



On the dynamics of phosphorus in vanadyl phosphates: a key property governing their catalytic behaviour

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Introduction

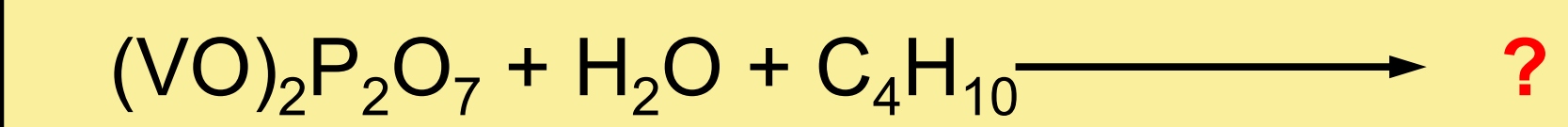
Industrial application of vanadyl pyrophosphate (VPP) catalysts (V:P=1:1) in the oxidation of n-butane to maleic anhydride (MA)

- Tendency to “de-selectivation” due to “over-activation” of VPP catalysts because of loss of phosphorus and formation of non-selective VPO phases (see [1, 2])
- Reasons for P loss:
 - Influence of water vapour [3], H₂O content of industrial effluent gas of butane oxidation: > 8 % (moisture and H₂O formed by reaction [1])
 - Formation of volatile P organic compounds [4] ?
- Avoidance of P loss: Addition of small amounts of esters of phosphoric acid to feed [1]

Approach and Aims

- Investigation of mobility and “household” of P in VPP catalysts

- Influence of water vapour
- Nature of volatile P compounds



Aims

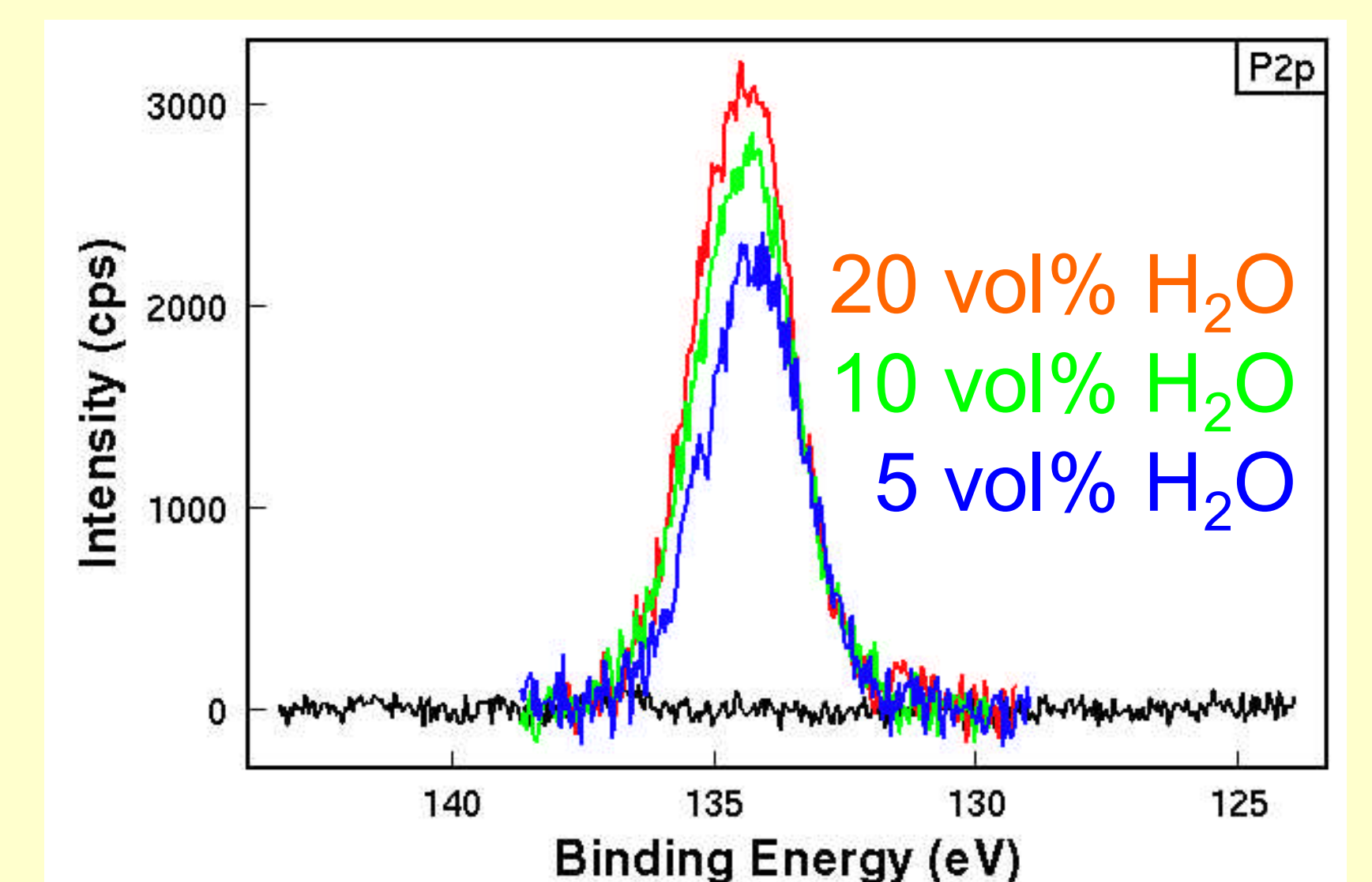
- Elucidation of the nature of volatile P compounds
- Determination of the P loss under model and industrial-like conditions
- Better understanding of the nature of the active sites

