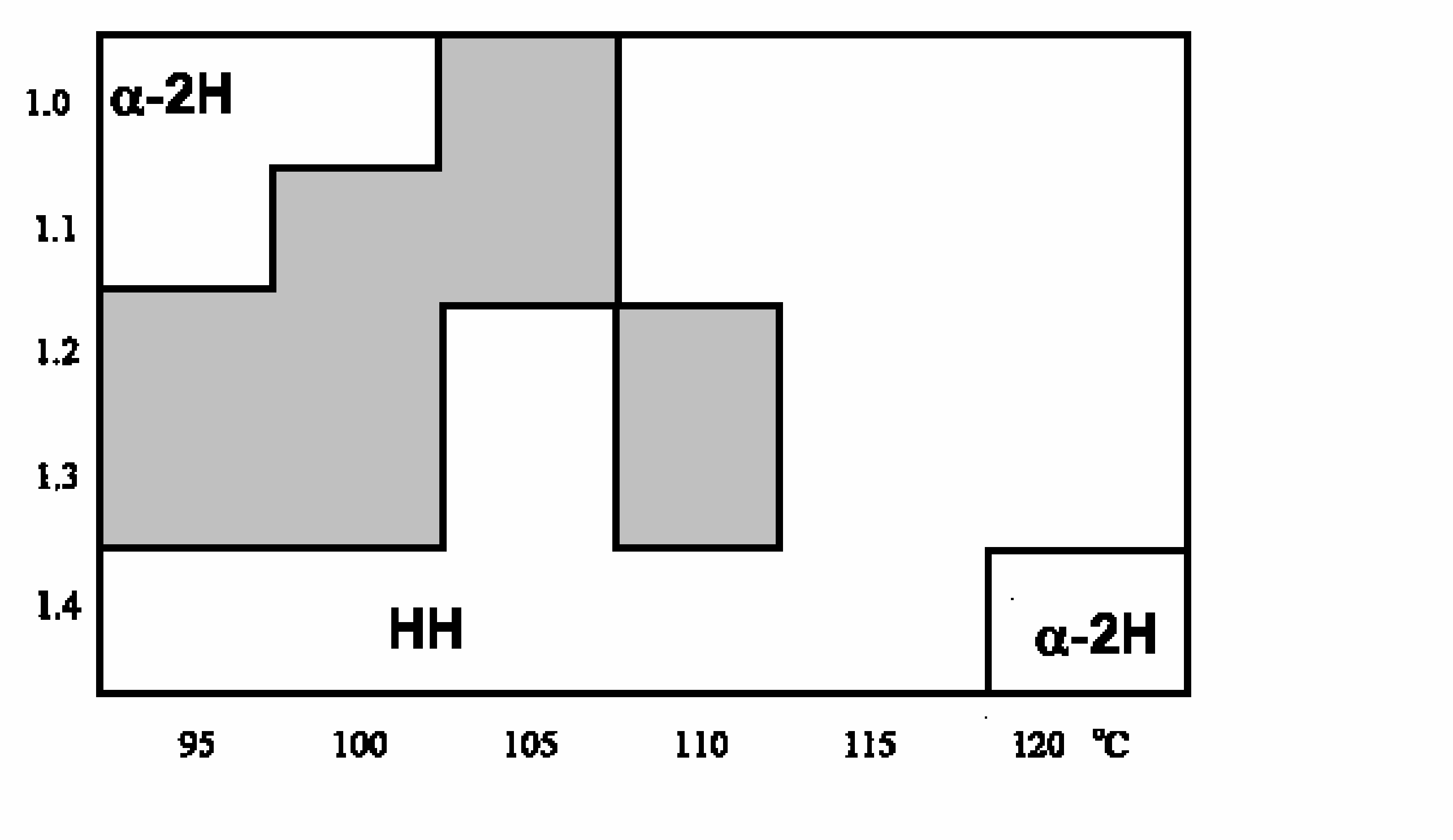
D. Fratzky, Th. Götze, H. Worzala, M. Meisel, Mater. Res. Bull. 33 (1998 635-643

# Determination of the crystallization temperature for $VOHPO_4$* 0,5 $H_2O$



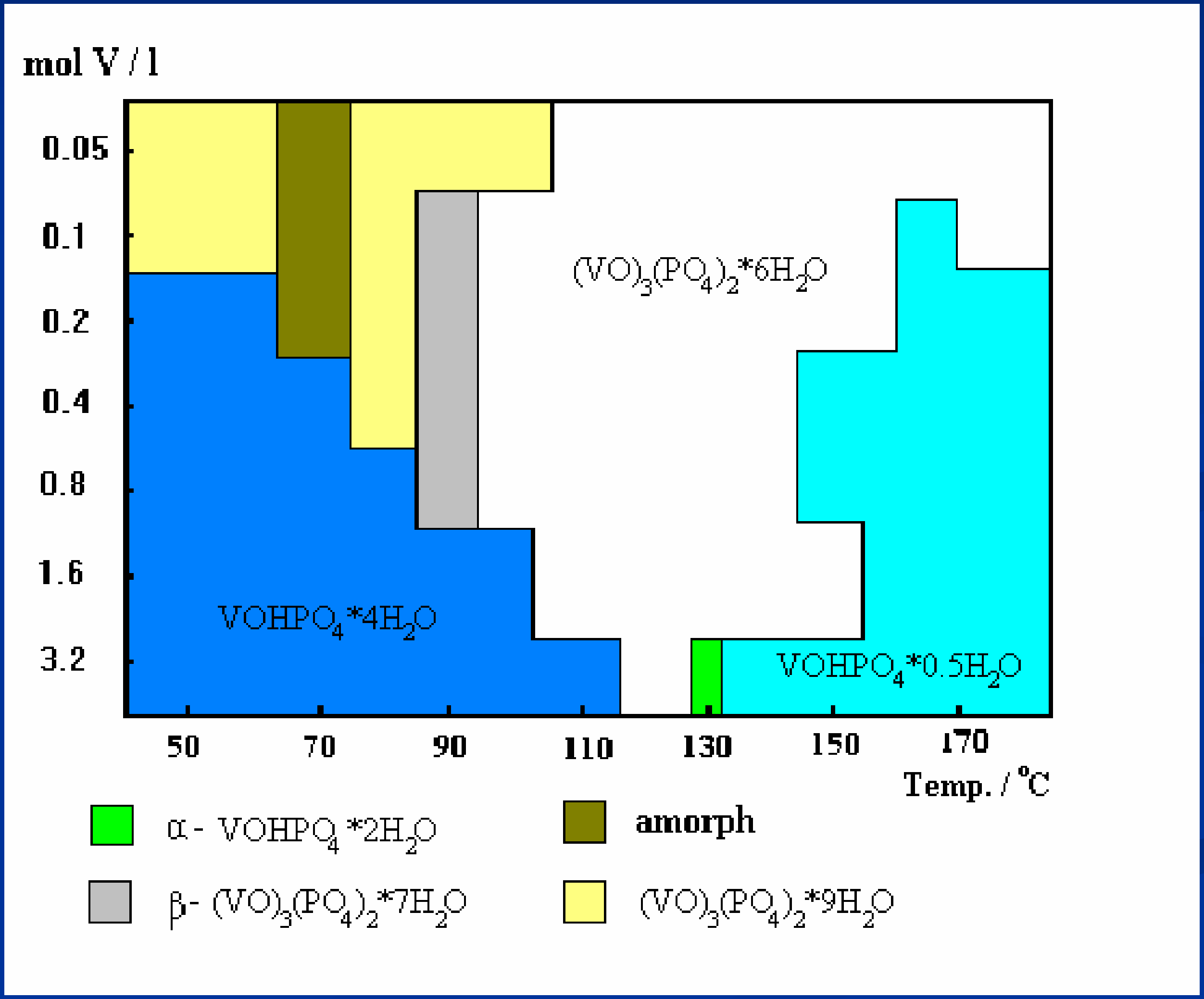
The formation of crystalline Hemihydrate takes place at 116 °C

# Detail from the phase formation diagram

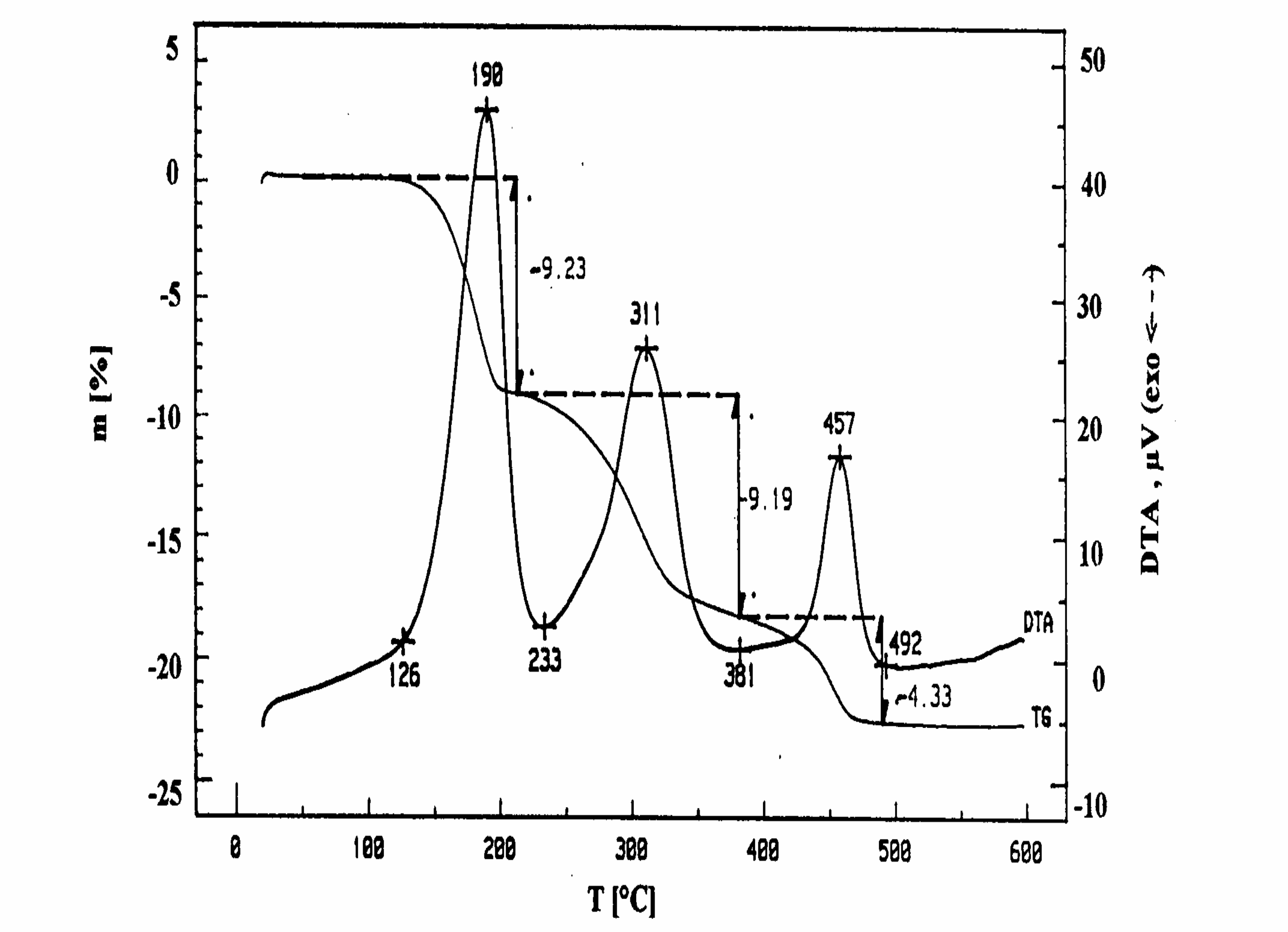


Molality of 1.0 corresponds 2.15 mol V/ kg ; Molality of 1.4 corresponds 3.0 mol V / Kg
HH = $VOHPO_4 * 0.5 H_2O$, α-2H = α-$VOHPO_4 * 2 H_2O$,
in the grey area both phases are formed

# Phase formation diagram of vanadium(IV) phosphates (crystallization at 100 bar)



# Thermal behaviour of hydrous vanadium(IV) hydrogenphosphates



DTA / DTG graph of α - VOHPO4 ∗ 2 $H_2O$

D. Fratzky, M. Meisel, unpublished

$$2\ \alpha\text{-}VOHPO_4{\times}2H_2O \xrightarrow{160^\circ C} 2\ VOHPO_4{\times}H_2O \xrightarrow{300^\circ C} 2\ VOHPO_4 \xrightarrow{450^\circ C} (VO)_2P_2O_7$$

