Accepted Manuscript

Title: α_{II} -(V_{1-x}W_x)OPO₄ catalysts for the selective oxidation of *n*-butane to maleic anhydride

Authors: C. Schulz, S.C. Roy, K. Wittich, R. Naumann d'Alnoncourt, S. Linke, V. Strempel, B. Frank, R. Glaum, F. Rosowski



Please cite this article as: Schulz C, Roy SC, Wittich K, d'Alnoncourt RN, Linke S, Strempel V, Frank B, Glaum R, Rosowski F, α_{II} -($V_{1-x}W_x$)OPO₄ catalysts for the selective oxidation of *n*-butane to maleic anhydride, *Catalysis Today* (2018), https://doi.org/10.1016/j.cattod.2018.05.040

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



α_{II} -(V_{1-x}W_x)OPO₄ catalysts for the selective oxidation of *n*-butane to maleic anhydride

C. Schulz^a, S. C. Roy^b, K. Wittich^b, R. Naumann d'Alnoncourt^a, S. Linke^{a,d}, V. Strempel^{a,d},

B. Frank^{a,*}, R. Glaum^{b,*}, F. Rosowski^{a,c}

a) BasCat - UniCat BASF JointLab, Technische Universität Berlin, 10623 Berlin, Germany

b) Institute for Inorganic Chemistry, Rheinische Friedrich-Wilhelms-Universität, 53121 Bonn, Germany

c) BASF SE, Process Research and Chemical Engineering, 67056 Ludwigshafen, Germany

d) Present address: BASF SE, Process Research and Chemical Engineering, 67056 Ludwigshafen, Germany

*) corresponding authors: BF: b.frank@bascat.tu-berlin.de; RG: rglaum@uni-bonn.de

Graphical Abstract



all-V1-xMxOPO4 (M=W,Mo)

Highlights

- solution combustion synthesis (SCS) leads to a variety of phase pure catalysts
- doping with Mo and W tunes the oxidation state of V in VOPO4 between 4+ and 5+
- αll-(V1-xWx)OPO4 reaches selectivities of maleic anhydride of more than 30%
- αll type solid solutions are a flexible platform for further research

Highlights

- A variety of phase pure catalysts for the selective oxidation of *n*-butane to maleic anhydride can be prepared via solution combustion synthesis (SCS)
- By doping with Mo and W the average oxidation state of V in VOPO₄ can be tuned between 4+ and 5+
- α_{II}-(V_{1-x}W_x)OPO₄ reaches selectivities of maleic anhydride of more than 30%, which is hardly achieved with other non-VPP based catalysts
- α_{II} type solid solutions are a flexible platform for further research in selective oxidation catalysis

The vanadyl pyrophosphate (VPP) based catalyst is unique in converting n-butane selectivity (60-70%) into maleic anhydride (MAN), whereas a MAN selectivity of 10-20% may be regarded as high for structurally different catalyst systems. We present novel vanadium phosphorous oxides and mixed metal phosphate solid solutions tested for n-butane oxidation to maleic anhydride with a selectivity of > 30%. The majority of the catalysts were prepared by solution combustion synthesis. (V_{1-x}W_x)OPO₄ with α_{II} structure was found to be more active and selective in selective oxidation of n-butane compared to β -VOPO₄. The oxidation state of vanadium in (V_{1-x}W_x)OPO₄ can be tuned between 4.74 and 4.99 by the tungsten content, which is regarded as the key for MAN production. All catalysts were structurally stable, but the specific surface area increased during the reaction, as detected by X-ray diffraction and N₂ physisorption, respectively. (V_{1-x}Mo_x)OPO₄ were also stable, but the selectivity for MAN was lower compared to β -VOPO₄. Low conversions result from low surface areas in the screening samples, however, could be overcome by advanced synthesis protocols.