Experimental

Preparation of C-free VPP (V:P=1:1.0) via VOHPO₄ · 0.5H₂O precursors from alcoholic and aqueous media, s. [1]

- Equilibration of VPP(1) for 8 d in n-butane (1.8 %)/air; V oxidation number: 4.17
- Pseudo-equilibration of VPP(2) for 2 h in O₂ (2 %)/N₂; V oxidation number: 4.01
- Shaping to granules (1.25 ... 4.5 mm)
- Use in quartz tube reactor (QR, i.D. 8 mm, 10 ml VPP(1),(2)) and stainless steel reactor (SR, i.D. 20 mm, 30 ml VPP(2))

- Treatment with water vapour addition
- atmospheres: N₂, He, Air, 1.5 % C₄H₁₀/air/H₂O-vapour (5 – 69 vol.-%, saturator),
- Conditions: model treatments: T until 650 °C (QR), 2-8 h similar to industrial conditions: T: 450 °C (SR), max.4 d
- Determination of P in effluent:
 - ³¹P NMR of liquid absorbents
 - XPS: Adsorption on Ag foil (reactor outlet)
- Characterization of catalysts:
 - ICP-OES
 - potentiometric titration
 - XRD



catalyst temperature: 600 °C, H₂O/N₂, 3 l h⁻¹, 2 h

- ★ P2p signal at 134.3 eV: characteristic for meta phosphates [5]
- ★ Increasing H₂O concentration: increasing peak intensity
- ★ Shift to lower binding energy: different PO_x species