# Thermal behaviour of hydrous vanadium(IV) hydrogenphosphates

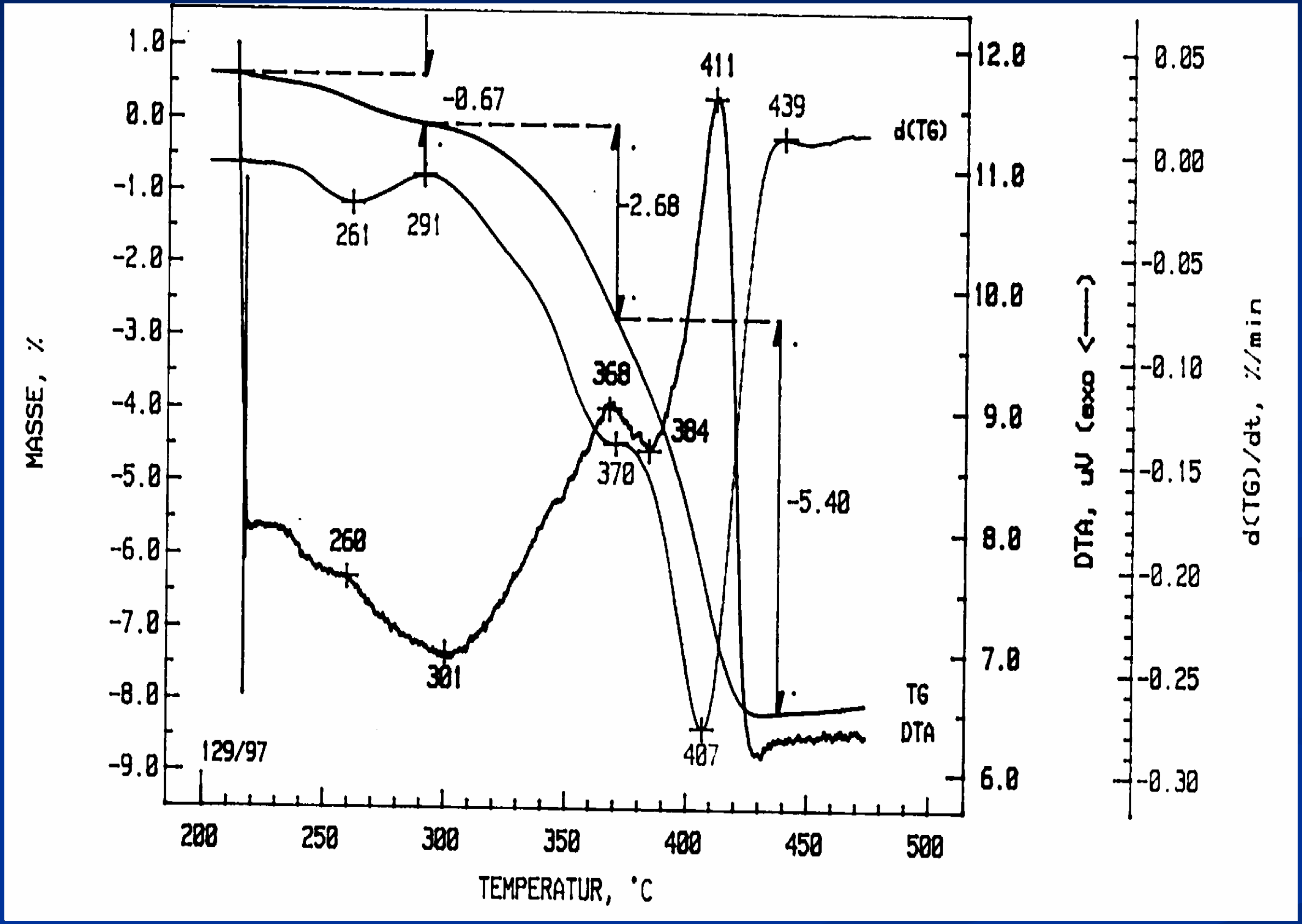
$$2\ \text{a-}VOHPO_4 * 2\ H_2O \xrightarrow{160^\circ\ C} 2\ VOHPO_4 * H_2O \xrightarrow{300^\circ\ C} 2\ VOHPO_4 \xrightarrow{450^\circ\ C} (VO)_2P_2O_7$$

$$2\ VOHPO_4 * H_2O \longrightarrow [2\ VOHPO_4 * 0{,}5\ H_2O] \longrightarrow (VO)_2P_2O_7 * H_2O$$

$$\longrightarrow (VO)_2P_2O_7$$

P. Amoros et al., Mater. Res. Bull. 24 (1989) 1347

# Thermal behaviour of hydrous vanadium(IV) hydrogenphosphates



DTA / DTG graph of the dehydrogenation of $VOHPO_4$* 0.5 $H_2O$ in vacuo

$VOHPO_4 \times 0.5H_2O \rightarrow (VO)_2P_2O_7 \times H_2O \rightarrow (VO)_2P_2O_7$

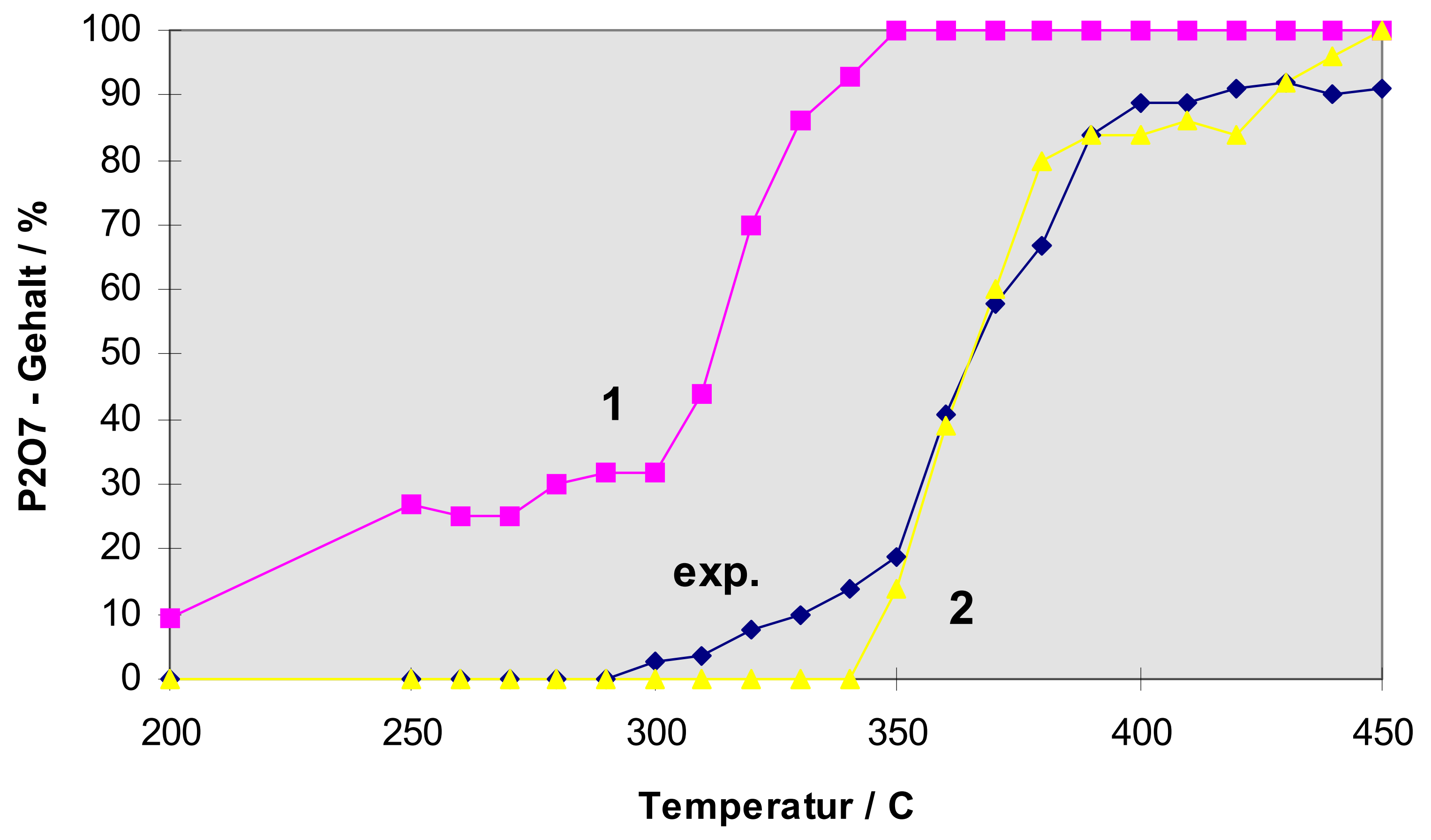
# Thermal behaviour of hydrous vanadium(IV) hydrogenphosphates

## Possible dehydration steps

(1) ➲ $2\ VOHPO_4 * 0{,}5\ H_2O \longrightarrow (VO)_2P_2O_7 * H_2O \longrightarrow (VO)_2P_2O_7 + H_2O$

(2) ➲ $2\ VOHPO_4 * 0{,}5\ H_2O \longrightarrow 2\ VOHPO_4 + H_2O \longrightarrow (VO)_2P_2O_7 + H_2O$

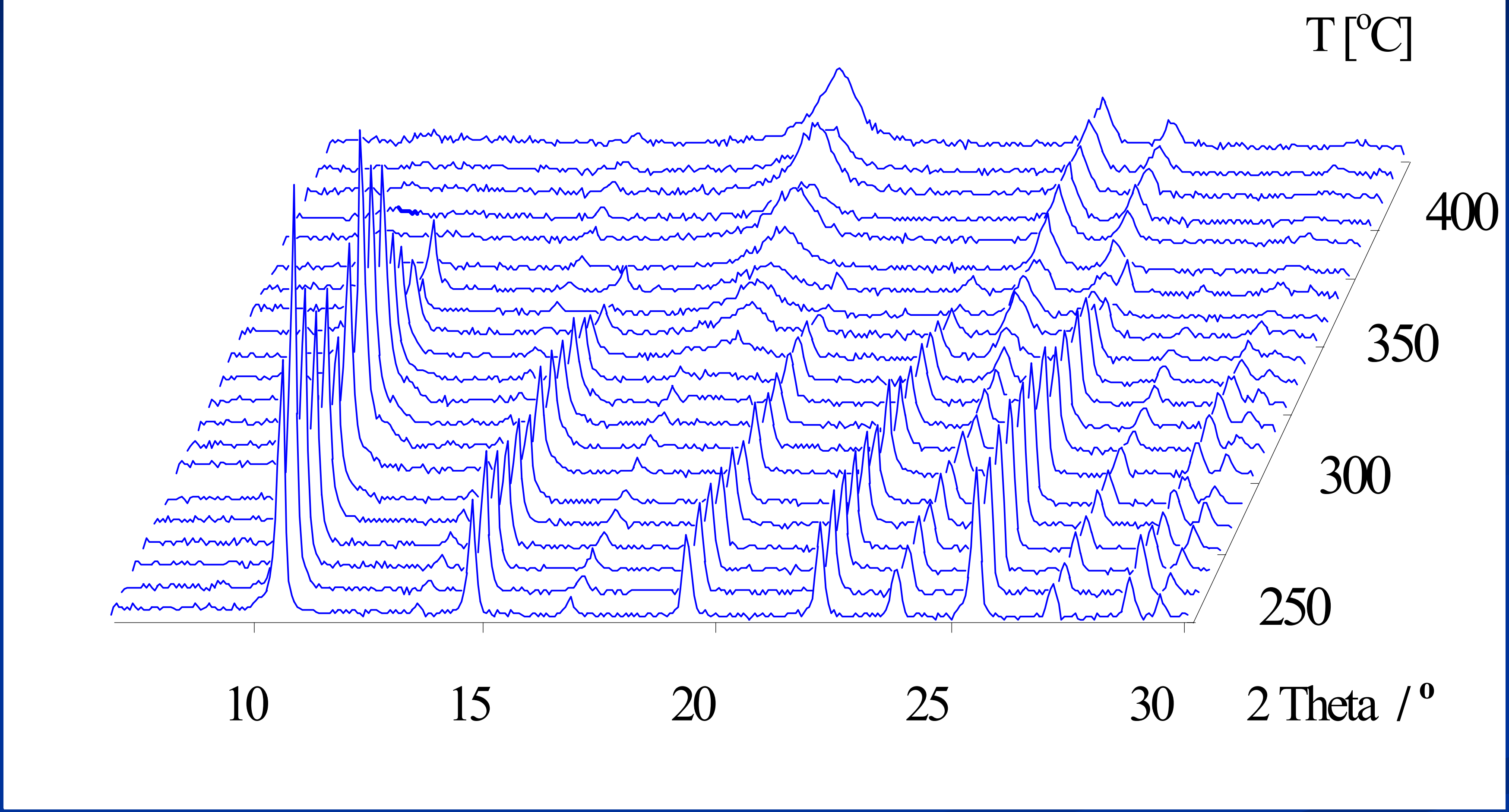
# Thermal behaviour of hydrous vanadium(IV) hydrogenphosphates



Formation of $P_2O_7{}^{4-}$ in dependence of the temperature

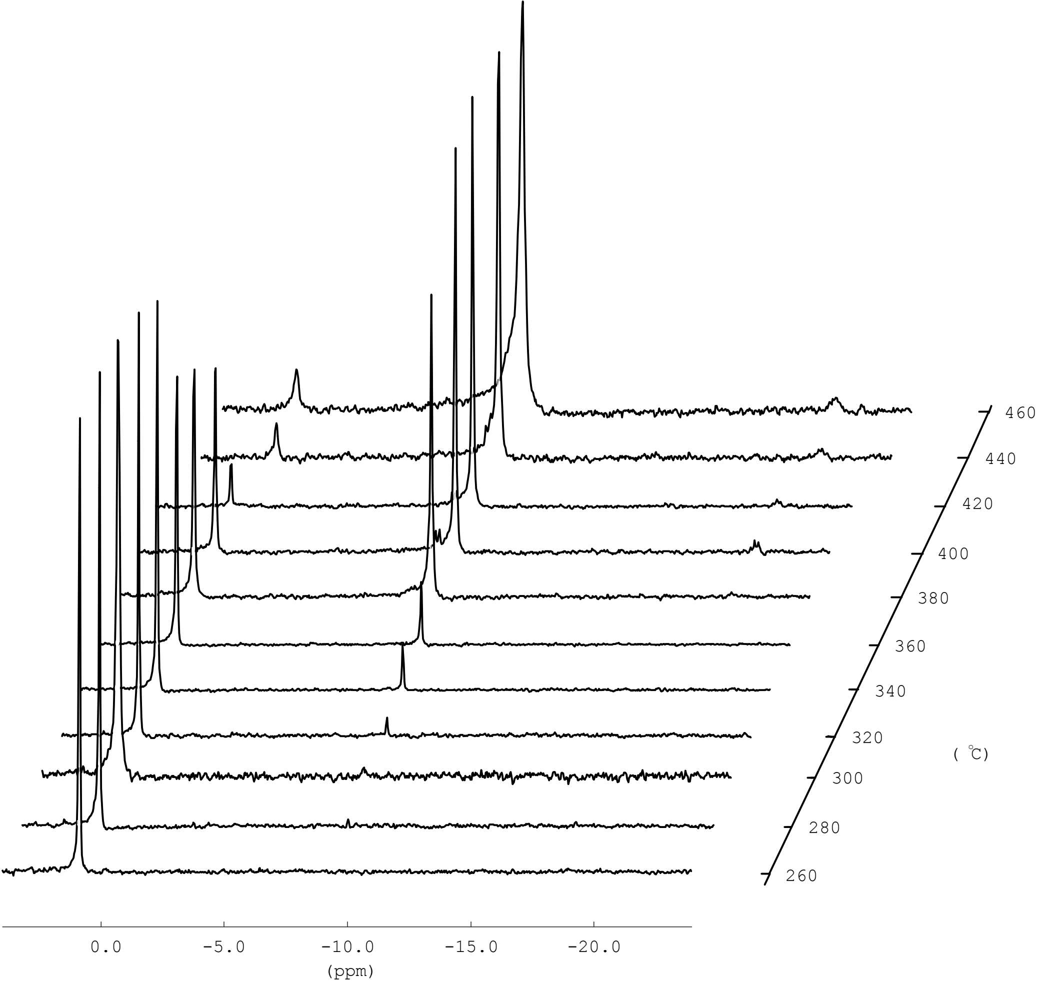
curve1: calc. from the weight loss related to eq. (1); curve 2: theor. Values related to eq. (2); black curve: exp. values