Key words: butane, maleic anhydride, selective oxidation, VPO, vanadium phosphorous oxide, solid solution, mixed metal phosphates

1. Introduction

The catalytic oxidation of *n*-butane to maleic anhydride (MAN) is the first and so far only industrial process of selective alkane oxidation and has an annual world capacity of more than 1 million tons [1]. Although the molar yield of the industrial process has been steadily improved over the past decades, the yields are still below 65%, which is mainly limited by product-selectivity [1–9]. The industrial state of the art catalyst is based on crystalline $(V^{IV}O)_2P_2O_7$ (vanadyl(IV) pyrophosphate, VPP). Due to several vanadium(V) orthophosphate by-phases, which are formed under reaction conditions, the catalyst is often referred to as vanadium phosphorous oxide (VPO). Significant improvements in activity and (by-)product selectivity with this catalyst system were achieved by increasing specific surface areas and by adding promotors like Nb [10], Co [11], Fe [12], and Sm [13]. As the extensive research on VPP-based systems missed a significant breakthrough within the past decades, a new perspective on this reaction is expected from the search for new materials rather than improving the VPO catalyst. In the literature the number of materials selectively converting *n*-butane to MAN is limited to VPO [14-21]. They can be subdivided into a) vanadyl(IV) pyrophosphate and b) vanadyl(V) orthophosphate with different structure types as α_r -VOPO₄, α_r -VOPO₄, β -VOPO₄, γ -VOPO₄, and δ -VOPO₄ [22]. All of them are well discussed in the literature with regard to their catalytic performance in *n*-butane oxidation as a by-phase in VPO [23-27].

Less effort was put into synthesis and catalytic testing of single phase bulk VOPO₄ catalysts. First results published by Shimoda *et al.* showed that single phase α_{ll} -VOPO₄ and β -VOPO₄ can produce maleic anhydride from *n*-butane. Starting from (NH₄)₂((VO)₂C₂O₄(HPO₄)₂)·5H₂O or NH₄HVPO₆ single phase α_{ll} -VOPO₄ and β -VOPO₄ were synthesized. Selectivities of MAN ranged from 14% to 20% [23].

Under reaction conditions most phases are stable and no indication for by-phases were found by *in situ* Raman studies [27].

On the search for novel materials with structural motifs similar for those of VOPO₄ and VPP were targeted. The crystal structure of VPP consists of a chain-ladder-motif of edge- and corner-sharing VO₆-octahedra, which are connected to pyrophosphate anions. Similar motifs are present in α_{ll} -VOPO₄. Here, the vanadium oxygen polyhedra are only connected by vertices. Pyrophosphate groups are replaced by orthophosphate anions (Figure 1).

Recently, Roy *et al.* reported a new class of V^{IV}/V^V containing mixed metal vanadium tungsten phosphate solid solutions. Solution combustion synthesis [30,31] starting from vanadium and tungsten precursors in nitric acid yields solid solutions V_{1-x}W_xOPO₄ (0.04 < x < 0.26), which crystallize with α_{ll} -VOPO₄- and β -VOPO₄-type structure (0 < x < 0.01), respectively [29]. XPS studies showed that the substitution of V^V by V^{IV}/W^{VI} in the α_{ll} -VOPO₄ lattice sensitively affects the average oxidation state of V, which can be finely adjusted between 4.74 and 4.96 (α_{ll} -VOPO₄-type) and 4.99 and 5.00 (β -VOPO₄type). NAP XPS showed that on the surface of VPO, V^{IV} and V^V are present with an average oxidation state of 4.3 [32]. The presence of V^V on the surface is crucial as it can be correlated with production of MAN [33]. Therefore, the introduction of bulk catalysts with a tunable vanadium oxidation state is a promising approach.

In the present study, triggered by this finding, further mixed metal (V, W, Mo, Fe) oxide phosphates in various oxidation states were synthesized and tested for their performance in the selective oxidation of *n*-butane. In particular, the substitution of V by Mo is of interest as Mo is a frequent constituent of many catalysts for hydrocarbon (amm)oxidation [34,35].