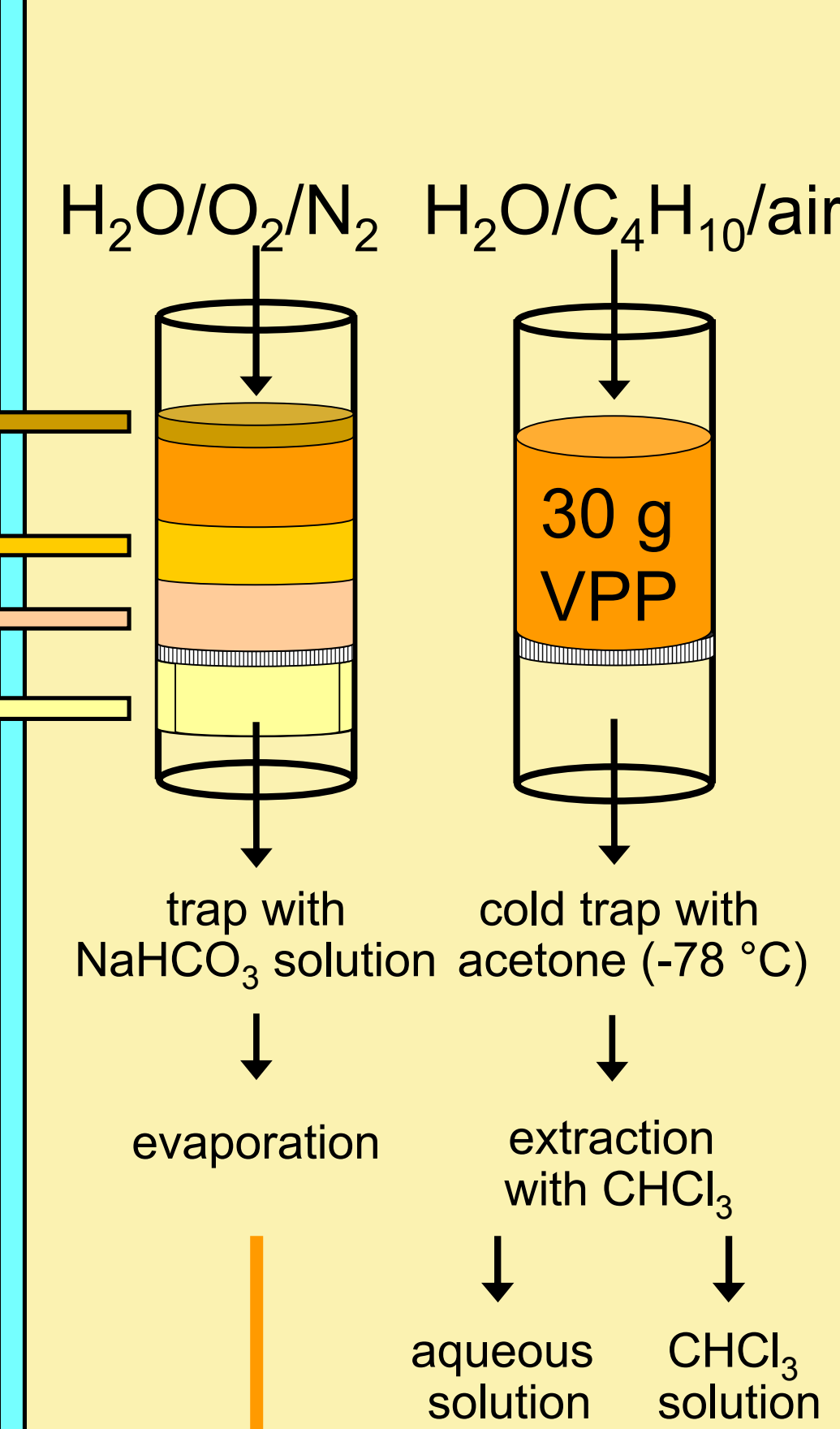
Methods of investigation

	ICP-OES	potent. Titration	XRD
	P:V	n in V ⁿ⁺	Determined phases
fresh samples	1,00	4,16	(VO) ₂ P ₂ O ₇ [PDF 34-1381] VOPO ₄ · 1,58 H ₂ O [3]
inlet	0,58	4,88	β-VOPO ₄ [PDF 27-948]
middle	0,90	4,87	β-VOPO ₄
outlet	~1,00	4,85	β-VOPO ₄ Si ₃ (PO ₄) ₄ [PDF 22-1380]