# Thermal behaviour of hydrous vanadium(IV) hydrogenphosphates



X-ray diagrams of the calcinates of $VOHPO_4$* 0.5 $H_2O$

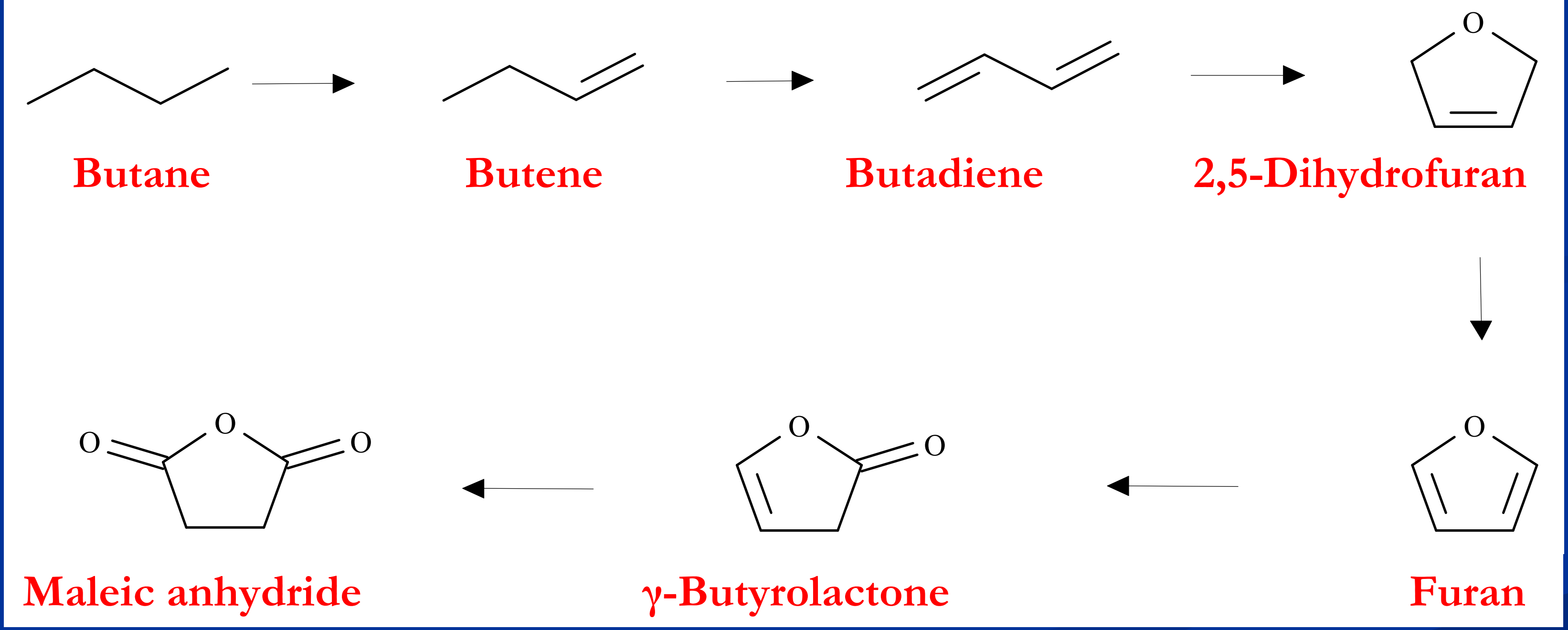
# Thermal behaviour of hydrous vanadium(IV) hydrogenphosphates



NMR-spectra of the dissolved calcinates of $VOHPO_4$* 0.5 $H_2O$

# Vanadium phosphates as catalysts in selective oxidation processes of aliphatic and aromatic hydrocarbons

## 1. Oxidation of n-Butane to Maleic Anhydride



# Vanadium phosphates as catalysts in selective oxidation processes of aliphatic and aromatic hydrocarbons

## Precursors and catalysts for the oxidation of butane

$$\mathrm{VOHPO_4 \times nH_2O} \xrightarrow{\Delta} \mathrm{VOHPO_4 \times 0.5H_2O}$$

precursor

$$2 \quad \mathrm{VOHPO_4 \times 0.5H_2O} \xrightarrow{480^{o}\mathrm{C}} \mathrm{(VO)_2P_2O_7} + 2\mathrm{H_2O}$$

catalyst

The transformation of the precursor (Hemihydrate) to the catalyst (Vanadyl pyrophosphate) occurs topotactical

# Preparation of vanadyl hydrogenphosphates, especially of the hemihydrate

- \- synthesis in aqueous medium ⇨ reduction of V(V)-compounds ($V_2O_5$, $HVO_3$) in the presence of $H_3PO_4$ followed by evaporating to dryness resp. crystallization.
  Reducing agents: HCl, hydroxylamine, hydrazine, oxalic acid, metallic vanadium

  Yields: 60-70%

- \- synthesis in organic medium ⇨ reduction of V(V)-compounds preferred in alcohols, e.g. isobutanol or isobutanol/benzyl alcohol

  Yields: quantitatively
  Problem: removing of intercalated alcohol

# Influence of the conditions of preparation of the precursor $VOHPO_4$* 0.5 $H_2O$ on the catalytic performance of $(VO)_2P_2O_7$ (VPP)

## Conditions of preparation of different precursors :

rate of crystalline growth

| symbol | average particle size | crystallization temperature | crystallization time | concentration / mol V / l |
|---|---|---|---|---|
| P1 | 54µm | 90 °C | 14 days | 6 |
| P2 | 8µm | 115 °C | 2 days | 3 |
| P3 | 2µm | 130 °C | < 12 h | 3 |

D. Fratzky, M. Meisel, unpublished

# Influence of the conditions of preparation of the precursor $VOHPO_4$* 0.5 $H_2O$ on the catalytic performance of $(VO)_2P_2O_7$ (VPP)

## Dependence of butane conversion on temperature and particle size of the catalyst precursors

| Temperature | $U_{Butan}$ P1<br>54 µm | $U_{Butan}$ P2<br>8 µm | $U_{Butan}$ P3*<br>2 µm |
|---|---|---|---|
| 380 | 21.8 | 69.1 | 75.6 |
| 400 | 31.7 | 85.6 | 88.7 |
| 437 | 54.2 | 99.1 | 99.1 |
| 498 | 93.5 | 100 | 100 |

* Preparation in an autoclave

# Influence of the conditions of preparation of the precursor $VOHPO_4$* 0.5 $H_2O$ on the catalytic performance of $(VO)_2P_2O_7$ (VPP)

## Results of the catalytic tests on the oxidation of n-butane

| Temperature / °C | Yield MSA P1 | Yield MSA P2 | Yield MSA P3 |
|---|---|---|---|
| 498 | 43,8 | | |
| 486 | 45,6 | | |
| 473 | 43,8 | | |
| 462 | 39,8 | | 19 |
| 461 | 39,6 | | 19,8 |
| 447 | 35,6 | | 27 |
| 437 | 32,6 | 44,7 | 32,5 |
| 431 | 30,4 | 48 | 35,8 |
| 426 | 28,3 | 50,6 | 37,6 |
| 414 | 24,1 | 53,4 | 42 |
| 399 | 19,5 | 54,7 | 44,6 |
| 384 | 14,8 | 53 | 45,3 |
| 381 | 13,9 | 52,3 | 44,8 |
| 372 | | 49,3 | 43,5 |
| 346 | | 32,8 | 33,3 |

# Influence of the conditions of preparation of the precursor $VOHPO_4$* 0.5 $H_2O$ on the catalytic performance of $(VO)_2P_2O_7$ (VPP)

## Investigation of recrystallization of $VOHPO_4$* 0.5 $H_2O$

## Influence of foreign phases ($VOHPO_4$*$H_2O$; a-$VOHPO_4$*$H_2O$; $VO(H_2PO_4)_2$)

**Preparation of the precursors:**

**K 1** ⇨ $VOHPO_4$* 0.5 $H_2O$ , from aqueous solution

**K 2** ⇨ K 1 treated with boiling water

**K 3** ⇨ K 2 treated with phosphoric acid
vanadium(IV) solution under the conditions of
formation of a-$VOHPO_4$ * 2 $H_2O$
(95°C, 3.13 mol V/l)

D. Fratzky, M. Meisel, unpublished

# Influence of the conditions of preparation of the precursor $VOHPO_4$* 0.5 $H_2O$ on the catalytic performance of $(VO)_2P_2O_7$ (VPP)

## Investigation of recrystallization of $VOHPO_4$* 0.5 $H_2O$

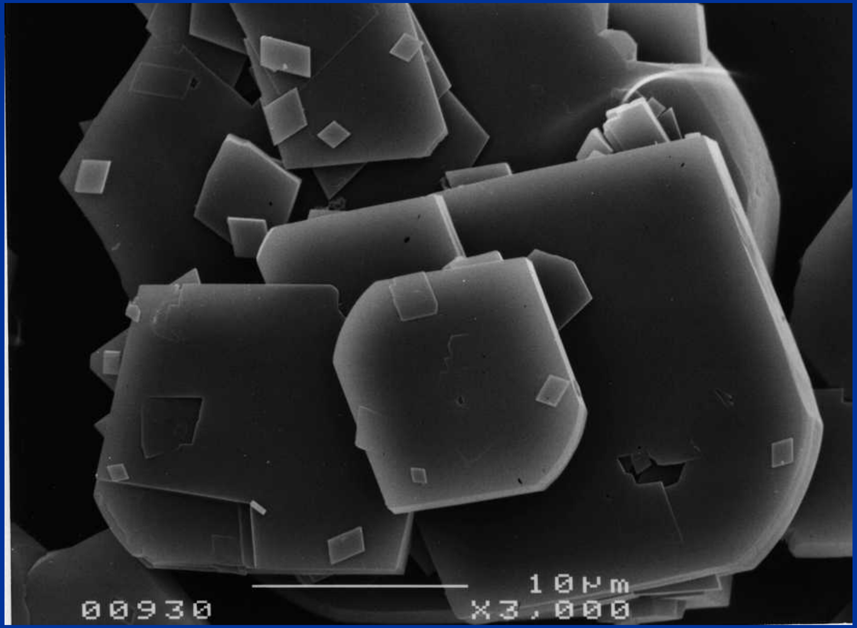
| Parameter | K1 | K2 | K3 | calculated |
|---|---|---|---|---|
| V(III) [%] | 0.14 | - | - | - |
| V(IV) [%] | 29.01 | 29.76 | 29.77 | 29.63 |
| V(V) [%] | - | 0.69 | 0.01 | - |
| $V_{ges}$ [%] | 29.15 | 30.45 | 29.78 | 29.63 |
| P [%] | 18.16 | - | 17.91 | 18.01 |
| P / V | 1.025 | - | 0.989 | 1 |
| $H_2O$ ( according to TG) | 11.57 | 10.88 | 11.23 | 10.47 |
| oxidation number | 3.995 | 4.023 | 4.000 | 4.000 |

analytical data of precursors K 1, K 2 und K 3

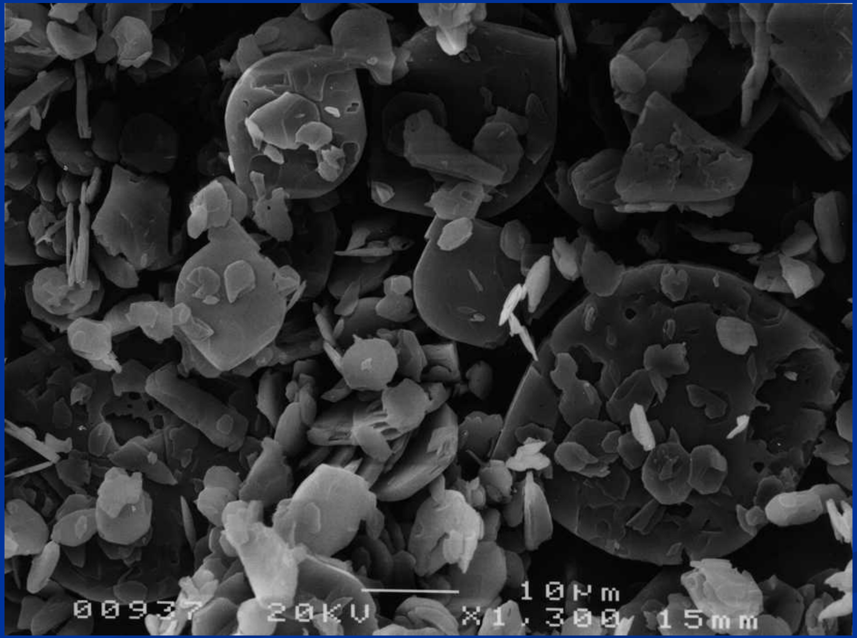
# Influence of the conditions of preparation of the precursor $VOHPO_4$* 0.5 $H_2O$ on the catalytic performance of $(VO)_2P_2O_7$ (VPP)