2. Experimental

2.1. Catalyst Preparation

Single phase solid solutions $(V_{1-x}W_x)OPO_4$ (α_{ll} and β -VOPO_4-type), $(V_{1-x}Mo_x)OPO_4$ (β - and γ -VOPO_4-type), $W_{0.67}Fe_{0.33}OPO_4$ (WOPO_4-type), $Fe(WO_2)_2(P_2O_7)(PO_4)$, and " $(V_{0.95}Mo_{0.05})_2P_2O_7$ " were obtained

by solid state synthesis or the solution combustion technique [29,36,37]. Single phase VPP was obtained by reducing β -VOPO₄ in Ar (p(O₂) = 10⁻⁵ mbar) at 750 °C for 2 days. Polycrystalline WOPO₄ was synthesized from W₂P₂O₁₀, WO₃, and P₄ in sealed silica tubes at 1000 °C for 7 days [38]. The reference catalyst VPO was synthesized according to patent *via* the organic synthesis route using *iso*-butanol [12]. Finally, the reduction of β -VOPO₄ in H₂, which was saturated with H₂O in a bubbler at ambient temperature (p_{sat} (H₂O) = 0.023 bar), at 500 °C for 1 day yields the thermodynamic metastable phase VPO₄-m1, which is structurally related to β -VOPO₄ [37].

The fine powders of the original catalyst samples were pelletized in a lab press (2.5 min, pressure equivalent to a weight of 2 t on a 12 mm tablet), respectively. Afterwards the pellets were crushed in an agate mortar and a 100-200 µm particle size fraction was obtained using analytical sieves made of stainless steel. The estimation of the Weisz-Prater criterion as well as previous pre-tests with more active catalysts indicate that this sieve fraction is appropriate to exclude mass and heat transfer limitations under the reaction conditions chosen.

2.2. Catalyst Characterization

Routine XRPD analyses (IP-Guinier technique [39]) were performed for phase identification and purity control. The patterns were recorded at ambient temperature using an image plate Guinier camera (HUBER G670, Cu-K_{a1} radiation, $\lambda = 154.059$ pm) with integrated read-out system [40]. The finely ground powder samples were spread on Mylar foil (Fluxana GmbH & Co. KG, type TF-160). Powder pattern were recorded for 15 min in the range of $4^{\circ} \le 2\theta \le 100^{\circ}$. The cell parameters were determined with the program SOS [41], α -SiO₂ (p. A., Merck) was used as an internal standard. Scherrer diameters (D) were calculated according to equation 1 with a Scherrer constant (K) of 0.94 for ω (FWHM) of spherical crystals with cubic symmetry. The FWHM ω was corrected for instrumental broadening with Y₂O₃ standard.

$$\mathsf{D} = \frac{\kappa_{\lambda}}{\omega\cos\theta} \tag{1}$$

BET measurements were carried out in a volumetric N₂ physisorption setup (Autosorb-6-B, Quantachrome) at the temperature of liquid N₂. The sample was degassed in a dynamic vacuum at 423 K for 2 h prior to physisorption. Full adsorption-desorption isotherms were recorded. The specific surface area according to the BET method was calculated from the linear range of the adsorption isotherm ($p/p_0=0.05-0.3$). All catalysts were characterized before and after catalytic testing (Table 1).

2.3. Catalyst Test Setup

Catalytic tests were performed in a fully automated, commercial 8-channel parallel testing setup (hte GmbH, Figure 2). It consists of a gas dosing unit, a reactor unit, an analytical unit. The gas dosing unit provides mixed feeds comprising N₂, O₂ (0-25 %), *n*-butane (0-10 %), Ar (as an internal standard), and H₂O (0-60 %). The typical range of gas hourly space velocities (GHSV) is 500-5000 h⁻¹. The test unit consists of 8 reactors for catalyst samples and one blank reactor filled with inert material (calcined corundum, 400-700 µm, CeramTec). Catalyst volumes of 1 mL were placed inside stainless steel reactors with inner diameter of 10 mm. Stainless steel thermowells (OD=1/8") are placed in the center of all reactors, which are used to guide thermocouples into the catalyst beds. The reactor temperature can be individually controlled in the range of 250-550 °C. The product gases are analyzed by two gas chromatographs (GC 7890A, Agilent). The effluent gas of the blank reactor, which corresponds to the inlet gas of all reactors, is also analyzed. Prior to the GC analysis, all effluent gas streams are diluted with hot inert gas to avoid the condensation of organic products or steam. Transfer lines between reactors and gas chromatographs are completely heated (200 °C). The GCs are optimized for the analysis of the product spectrum of the oxidation of *n*-butane to MAN.