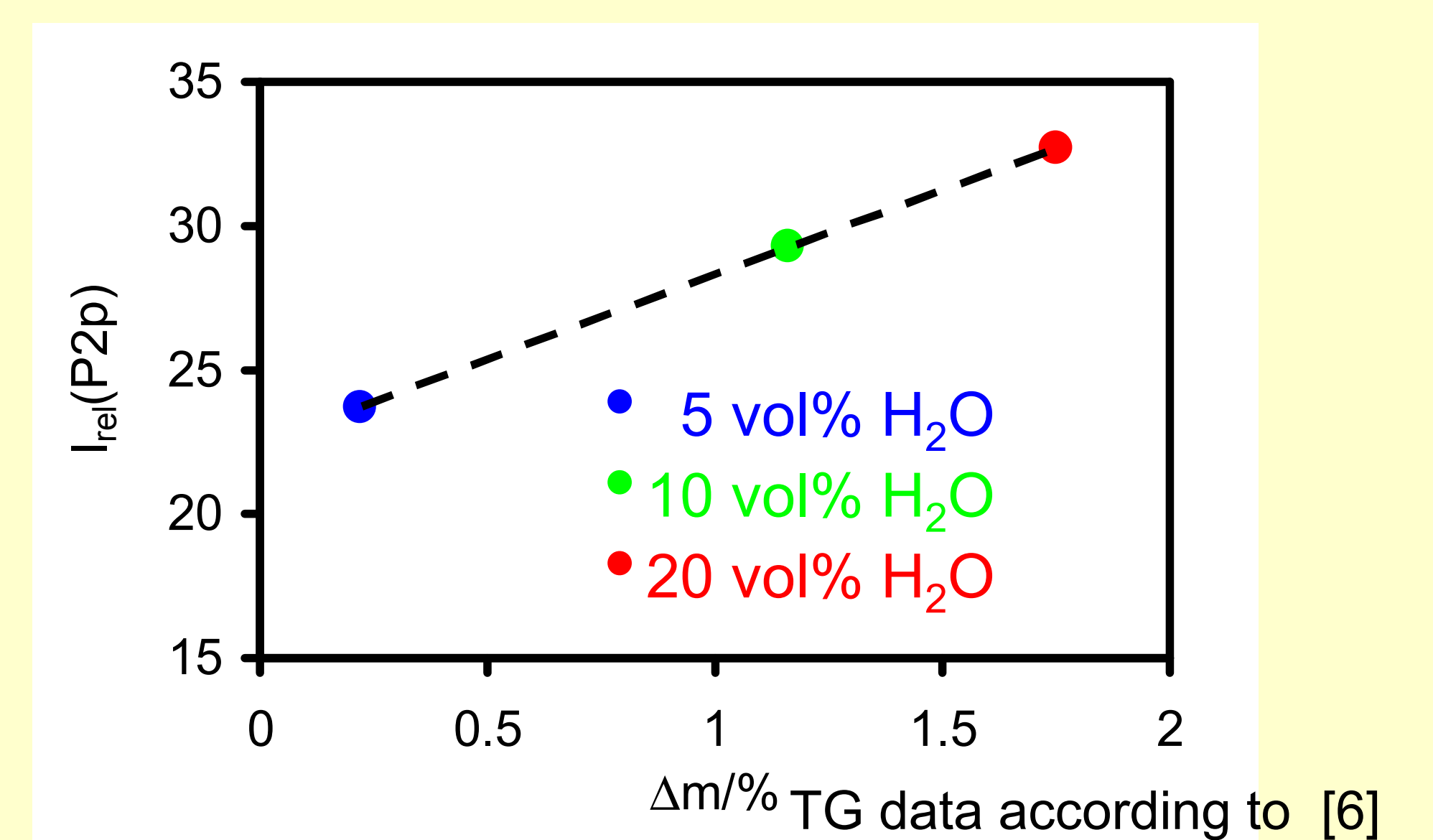