## Investigation of recrystallization of $VOHPO_4$* 0.5 $H_2O$

Electron micrographs of the precursors



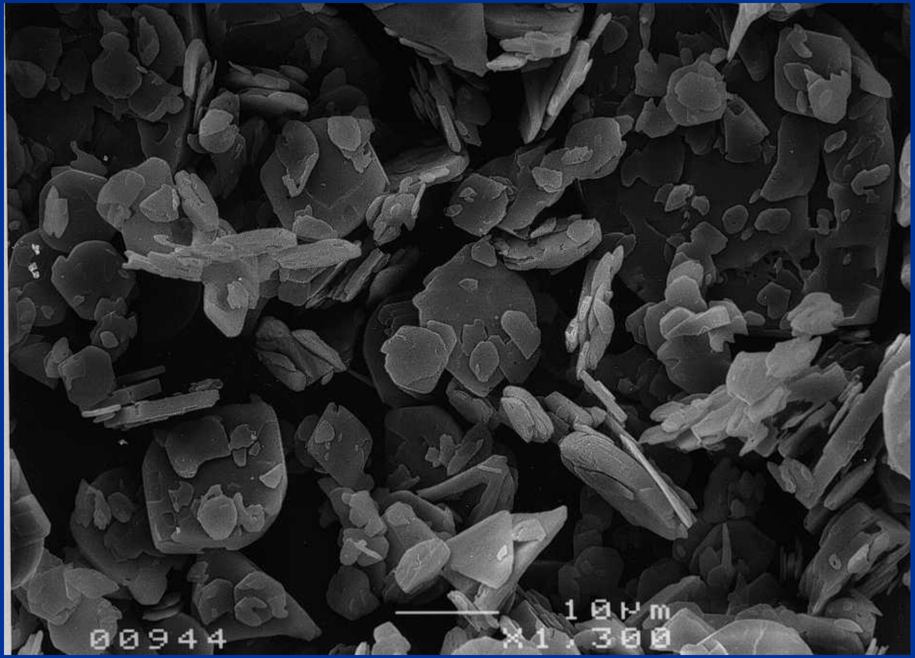
K 1 (untreated precursor)



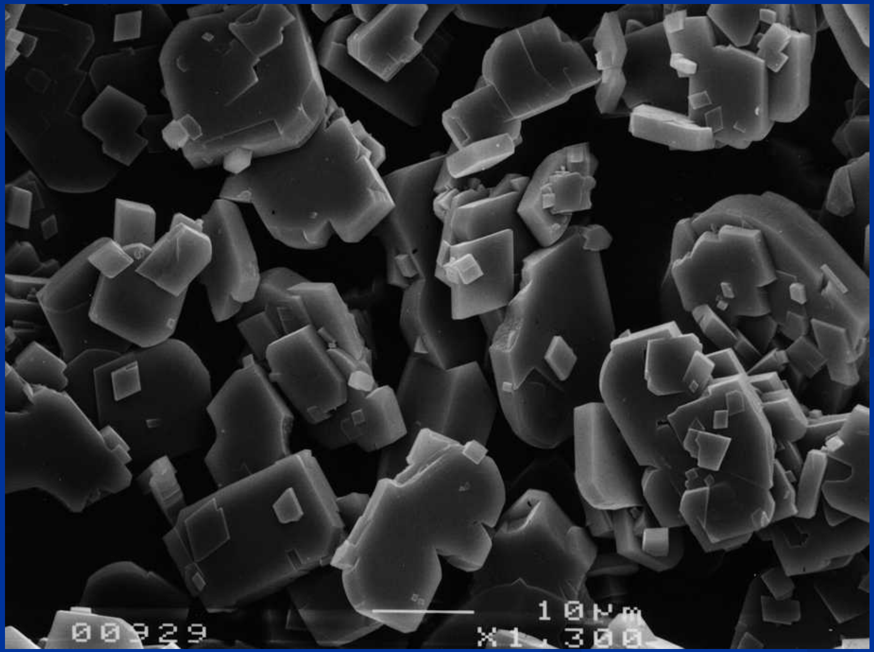
K 2 (after treatment with boiling water)

# Influence of the conditions of preparation of the precursor $VOHPO_4 * 0.5\ H_2O$ on the catalytic performance of $(VO)_2P_2O_7$ (VPP)

## Investigation of recrystallization of $VOHPO_4 * 0.5\ H_2O$



K 2 (after treatment with boiling water)



K 3 (after treatment with $H^+/V^{4+}/PO_4^{3-}$ / $C_2O_4^{2-}$ solution)

# Influence of the conditions of preparation of the precursor $VOHPO_4$* 0.5 $H_2O$ on the catalytic performance of $(VO)_2P_2O_7$ (VPP)

## Surfaces of precursors K 1 and K 3and surfaces of the corresponding VPP catalysts prepared by calcination

| | K 1 | K 3 |
|---|---|---|
| surface precursor $VOHPO_4$* 0,5 $H_2O$ [ $m^2$ ] | 1.3 | 1.7 |
| surface catalyst $(VO)_2P_2O_7$ [ $m^2$ ] | 7.3 | 8.5 |

# Influence of the conditions of preparation of the precursor $VOHPO_4$* 0.5 $H_2O$ on the catalytic performance of $(VO)_2P_2O_7$ (VPP)

## Catalytic properties of VPP from the precursors K 1 und K 3

| | K 1 | | | | K 3 | | |
|---|---|---|---|---|---|---|---|
| **Reaction temperature [°C]** | **$U_{butan}$ [%]** | **$Y_{MSA}$ [%]** | **$S_{MSA}$ [%]** | **Reaction temp. [°C]** | **$U_{butan}$ [%]** | **$Y_{MSA}$ [%]** | **$S_{MSA}$ [%]** |
| 435 | 93,2 | 47,9 | 51,4 | 431 | 97,0 | 50,5 | 52,1 |
| 423 | 85,4 | 48,1 | 56,3 | 417 | 90,8 | 52,7 | 58,1 |
| 410 | 75,7 | 44,5 | 58,8 | 403 | 81,9 | 52,9 | 64,5 |
| 397 | 65,6 | 40,5 | 61,7 | 378 | 62,2 | 40,7 | 65,5 |
| 352 | 31,6 | 20,8 | 65,7 | | | | |

# Preparation of the Hemihydrate by the method of controlled crystallization

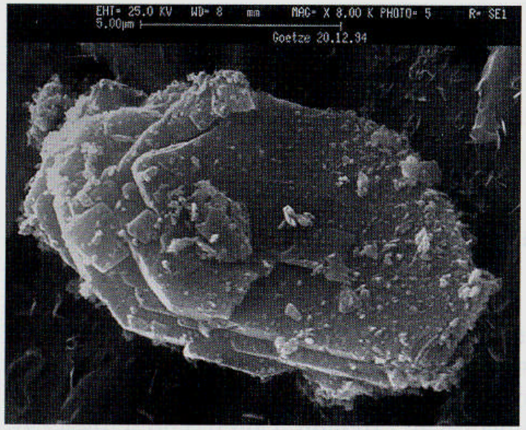


Bild 2. REM-Aufnahme des unter vollständigem Eindampfen der Lösung erhaltenen $VOHPO_4 \cdot 0{,}5\ H_2O$-Precursors *1*

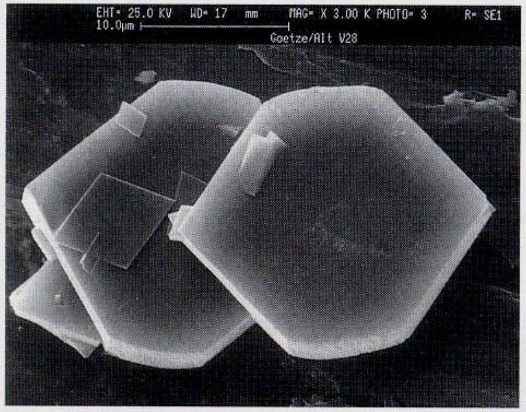
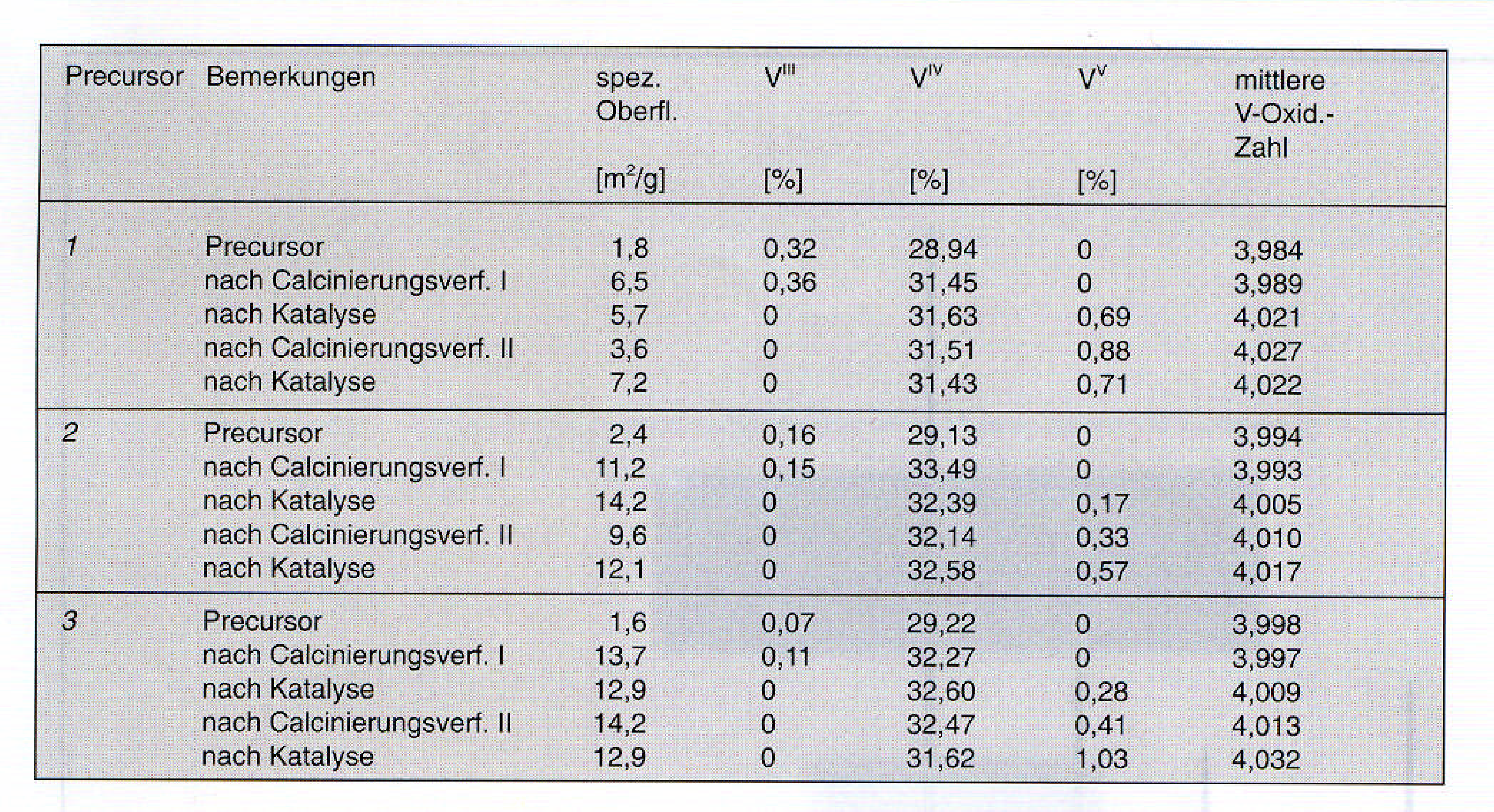


Bild 3. REM-Aufnahme des unter kontrollierten Kristallisationsbedingungen erhaltenen $VOHPO_4 \cdot 0{,}5\ H_2O$-Precursors *2*

Crystallization in a rotary evaporator in a temperatur range of 120...140°C

Th. Götze, H. Wolf, B. Kubias, M. Meisel, Chem. Technik 49 (1997) 62-67

# Precursor 2 and 3 prepared by controlled crystallization, Precursor 1 via the conventionel aqueous route



| Precursor | Bemerkungen | spez. Oberfl. [$m^2/g$] | $V^{III}$ [%] | $V^{IV}$ [%] | $V^{V}$ [%] | mittlere V-Oxid.-Zahl |
|---|---|---|---|---|---|---|
| 1 | Precursor | 1,8 | 0,32 | 28,94 | 0 | 3,984 |
| | nach Calcinierungsverf. I | 6,5 | 0,36 | 31,45 | 0 | 3,989 |
| | nach Katalyse | 5,7 | 0 | 31,63 | 0,69 | 4,021 |
| | nach Calcinierungsverf. II | 3,6 | 0 | 31,51 | 0,88 | 4,027 |
| | nach Katalyse | 7,2 | 0 | 31,43 | 0,71 | 4,022 |
| 2 | Precursor | 2,4 | 0,16 | 29,13 | 0 | 3,994 |
| | nach Calcinierungsverf. I | 11,2 | 0,15 | 33,49 | 0 | 3,993 |
| | nach Katalyse | 14,2 | 0 | 32,39 | 0,17 | 4,005 |
| | nach Calcinierungsverf. II | 9,6 | 0 | 32,14 | 0,33 | 4,010 |
| | nach Katalyse | 12,1 | 0 | 32,58 | 0,57 | 4,017 |
| 3 | Precursor | 1,6 | 0,07 | 29,22 | 0 | 3,998 |
| | nach Calcinierungsverf. I | 13,7 | 0,11 | 32,27 | 0 | 3,997 |
| | nach Katalyse | 12,9 | 0 | 32,60 | 0,28 | 4,009 |
| | nach Calcinierungsverf. II | 14,2 | 0 | 32,47 | 0,41 | 4,013 |
| | nach Katalyse | 12,9 | 0 | 31,62 | 1,03 | 4,032 |

# Catalytic performance of catalysts prepared from precursors from conventionel „aqueous“ (P 1) or „organic“preparation (Table 4) compared with those from the method of controlled crystallization (P 2, P 3)