The conversion (*X*) of *n*-butane (Eqs. 1 and 3) and the selectivities (*S*) of the respective products are calculated from the concentrations measured with reference to the internal standard Ar (Eqs. 2 and 4). The latter are averaged over 5 runs measured at each temperature step, respectively. The selectivities of the (by)products (Eq. 2) were normalized to the number of carbon atoms (N_c) in the (by)products

and *n*-butane, respectively. Depending on the catalyst, byproducts include butenes, acrylic acid, propionic acid, acetic acid, acrolein, acetaldehyde, propane, propene, acetylene, ethylene, ethane, carbon monoxide, and carbon dioxide. There are no unidentified peaks in the gas chromatograms. At low levels of *n*-butane conversion, the product-based analysis of selectivities and conversions (Eqs. 3 and 4) is preferred.

2.4. Catalytic Testing

All catalysts were tested in groups of 8 samples following the same testing protocol. Catalyst volumes of 1 mL were kept in their position in the reactor tubes by two layers of inert corundum particles, respectively. The GHSV was fixed at 2000 h⁻¹. The catalysts were ramped at 2 K min⁻¹ in a lean air mix of 5 % O_2/N_2 to 250 °C. At 250 °C the feed gas was changed to 2 % *n*-butane, 20 % O_2 , 3 % H₂O, 3 % Ar with N₂ balance and subsequently the reactor temperature was further increased to 375 °C. After an initial equilibration period of 30 min the catalytic measurements were started. The standard testing procedure includes 5 GC analyses per reactor and temperature with the reactor temperature ramping up in 25 K steps up to a maximum temperature of 450 °C, followed by ramping down to 400 °C. Finally, the reactors were cooled down to ambient temperature in 5% O_2/N_2 . Thus, information on activity, selectivity and thermal stability/deactivation of the catalysts is obtained. One testing cycle takes 8 days including the (dis)charging and cleaning of the reactors.

3. Results and Discussion

According to crystal structure and chemical composition of the catalysts, the results of characterization and catalytic testing are collected in two categories:

3.1. Vanadium Phosphorous Oxides

The group of vanadium phosphorous oxides investigated in our study comprises vanadium(III) orthophosphate VPO₄-m1 and vanadyl(IV) pyrophosphate (VO)₂P₂O₇. VPO₄-m1 is a new polymorph

of VPO₄ and a promising model catalyst with V in the low oxidation state +III and absence of vanadyl oxygen atoms. The latter, however, are often discussed as crucial functional groups for the activation of *n*-butane [3,42]. XRPD analysis of the as-prepared sample clearly identifies "single phase" VPO₄-m1 (Figure 3). VPO₄-m1 and its structure are part of ongoing investigations and not clarified to its full extend. Therefore, it is unclear if the additional reflections in the XRPD pattern indicate a superstructure or an adphase. The main reflections of its XRPD pattern are assigned on the basis of the *β*-VOPO₄ structure (*Pnma*, with z = 4, lattice parameters a = 7.7863(5) Å , b = 6.1329(3) Å, c = 6.9673(5) Å). Under reaction conditions VPO₄-m1 is oxidized to (VO)₂P₂O₇, *β*-VOPO₄. This oxidation is accompanied by a more than two-fold increase of the specific surface area (Table 2). In parallel, the conversion of *n*-butane as well as the selectivity for MAN steadily increases during the reaction. Likely the significant boost of activity can be correlated to both the increased surface area and the formation of highly active (VO)₂P₂O₇ and *β*-VOPO₄, respectively. This is confirmed by the final performance matching the reference VPO from solution combustion synthesis with regard to the selectivity for MAN (Table 2).