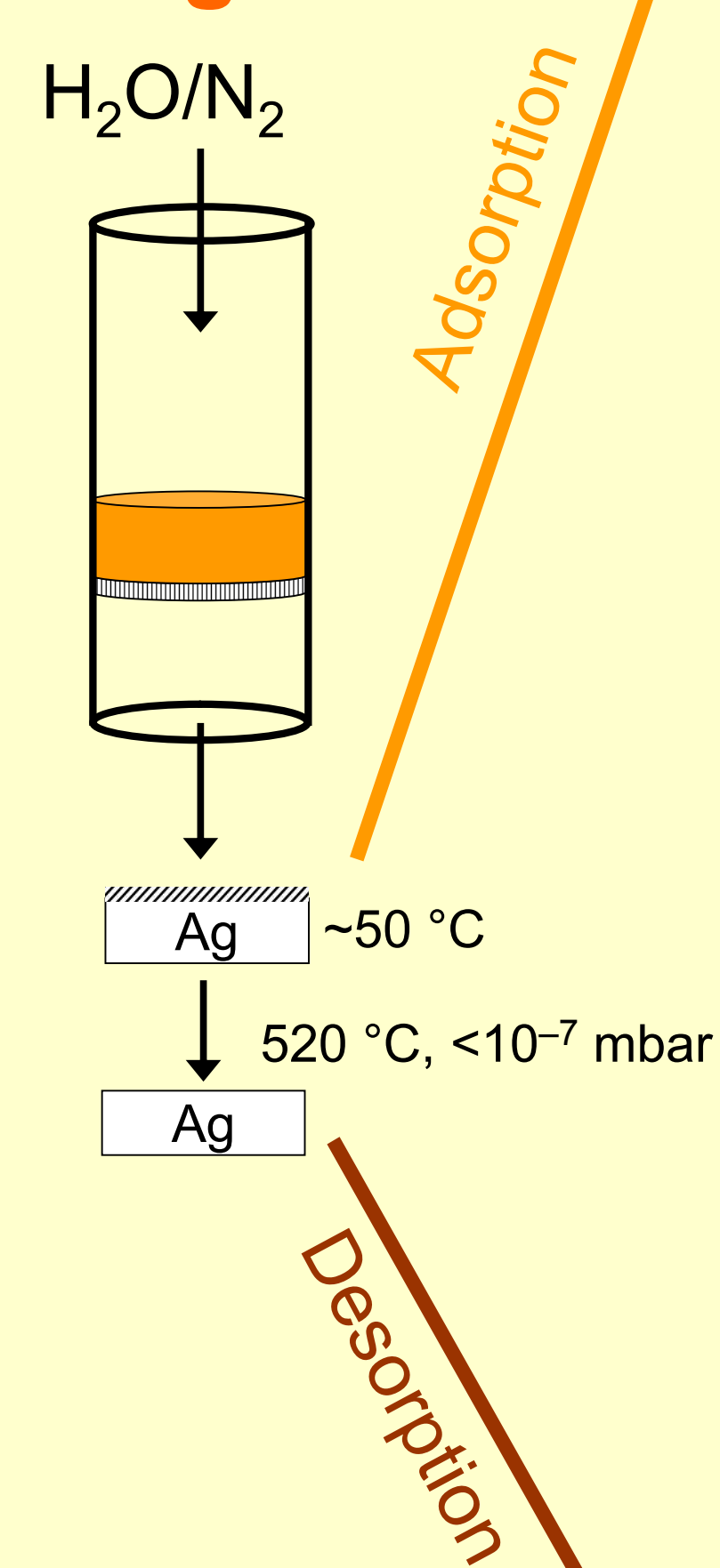
Effect of H₂O/O₂/N₂ treatment on VPP:

- ★ P impoverishment (very strong at reactor inlet)
- ★ Vanadium oxidation in presence of oxygen: formation of VOPO₄ in whole catalyst bed
- ★ Formation of silicophosphates by reaction of hot quartz-reactor walls with released PO_x species

³¹P NMR



XPS of Ag foil



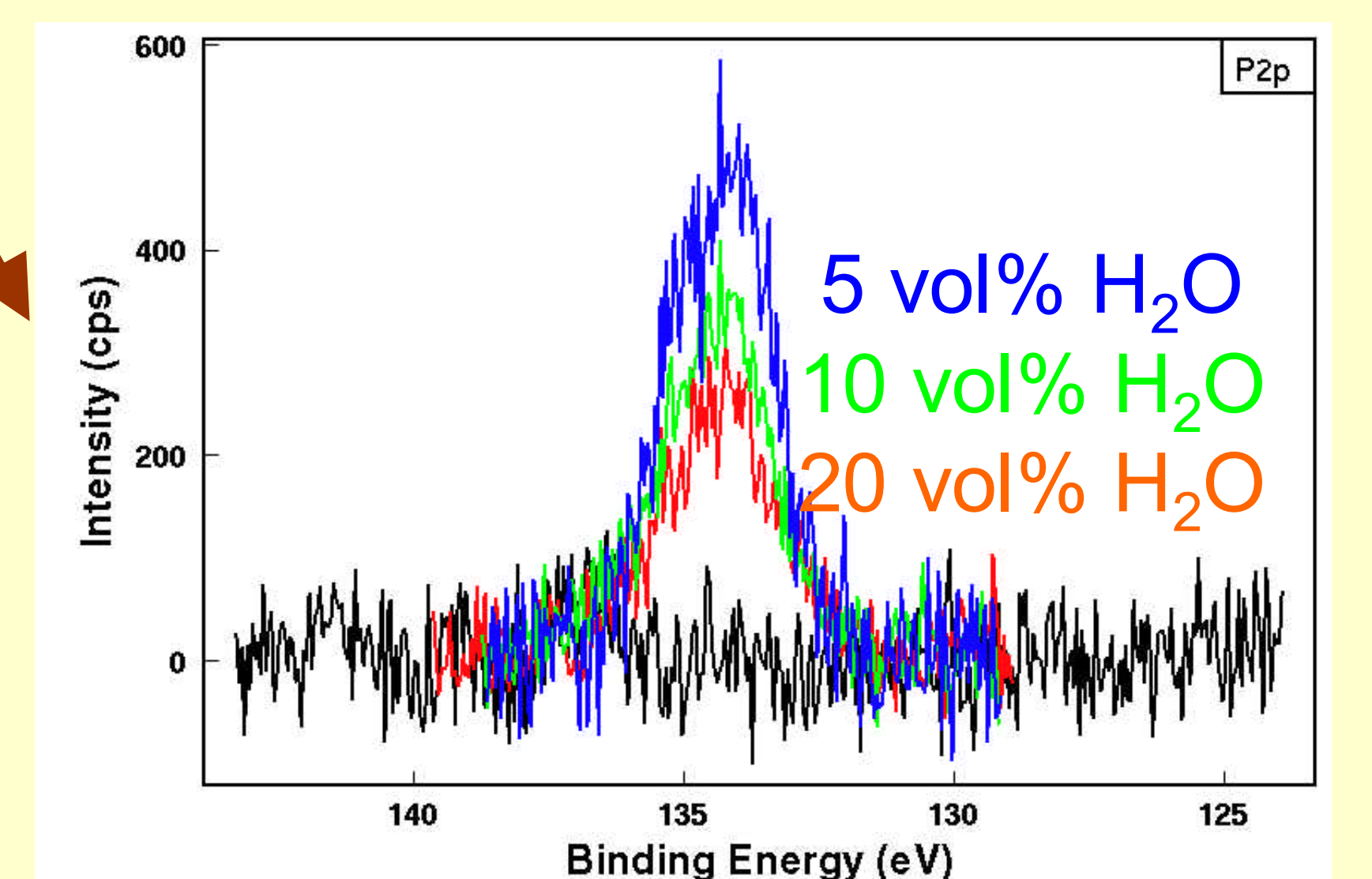
- ★ Correlation of mass loss (determined by TG using the same catalyst [6]) and P2p XPS signal intensity: volatile species contain P

Determination of P_xO_y ions in aqueous solution:

- ★ Increasing intensity of ³¹P NMR PO₄³⁻ signals with increasing duration of catalyst treatments with H₂O at higher temperature
- ★ Determination of small fraction of P₂O₇²⁻ at prolonged treatment times

time/h	chem. shift/ppm	assignment	intensity
22	–	–	0.00
43	3.80	PO ₄ ³⁻	0.01
62	3.76	PO ₄ ³⁻	0.40
86	3.80/–4.20	PO ₄ ³⁻ /P ₂ O ₇ ²⁻	0.60/0.30

- Reaction gas of butane oxidation: ³¹P NMR: no organic compounds in CHCl₃



catalyst temperature: 600 °C, H₂O/N₂, 3 l h⁻¹, 2 h (Adsorption)

- ★ Decreasing intensity of peaks with increasing content of water vapour
- ★ Different desorption of PO_x from different treated VPP samples: formation of different PO_x species

Conclusions

- Reason for the P loss of VPP catalysts during oxidation of butane to MA: hydrolysis of (VO)₂P₂O₇ to V: P >1 phases up to the formation of VO_x (see [7])
- Nature of the volatile P species: P₁O_x species predominates, P₂O_x species to a minor extent
- Dual role of P in VPO catalysts:
 - Stabilizing the active and selective form of the VPP catalyst by preventing the formation of extended surfaces of binary vanadium oxides. The latter ones are thought to form the active and selective sites as long as they are of nanoscopic dimension [8]
 - Being mobile what may be used to redistribute P over the whole catalyst bed in the case of a previous “overdosing” of phosphorus [9]

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