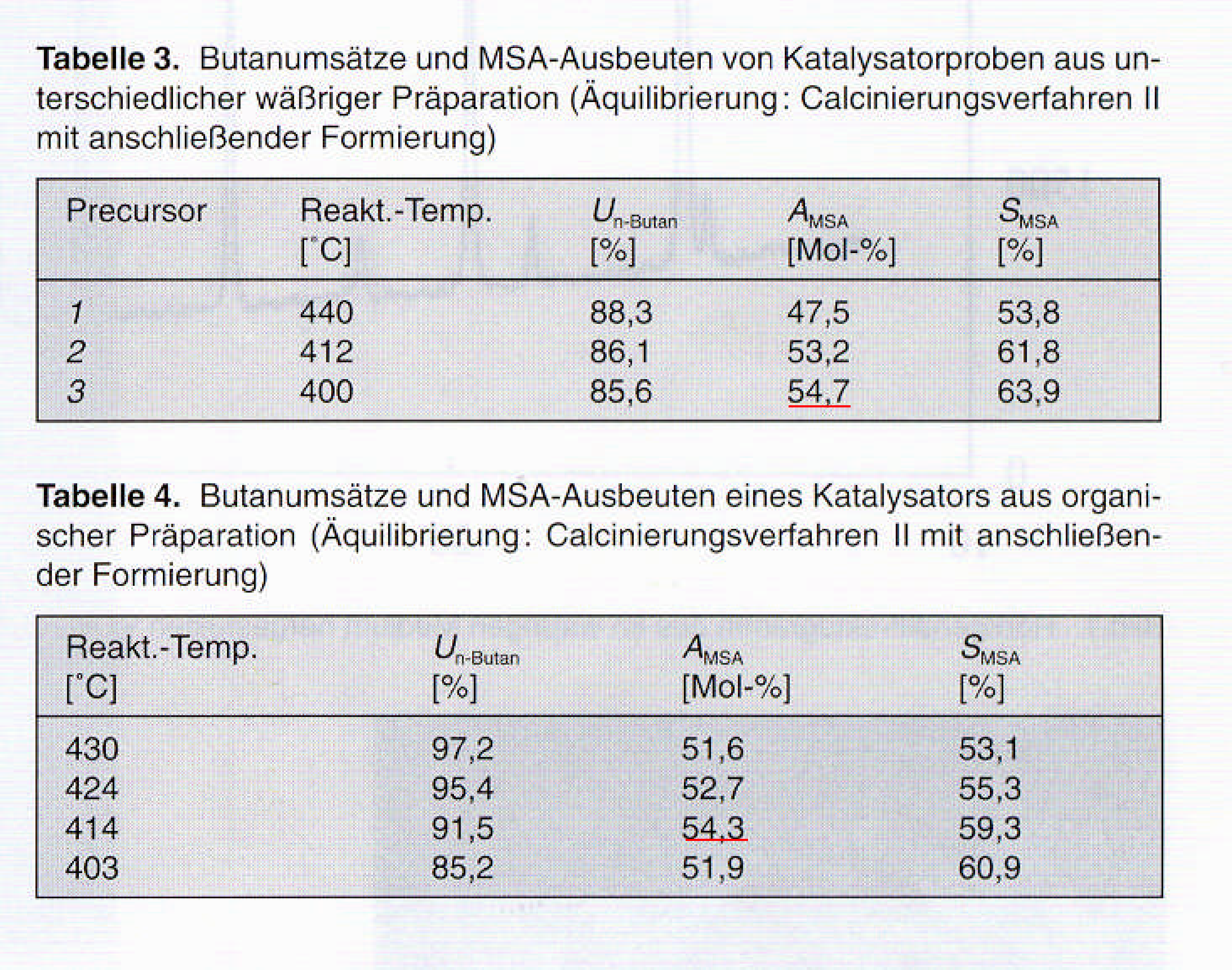


**Tabelle 3.** Butanumsätze und MSA-Ausbeuten von Katalysatorproben aus unterschiedlicher wäßriger Präparation (Äquilibrierung: Calcinierungsverfahren II mit anschließender Formierung)

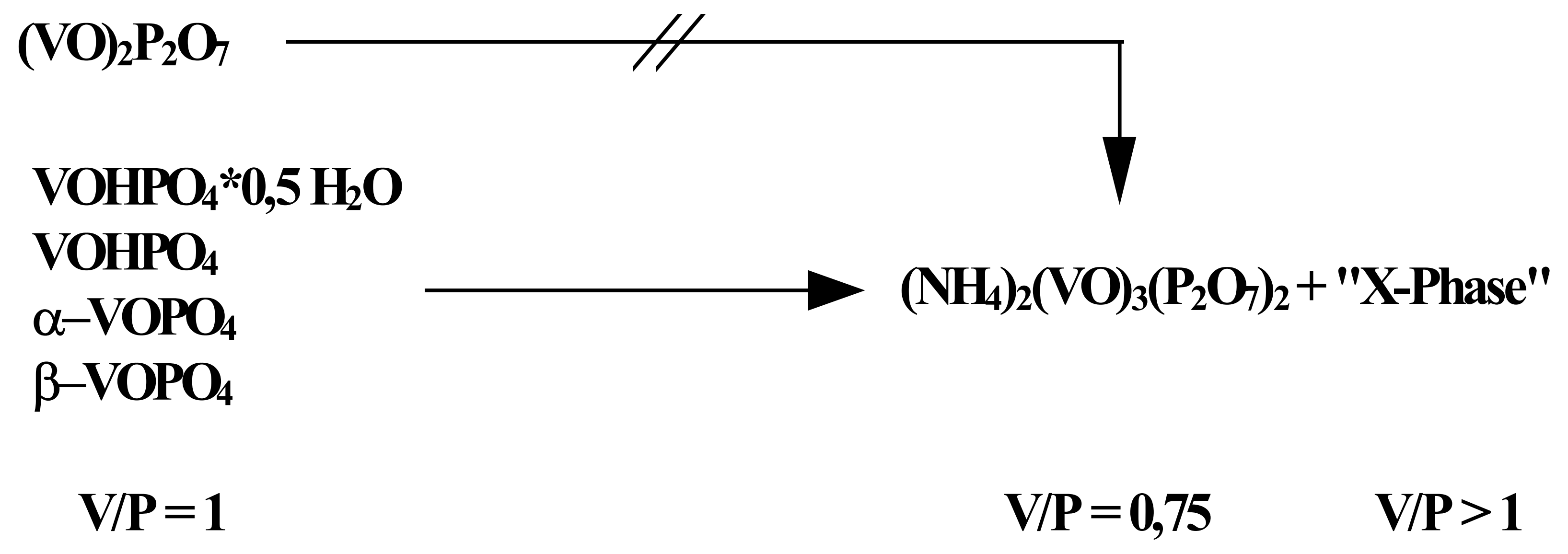
| Precursor | Reakt.-Temp. [°C] | $U_{n\text{-Butan}}$ [%] | $A_{MSA}$ [Mol-%] | $S_{MSA}$ [%] |
|---|---|---|---|---|
| *1* | 440 | 88,3 | 47,5 | 53,8 |
| *2* | 412 | 86,1 | 53,2 | 61,8 |
| *3* | 400 | 85,6 | 54,7 | 63,9 |

**Tabelle 4.** Butanumsätze und MSA-Ausbeuten eines Katalysators aus organischer Präparation (Äquilibrierung: Calcinierungsverfahren II mit anschließender Formierung)

| Reakt.-Temp. [°C] | $U_{n\text{-Butan}}$ [%] | $A_{MSA}$ [Mol-%] | $S_{MSA}$ [%] |
|---|---|---|---|
| 430 | 97,2 | 51,6 | 53,1 |
| 424 | 95,4 | 52,7 | 55,3 |
| 414 | 91,5 | 54,3 | 59,3 |
| 403 | 85,2 | 51,9 | 60,9 |

# 2. Ammoxidation of Methylaromatics, e.g. Toluene to Benzonitrile

## Precursors and Catalysts



$(VO)_2P_2O_7$

$VOHPO_4 * 0{,}5\ H_2O$

$VOHPO_4$

$\alpha-VOPO_4$

$\beta-VOPO_4$

$(NH_4)_2(VO)_3(P_2O_7)_2$ + "X-Phase"

$V/P = 1$

$V/P = 0{,}75$

$V/P > 1$

Scheme of the solid state transformation of vanadium phosphates under the conditions of ammoxidation of methylaromatics

# Ammoxidation

Solid state transformation of the different VPO precursors

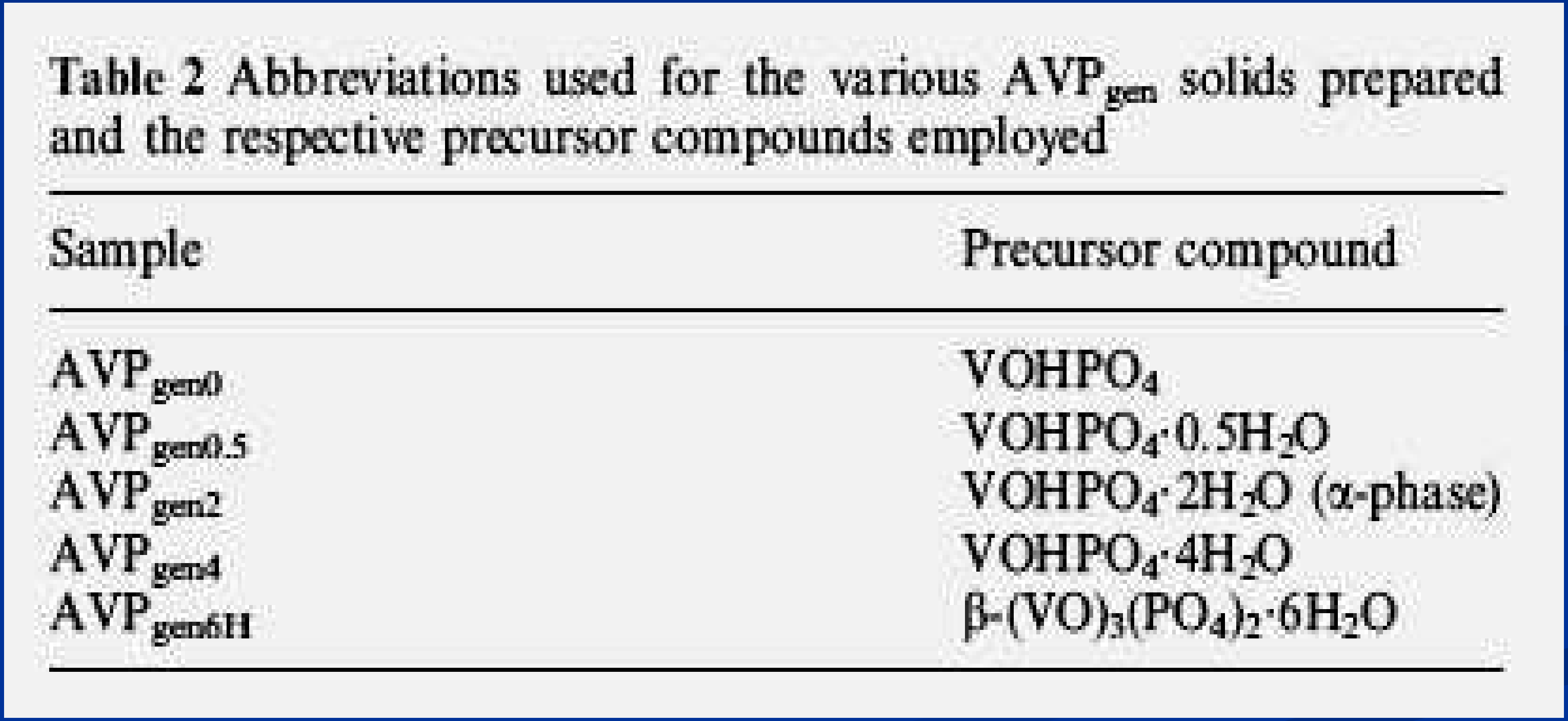


Table 2 Abbreviations used for the various $AVP_{gen}$ solids prepared and the respective precursor compounds employed

| Sample | Precursor compound |
|---|---|
| $AVP_{gen0}$ | $VOHPO_4$ |
| $AVP_{gen0.5}$ | $VOHPO_4\cdot 0.5H_2O$ |
| $AVP_{gen2}$ | $VOHPO_4\cdot 2H_2O$ (α-phase) |
| $AVP_{gen4}$ | $VOHPO_4\cdot 4H_2O$ |
| $AVP_{gen6H}$ | $\beta$-$(VO)_3(PO_4)_2\cdot 6H_2O$ |

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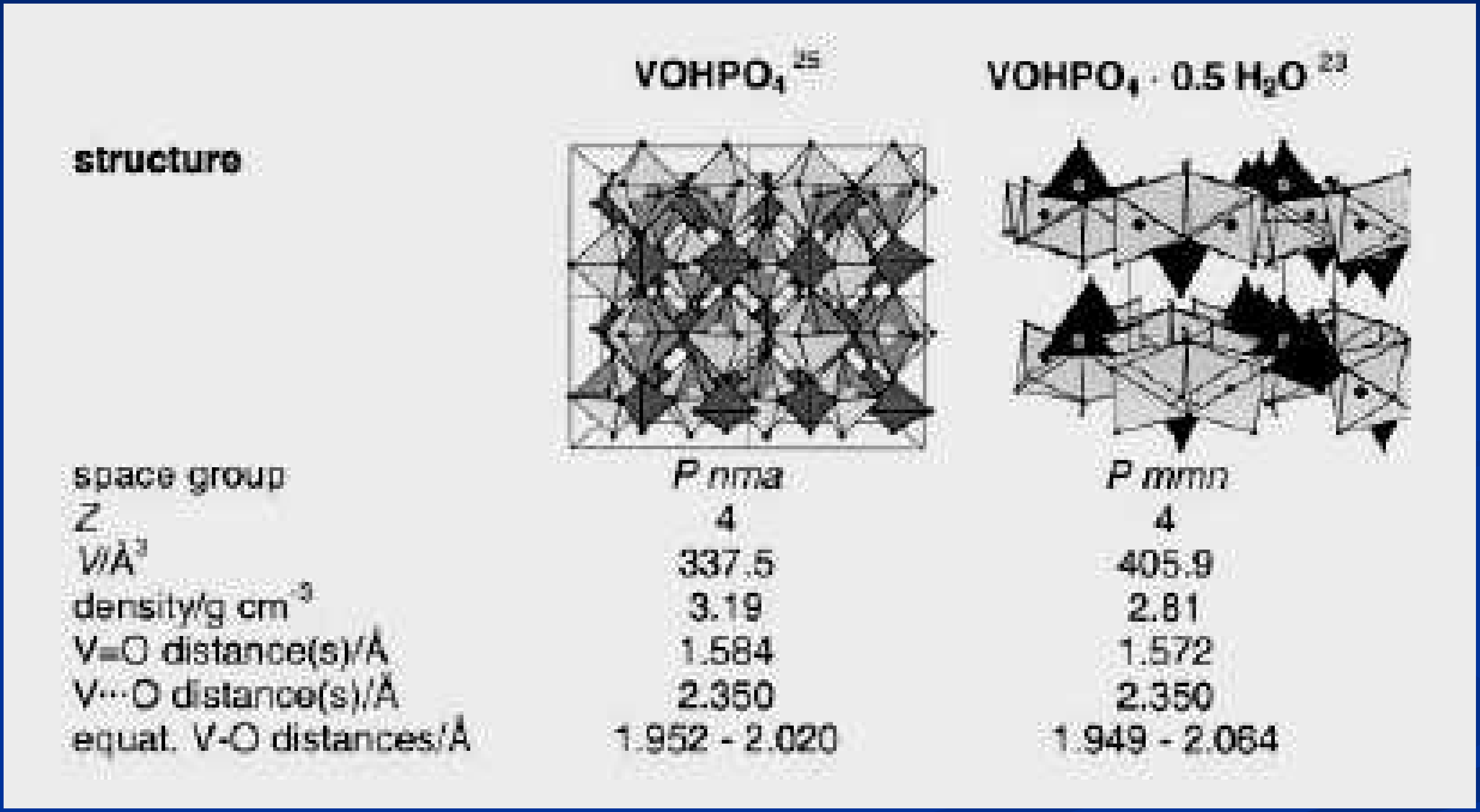
# Ammoxidation