In principle (VO)₂P₂O₇ can be synthesized *via* two different routes [43–49]. In the aqueous route V₂O₅ is reduced by NH₂OH in the presence of H₃PO₄ yielding highly crystalline (VO)₂P₂O₇ after calcination of the VOHPO₄·0.5H₂O precursor [44,48–52]. Instead, the organic route uses *iso*-butanol as the reducing agent [44,53,54]. Here, V₂O₅, H₃PO₄, and *iso*-butanol are refluxed for several hours and converted to VOHPO₄·0.5H₂O, which similarly forms (VO)₂P₂O₇ in the calcination process. However, the crystallinity of the "organic" material is significantly lower as shown by XRPD measurements, and typically leads to a higher surface area enhancing catalyst performance [44]. Single-phase (VO)₂P₂O₇ with a high crystallinity can also be synthesized by the reduction of *β*-VOPO₄ in Ar at 750 °C, as done in the present study. The selectivity for MAN obtained over this material is lower compared to the industrial reference system VPO from the organic route (Table 2). However, it is in the same range as VPO catalysts synthesized via the water route with a P:V ratio of 1:1 [55].

For $(VO)_2P_2O_7$ the effect of Mo doping was tested. The sample with 5 % of V substituted by Mo $(V_{0.95}Mo_{0.05}O)_2P_2O_7$ was prepared by solution combustion synthesis (SCS). The influence on crystallinity and specific surface area is negligible (Table 2). However, in terms of catalyst performance the surface area-corrected conversion of *n*-butane normalized is similar as compared to the undoped material, whereas the selectivity for MAN is reduced to 30 %. Selectivity loss is mainly contributed to formation of acrylic(*S*(acrylic acid)=17%) and acetic acid (*S*(acetic acid)=10%). The formation of CO_x is also reduced, which indicates on the one hand inhibition of total oxidation of *n*-butane or MAN by Mo. On the other hand Mo enhances C-C cleavage of reaction intermediates. Since the amount of Mo is small and the results match the undoped material quiet well it cannot be ruled out that Mo is not incorporated at all.

3.2. Mixed Metal Phosphate Solid Solutions

The most extensively investigated sub-category within this class is based on the substitution of V by W according to the formula (V_{1-x}W_xOPO₄) [29]. XRPD patterns of these materials indicate single phases (β for $x \le 0.01$, α_{II} for $0.04 \le x \le 0.26$) with a mean crystallite size in the range of 37 (x = 0.2) to 54 nm (x = 0.06). These phases are stable and neither phase transformation nor formation of an adphase was observed after the catalytic testing (Figure 4).

The BET surface area of the as-prepared samples, which are generally very low in the range of 1–4 $m^2 g^{-1}$, occasionally changed during the catalytic process (Table 3). An almost doubled specific surface area as well as activation is observed for the tungsten-rich V_{0.8}W_{0.2}OPO₄. On the one hand our results could indicate a dramatic reconstruction of the morphologies of particle and surface during the catalytic process. On the other hand pores might be blocked by residual organic compounds from synthesis. Calcination of all samples at higher temperatures compared to reaction temperatures should be sufficient for carbon removal from synthesis. However, the effect on surface area is small. With decreasing W content within these solid solution-type catalysts the effect of reaction conditions on the specific surface area is reduced, which is almost absent on $V_{0.99}W_{0.01}OPO_4$ and even negative

(reduction of S_{BET}) for the tungsten-free VOPO₄ catalyst. Instead, the industrial reference VPO, owing to elaborated synthesis protocols, has an approximately 10-fold higher and stable specific surface area of 26 m² g⁻¹, which is retained after the catalytic test.