## Structures of the different VPO precursor phases

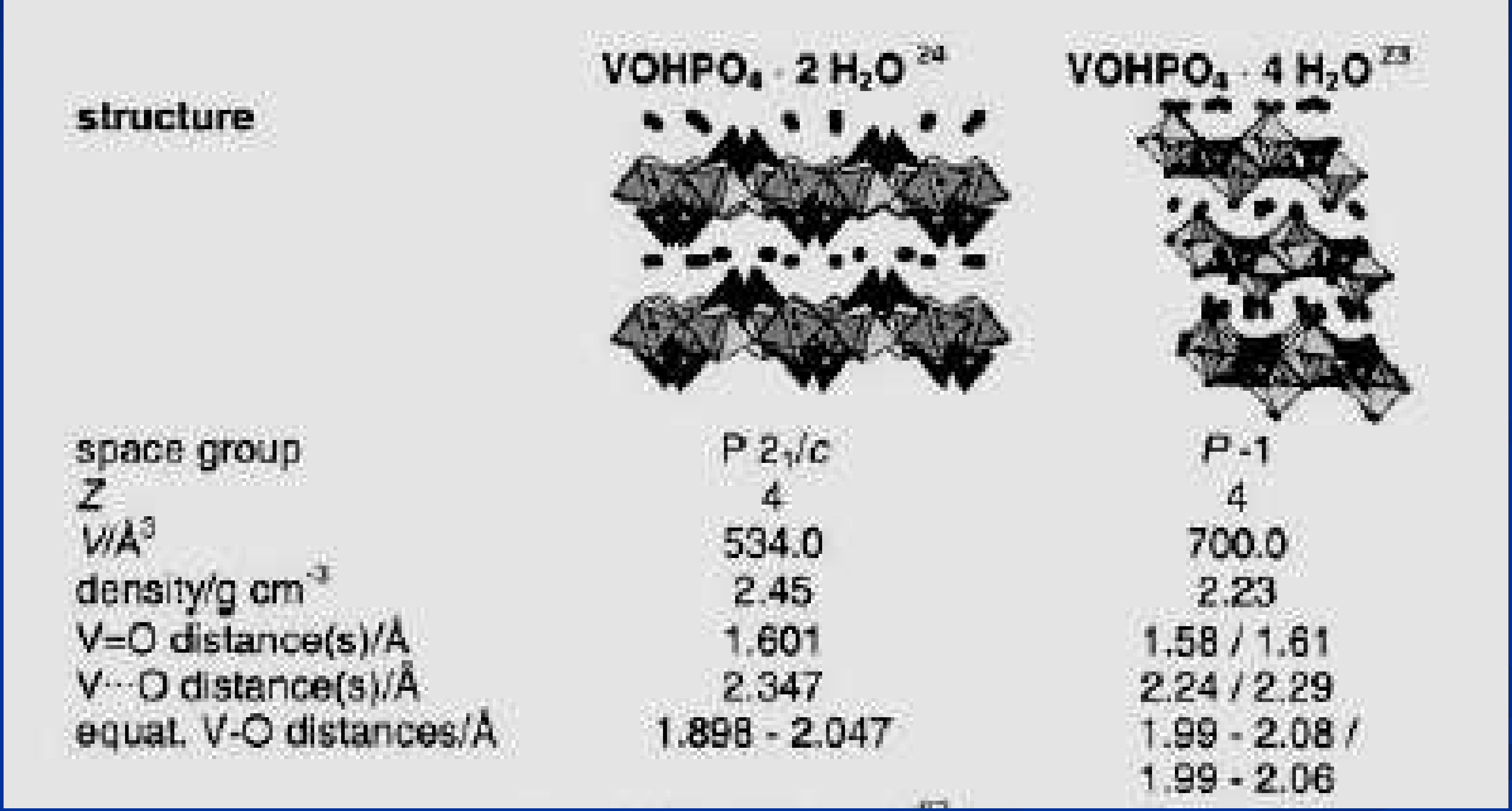


| | $VOHPO_4$ [25] | $VOHPO_4 \cdot 0.5\ H_2O$ [23] |
|---|---|---|
| **structure** | | |
| space group | *P nma* | *P mmn* |
| $Z$ | 4 | 4 |
| $V$/Å$^3$ | 337.5 | 405.9 |
| density/g cm$^{-3}$ | 3.19 | 2.81 |
| V=O distance(s)/Å | 1.584 | 1.572 |
| V···O distance(s)/Å | 2.350 | 2.350 |
| equat. V-O distances/Å | 1.952 - 2.020 | 1.949 - 2.064 |

A. Martin, L. Wilde, U. Steinike, J. Mater. Chem. 10 (2000) 2368-2374

# Ammoxidation

## Structures of the different VPO precursor phases



| | $VOHPO_4 \cdot 2\,H_2O$ [24] | $VOHPO_4 \cdot 4\,H_2O$ [23] |
|---|---|---|
| structure | | |
| space group | $P\,2_1/c$ | $P\,\bar{1}$ |
| $Z$ | 4 | 4 |
| $V/Å^3$ | 534.0 | 700.0 |
| density/g cm$^{-3}$ | 2.45 | 2.23 |
| V=O distance(s)/Å | 1.601 | 1.58 / 1.61 |
| V···O distance(s)/Å | 2.347 | 2.24 / 2.29 |
| equat. V-O distances/Å | 1.898 - 2.047 | 1.99 - 2.08 /<br>1.99 - 2.06 |

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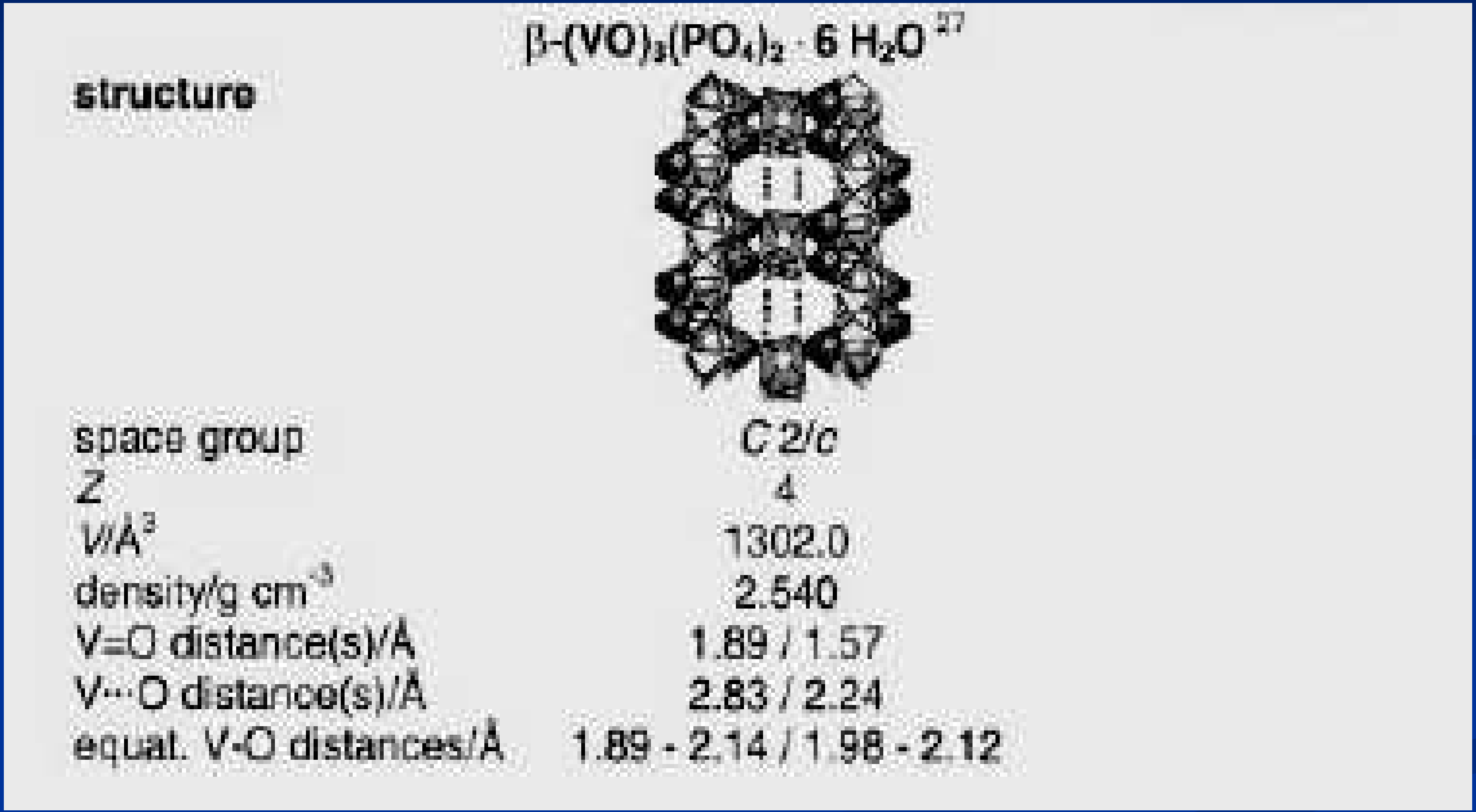
# Ammoxidation

## Structures of the different VPO precursor phases



| | $\beta$-$(VO)_3(PO_4)_2 \cdot 6\,H_2O$ [27] |
|---|---|
| structure | |
| space group | *C* 2/*c* |
| *Z* | 4 |
| *V*/Å$^3$ | 1302.0 |
| density/g cm$^{-3}$ | 2.540 |
| V=O distance(s)/Å | 1.89 / 1.57 |
| V···O distance(s)/Å | 2.83 / 2.24 |
| equat. V-O distances/Å | 1.89 - 2.14 / 1.98 - 2.12 |

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# Ammoxidation

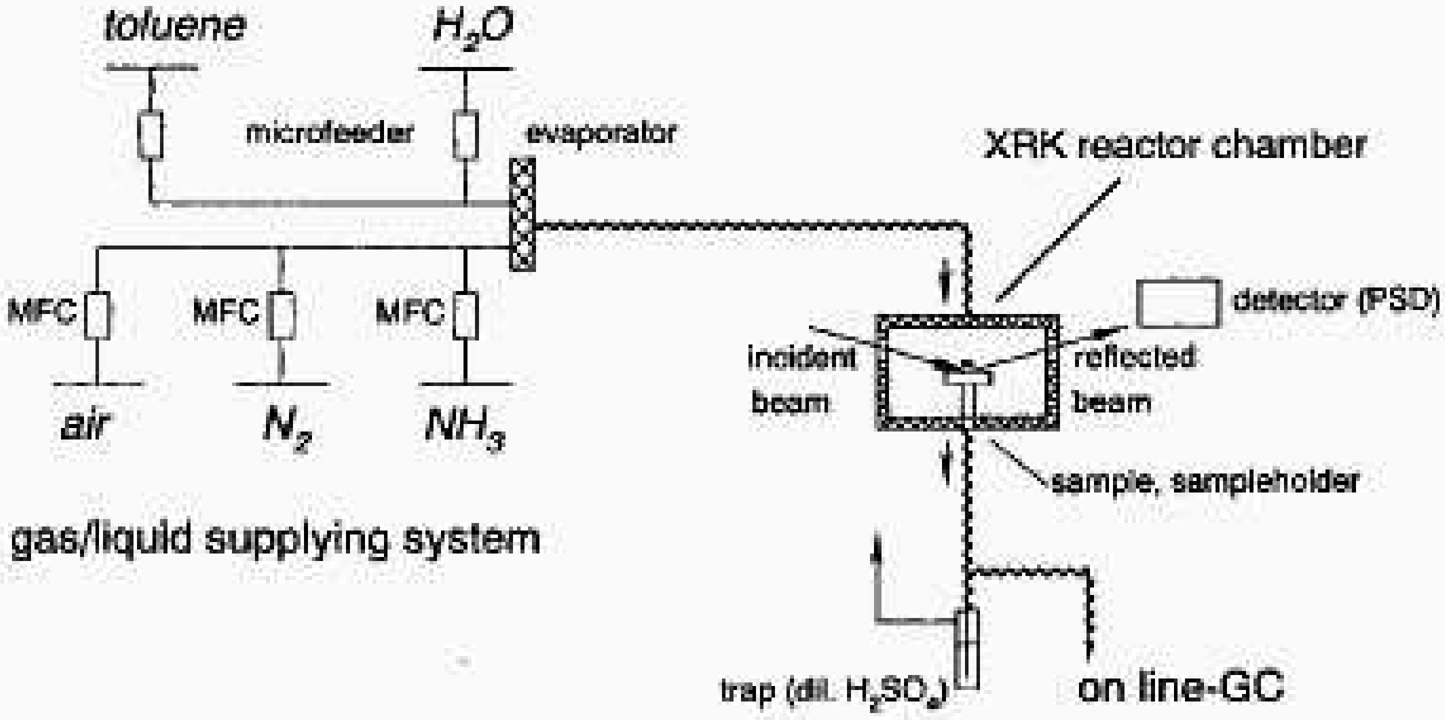

Fig. 2 Scheme of the *in situ* XRD/catalytic reactor set-up.