Catalytic tests of samples of compositions V_{1-x}W_xOPO₄ show a remarkably high selectivity for MAN in the range of 20-31% (Figure 5). XPS studies showed that W⁵⁺ is oxidized to W⁶⁺ in V_{1-x}W_xOPO₄ reducing an equimolar amount of V⁵⁺ to V⁴⁺ [29]. The comparison of V_{0.8}W_{0.2}OPO₄ and VOPO₄ clearly shows an increased selectivity of MAN, which might be attributed to the reduced (average) oxidation state of vanadium [29]. Activation energy can be correlated with tungsten content or the amount of V⁴⁺. Isotope labeling studies of *n*-butane showed that C-H activation of methylene groups is the rate determining step and the activation is correlated with the presence of V^V [6]. By substitution of vanadium by tungsten, the oxidation state of vanadium is reduced, which explains the higher activation energy. Nevertheless, a direct correlation between substituted V and selectivity for MAN is hardly possible. Our results indicate a maximum selectivity near 20% substitution of V by W (V1-xWxOPO4 with x = 0.2). On the other hand, vanadium-free WOPO₄ does not convert *n*-butane to maleic anhydride, which underlines that W plays not an active role in the catalytic cycle. The change in surface area on the course of the reaction, which is observed for several samples, is typically accompanied by a corresponding change in activity, whereas selectivity for MAN remains constant. Notably, the activity of most of these catalysts if referred to the specific surface area is comparable or even higher than for the reference VPO. For instance, the most selective V_{0.8}W_{0.2}OPO₄ provides a conversion and specific surface area (after reaction) of 42% and 3.4 m² g⁻¹, however, 80% of butane conversion over VPP can be considered mainly as a result of the superior surface area (26 m² g⁻¹) [12]. Thus, a high potential for improvement of these catalysts is expected from the optimization of synthetic strategies.

The main by-products are CO_x. The organic by-products of *n*-butane oxidation over $V_{1-x}W_xOPO_4$ -type materials comprise acrylic and acetic acids (< 8%), as well as traces of 1-butene, ethylene, furan, and propene (< 1%).

Molybdenum is a common constituent of selective oxidation catalysts, such as MoVTeNb mixed oxides for ammoxidation of propane to acrylonitrile, oxidation of propane to acrylic acid, or oxidative dehydrogenation of ethane to ethylene[56–60]. Thus, Mo was in our focus for the substitution of V in VOPO₄. We tested the γ - and the β -phase with 20% substitution (V_{0.8}Mo_{0.2}OPO₄), respectively (Figure 6)[61].

Neither phase changes, decomposition nor significant changes in specific surface area were observed after exposure to reaction conditions (Table 2). However, the catalysts were nearly inactive, which might be explained by the very low surface areas and/or by a negative effect of Mo. Compared to the mixed-metal phosphates $V_{1-x}W_xOPO_4$, the selectivity for MAN drops significantly. Similar to $(V_{0.95}Mo_{0.05}O)_2P_2O_7$ selectivity for acetic and acrylic acid is enhanced whereas CO and CO₂ formation is reduced. The surface-corrected net activity is also much lower than for the W-substituted vanadyl phosphates. However, the level of selectivity for MAN of the mixed-metal phosphates $V_{1-x}W_xOPO_4$ and β -VOPO₄ is in good agreement with single phase α -VOPO₄ and β -VOPO₄ catalysts as shown by Shimoda.¹⁶ Finally, we tested the substitution of W⁵⁺ by (Fe³⁺_{1/3}W⁶⁺_{2/3}) in WOPO₄ (W_{1-x}Fe_xOPO₄ with x = 0.33). This sample, which was obtained by SCS, provides a relatively high specific surface area of 6.2 m² g⁻¹ but is unstable under reaction conditions. This instability under the testing conditions is rather surprising since zero activity for *n*-butane activation indicates little interaction with the gas phase. Although Fe [62] and W [63] are known as efficient promotors for selective oxidation catalysts, this is further indication for the active role of V in the activation of *n*-butane as stated by Centi *et al.*[3]