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# Ammoxidation

## Formation of the ammonium vanadyl(IV) phosphate catalysts

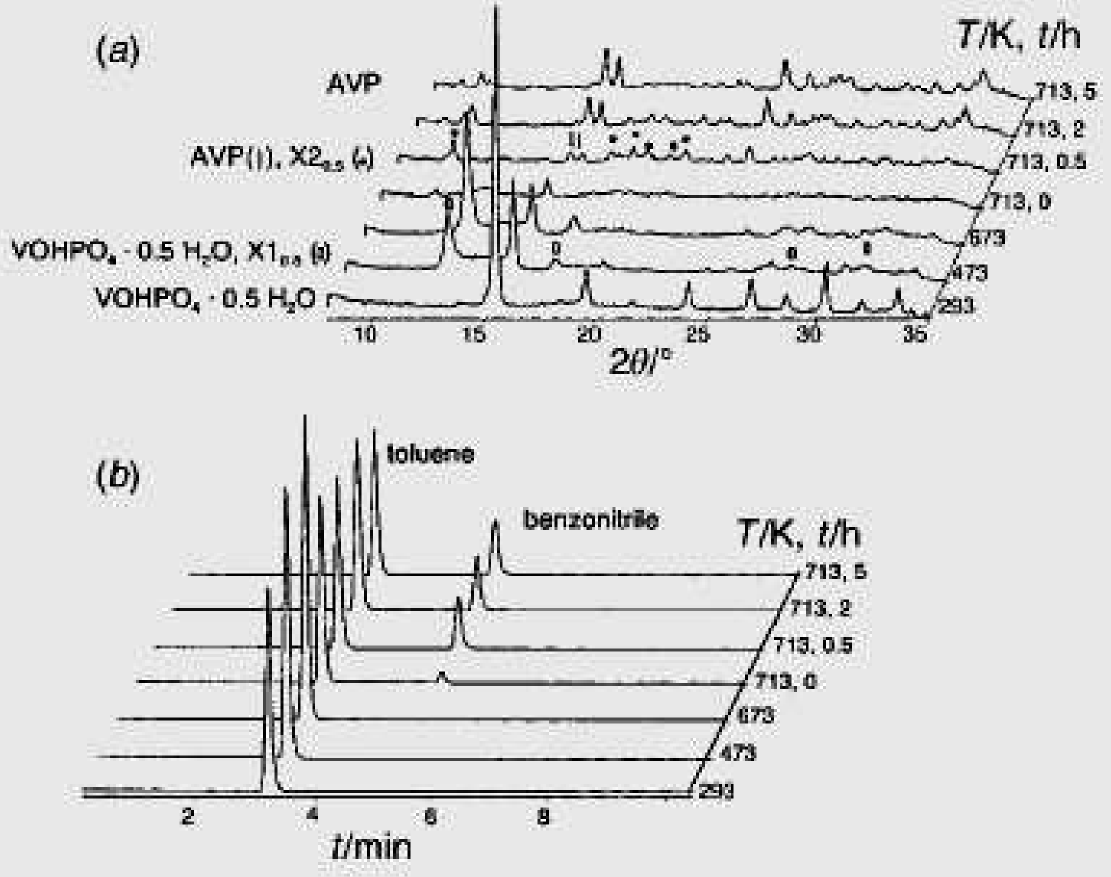


Fig. 3 XRD pattern of (a) the $VOHPO_4{\cdot}0.5H_2O$ to $AVP_{gen0.5}$ transformation process and (b) gas chromatographic analysis of the product stream as a function of time-on-stream.

# Ammoxidation

## Formation of the ammonium vanadyl(IV) phosphate catalysts

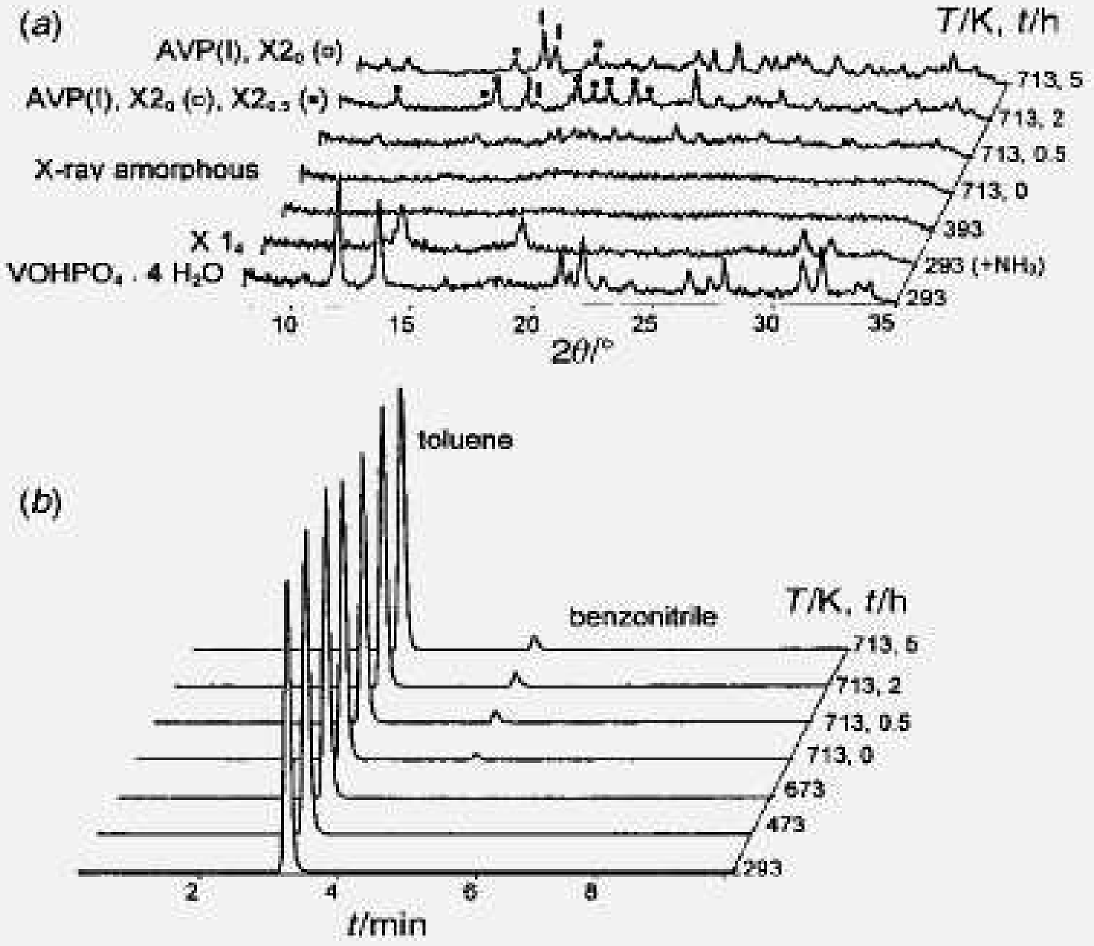


Fig. 4 XRD pattern of (a) the $VOHPO_4{\cdot}4H_2O$ to $AVP_{gen4}$ transformation process and (b) gas chromatographic analysis of the product stream as a function of time-on-stream.

# Ammoxidation

## Formation of the ammonium vanadyl(IV) phosphate catalysts – observed intermediate phases and final products

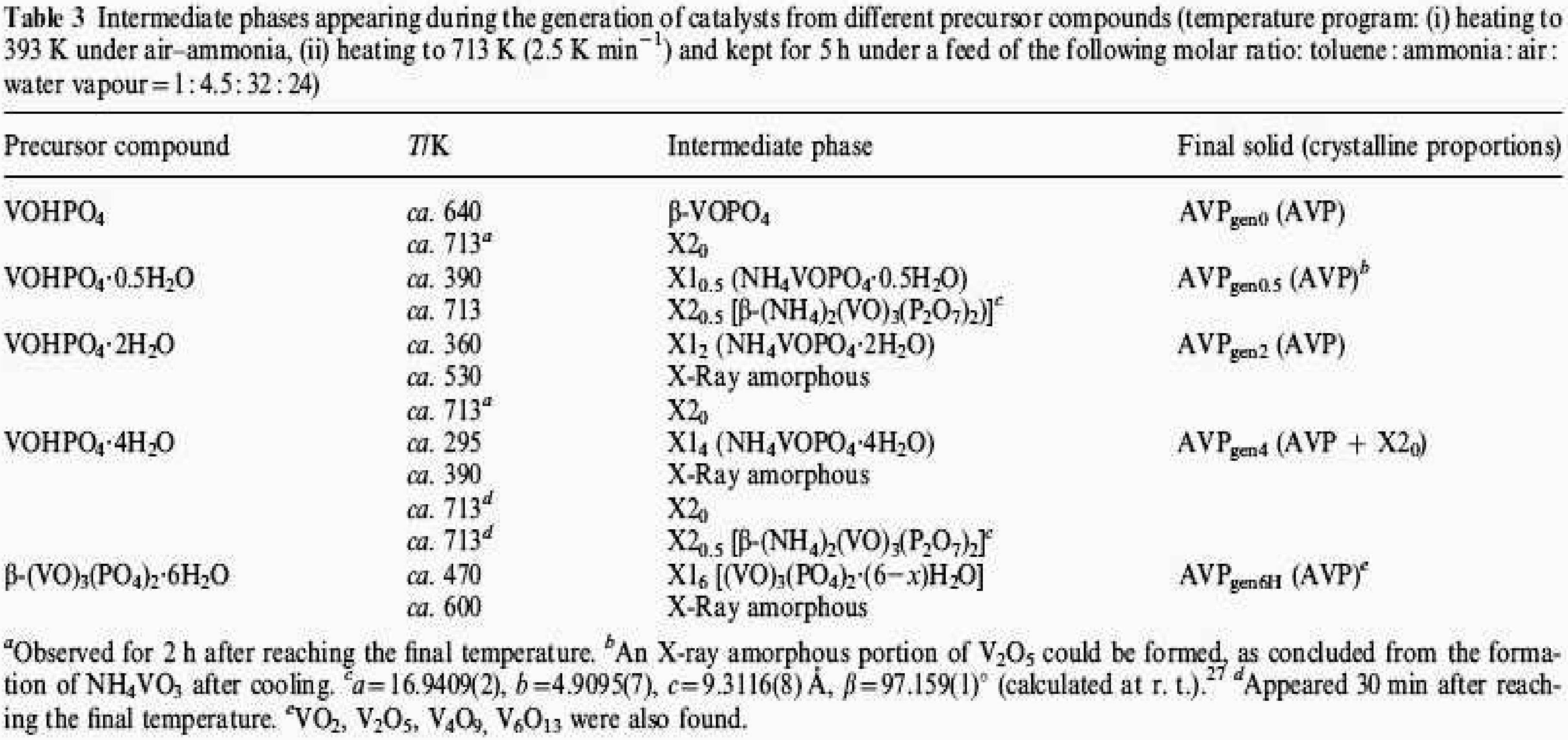


Table 3 Intermediate phases appearing during the generation of catalysts from different precursor compounds (temperature program: (i) heating to 393 K under air–ammonia, (ii) heating to 713 K (2.5 K $min^{-1}$) and kept for 5 h under a feed of the following molar ratio: toluene : ammonia : air : water vapour = 1 : 4.5 : 32 : 24)

| Precursor compound | *T*/K | Intermediate phase | Final solid (crystalline proportions) |
|---|---|---|---|
| $VOHPO_4$ | *ca.* 640 | $\beta$-$VOPO_4$ | $AVP_{gen0}$ (AVP) |
| | *ca.* 713[a] | $X2_0$ | |
| $VOHPO_4 \cdot 0.5H_2O$ | *ca.* 390 | $X1_{0.5}$ ($NH_4VOPO_4 \cdot 0.5H_2O$) | $AVP_{gen0.5}$ (AVP)[b] |
| | *ca.* 713 | $X2_{0.5}$ [$\beta$-$(NH_4)_2(VO)_3(P_2O_7)_2$)][c] | |
| $VOHPO_4 \cdot 2H_2O$ | *ca.* 360 | $X1_2$ ($NH_4VOPO_4 \cdot 2H_2O$) | $AVP_{gen2}$ (AVP) |
| | *ca.* 530 | X-Ray amorphous | |
| | *ca.* 713[a] | $X2_0$ | |
| $VOHPO_4 \cdot 4H_2O$ | *ca.* 295 | $X1_4$ ($NH_4VOPO_4 \cdot 4H_2O$) | $AVP_{gen4}$ (AVP + $X2_0$) |
| | *ca.* 390 | X-Ray amorphous | |
| | *ca.* 713[d] | $X2_0$ | |
| | *ca.* 713[d] | $X2_{0.5}$ [$\beta$-$(NH_4)_2(VO)_3(P_2O_7)_2$][c] | |
| $\beta$-$(VO)_3(PO_4)_2 \cdot 6H_2O$ | *ca.* 470 | $X1_6$ [$(VO)_3(PO_4)_2 \cdot (6-x)H_2O$] | $AVP_{gen6H}$ (AVP)[e] |
| | *ca.* 600 | X-Ray amorphous | |

[a] Observed for 2 h after reaching the final temperature. [b] An X-ray amorphous portion of $V_2O_5$ could be formed, as concluded from the formation of $NH_4VO_3$ after cooling. [c] $a = 16.9409(2)$, $b = 4.9095(7)$, $c = 9.3116(8)$ Å, $\beta = 97.159(1)°$ (calculated at r. t.).[27] [d] Appeared 30 min after reaching the final temperature. [e] $VO_2$, $V_2O_5$, $V_4O_9$, $V_6O_{13}$ were also found.

# Ammoxidation

Solid state transformation of oxovanadium hydrogen-phosphate hemihydrate under ammoxidation conditions

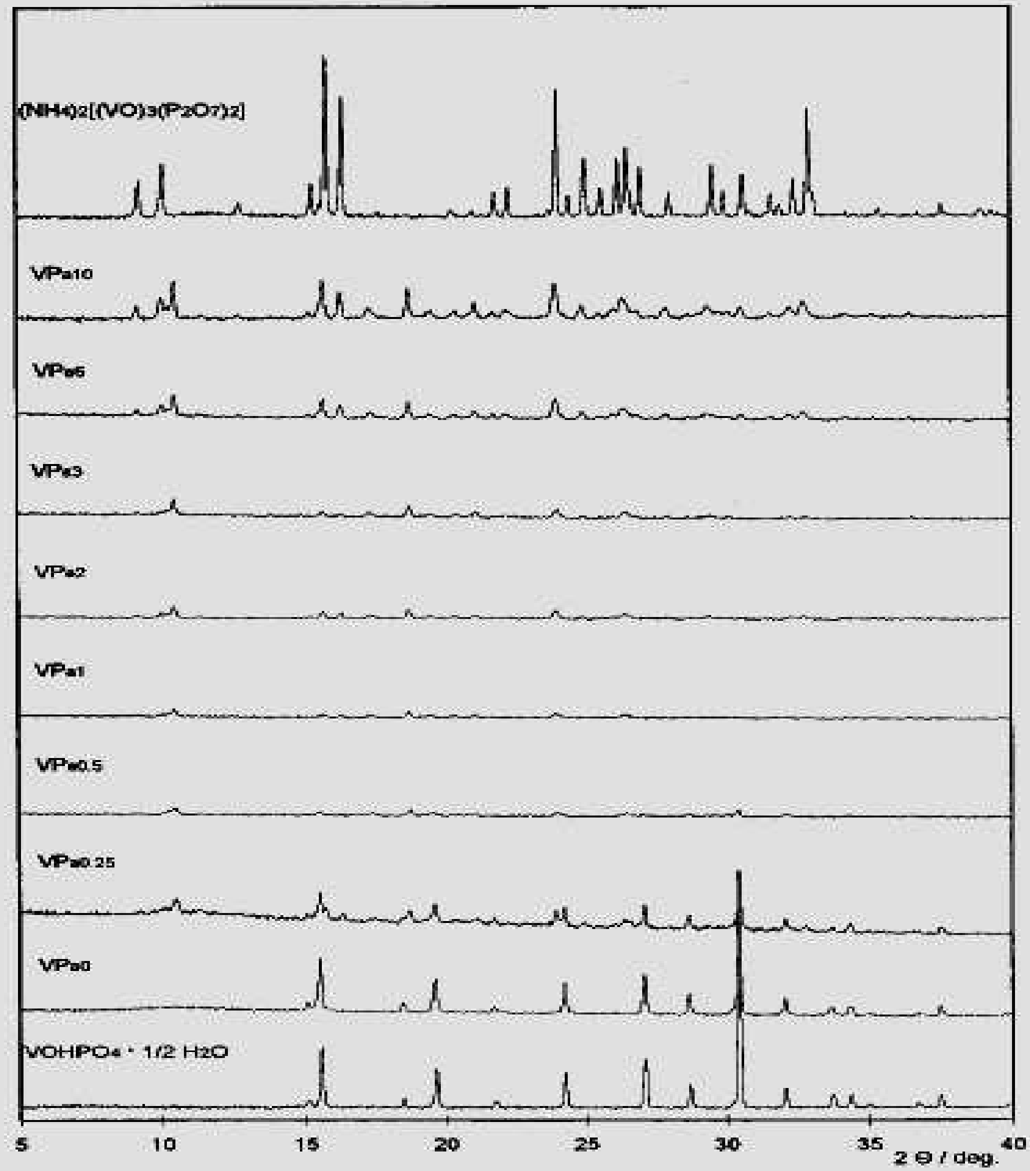


**Figure 1.** X-ray powder diffraction patterns of $VOHPO_4 \cdot {}^1/_2H_2O$, hemihydrate samples treated with ammoxidation gas flow ($VP_{a0}$—$Vp_{a10}$, run a) and the as-synthesized $(NH_4)_2[(VO)_3(P_2O_7)_2]$.

Y. Zhang, A. Martin, G.-U. Wolf, S. Rabe, H. Worzala, B. Lücke, M. Meisel, K. Witke; Chem. Mater. 8 (1996) 1135-1140

# Ammoxidation

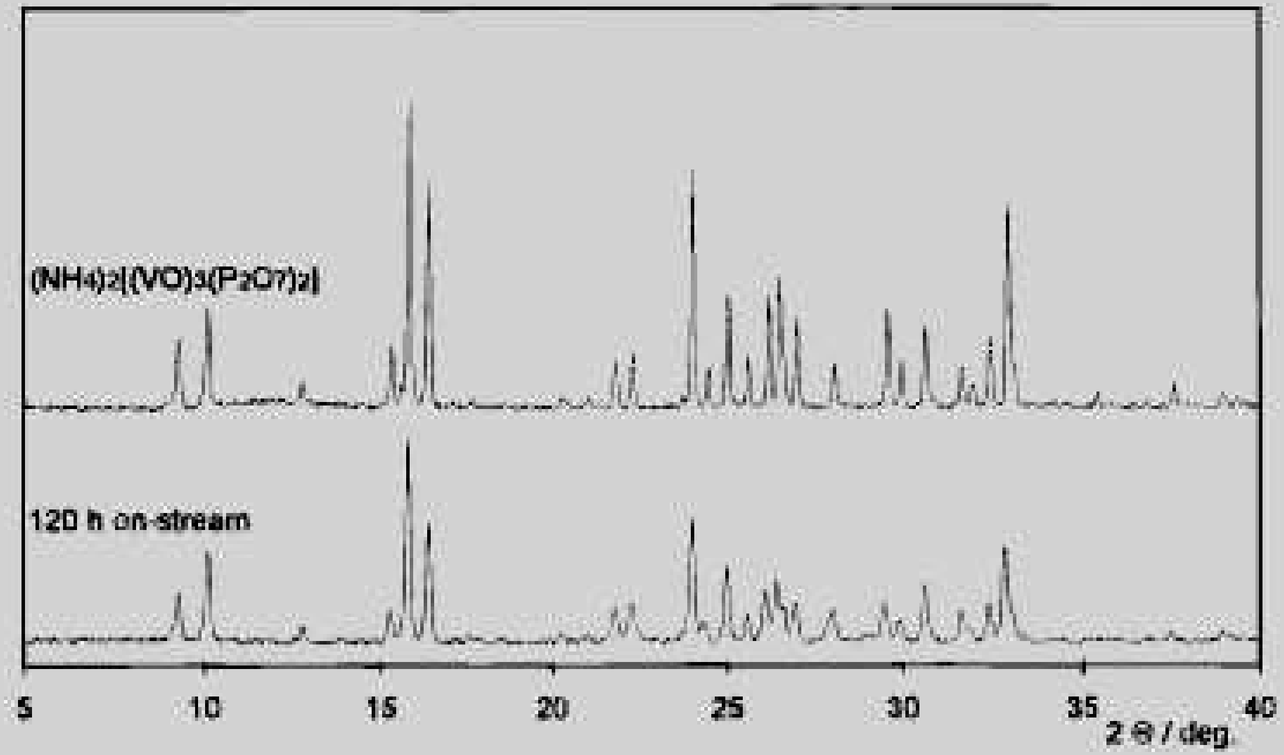
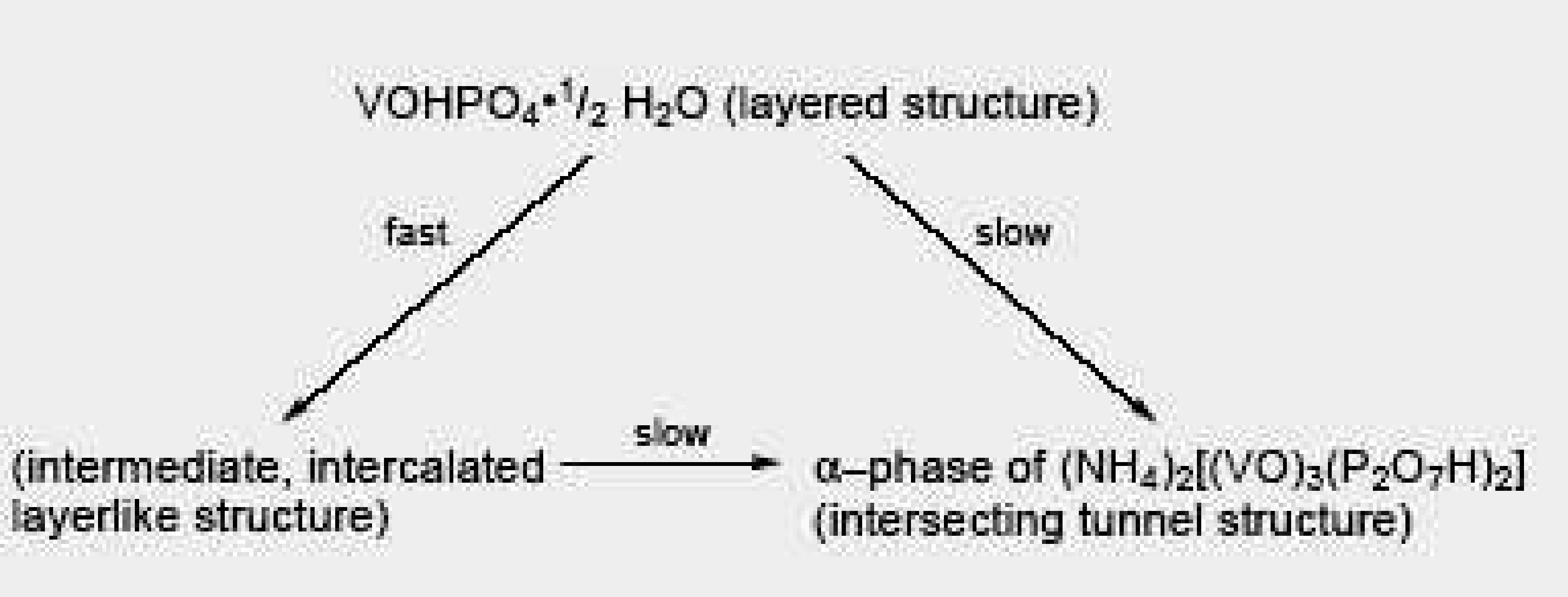


**Figure 2.** X-ray powder diffraction patterns of an ammoxidation catalyst ($VOHPO_4 \cdot {}^1/_2H_2O$ precursor) proceeding 120 h on-stream in comparison to the as-synthesized $(NH_4)_2[(VO)_3(P_2O_7)_2]$.

# Ammoxidation

Paths of the solid state transformation of the Hemihydrate

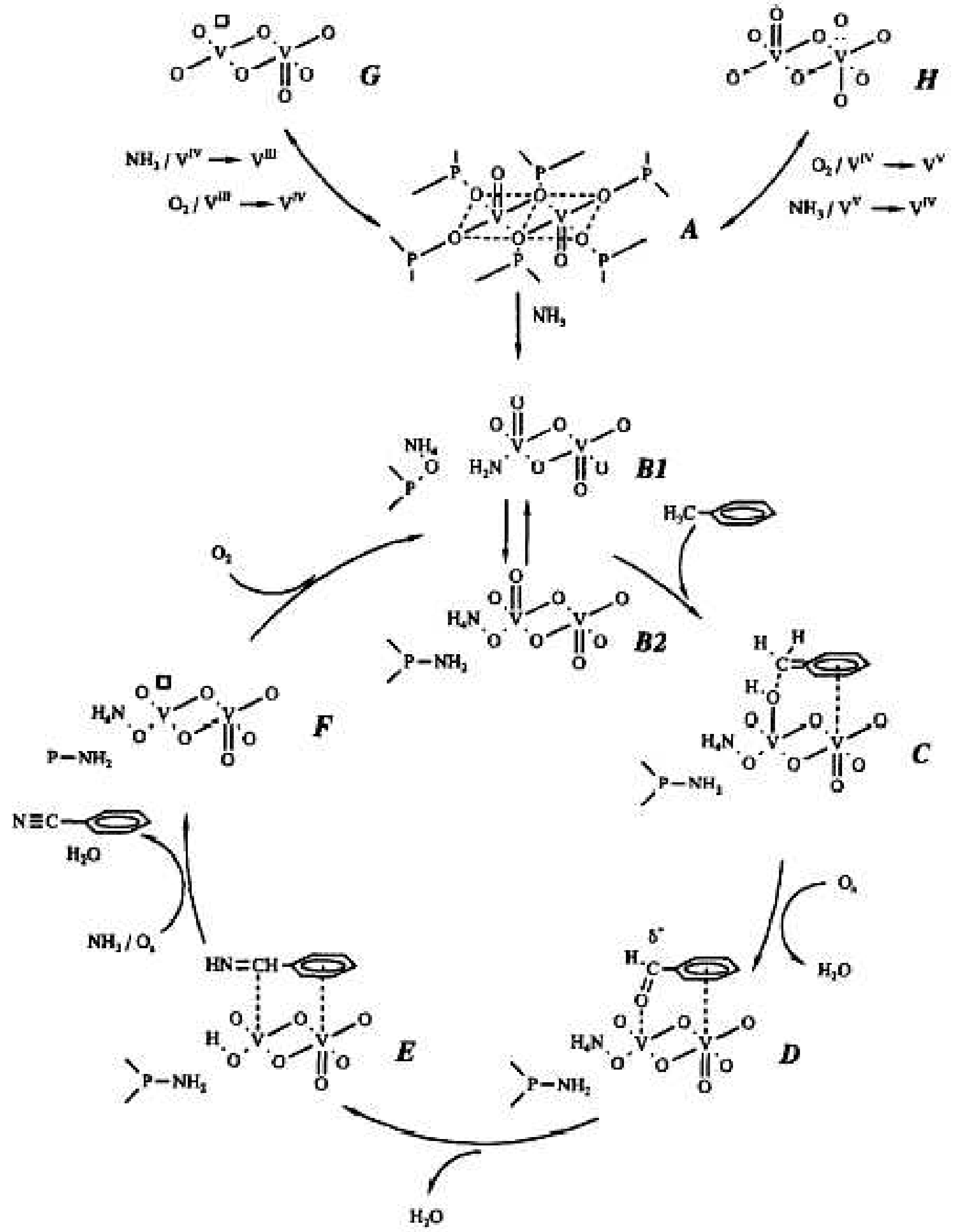


**Reaction scheme:**

$$VOHPO_4 \cdot {}^1/_2H_2O + NH_3/O_2/(H_2O) \rightarrow \alpha\text{-}(NH_4)_2[(VO)_3(P_2O_7)_2] + \text{“}V_xO_y\text{”}$$

# Ammoxidation

Proposed Mechanism of the ammoxidation of toluene to benzonitril on NVP-catalysts



Scheme 1.

Y. Zhang, A. Martin, H. Berndt, B. Lücke, M. Meisel, J. Mol. Catal. A: Chemical, 118 (1997) 205-214