4. Conclusion

A variety of catalysts were synthesized and tested for selective oxidation of *n*-butane based on (VO)₂P₂O₇ and VOPO₄. Vanadium was substituted or replaced by other transition metals like tungsten, molybdenum or iron. Substitution of V by W leads to $V_{1-x}W_xOPO_4$ with α_{ll} structure type, which is a novel class of catalysts for selective oxidation of *n*-butane to MAN. The amount of tungsten can be tuned in the range from $0.04 \le x \le 0.26$. All catalysts are phase stable under reaction conditions, although the specific surface area increases during the reaction, which needs to be studied in detail. Reducing the oxidation state of vanadium increase the apparent activation energy for n-butane conversion. Compared to β -VOPO₄, the selectivity for MAN could be increased from 20% up to 31%. Nevertheless, V_{1-x}W_xOPO₄ catalysts are less selective and active than VPO reference. However, it could be shown that the oxidation state of vanadium influences the selectivity for MAN. Substitution of V with Mo in (VO)₂P₂O₇ and VOPO₄ showed different results. In VOPO₄, V by Mo can be easily substituted leading to pure β - and γ -phases, which are more stable under reaction conditions compared to $V_{1-x}W_xOPO_4$. In case of $(V_{0.95}Mo_{0.05}O)_2P_2O_7$ there is no evidence in the XRPD that Mo is incorporated in the $(VO)_2P_2O_7$ crystal structure. In both cases, the effect on catalysis is comparable. Selectivity for MAN and CO_x is reduced compared to the non-substituted catalysts. Further, addition of Mo strongly influences the C-C cleavage leading to the formation products like acetic and acrylic acid. Additionally, we could show that vanadyl pyrophosphate synthesized by solution combustion synthesis is similar to VPO from aqueous routes. Differences in activity can be explained by low surface areas. The reduced selectivity for MAN might be correlated with a 1:1 ratio of P:V since an excess of phosphor enhances the selectivity. VPO₄-m1 is a new polymorph of VPO, which was introduced by removing the vanadyl oxygen atoms of β -VOPO₄. Under reaction conditions it is oxidized to $(VO)_2P_2O_7$ and β -VOPO₄. The performance is comparable to VPO by SCS and stresses the importance of stable catalysts as well as the inflexibility of (VO)₂P₂O₇. Complete substitution of V in $(VO)_2P_2O_7$ and VOPO₄ with iron or tungsten yields phase-stable materials that are not active in the selective oxidation of *n*-butane. In general, the combination of vanadium in the oxidation state +4 and +5 and the ratio of vanadium and phosphate are crucial parameters for selective oxidation of *n*-butane to MAN. Although, VPO is the best catalyst known, it has limited options for optimization due to the

inflexible crystal structure and limited effect of promotors [62]. Therefore, mixed transition metal $V_xM_{1-x}OPO_4$ might be a good starting point for novel catalysts with higher potential for improvement. It could be shown that solid state synthesis methods like solution combustion synthesis might be a good way to access mentioned new materials/structure motifs for catalysis. However, surface areas are quite low. Consequently, other synthesis methods like hydrothermal routes should be considered as well as supporting of the active catalyst. Transition metals should be selected based on their catalytic performance in oxidation catalysis or by their potential for reduction of vanadium since recent NAP XPS studies of VPO showed that under working conditions the average oxidation state of surface vanadium is +4.3 [32].

From a mechanistic point of view, kinetics and reaction networks of the newly found mixed-metal phosphates $V_{1-x}W_xOPO_4$ should be analyzed and compared to VPO as well as β -VOPO₄, which could be a crucial step towards understanding the active site. Especially, the surface composition and oxidation state under reaction conditions needs to be analyzed in detail.

References

- N. Ballarini, F. Cavani, C. Cortelli, S. Ligi, F. Pierelli, F. Trifirò, C. Fumagalli, G. Mazzoni, T. Monti, Top. Catal. 38 (2006) 147–156.
- [2] F. Trifirò, R.K. Grasselli, Top. Catal. 57 (2014) 1188–1195.
- [3] G. Centi, Catal. Today 16 (1993) 5–26.
- [4] C.H. Bartholomew, R.J. Farrauto, Fundamentals of Industrial Catalytic Processes, John Wiley & Sons, Inc, Hoboken, NJ, USA, 2005.
- [5] J.-C. Volta, Comptes Rendus de l'Académie des Sciences Series IIC Chemistry 3 (2000) 717–723.
- [6] G. Centi, F. Trifiro, J.R. Ebner, V.M. Franchetti, Chem. Rev. 88 (1988) 55–80.
- [7] M.A. Pepera, J.L. Callahan, M.J. Desmond, E.C. Milberger, P.R. Blum, N.J. Bremer, J. Am. Chem. Soc. 107 (1985) 4883–4892.

- [8] R. Glaum, C. Welker-Nieuwoudt, C.-K. Dobner, M. Eichelbaum, F. Gruchow, C. Heine, A. Karpov, R. Kniep, F. Rosowski, R. Schlögl, S.A. Schunk, S. Titlbach, A. Trunschke, Chem. Ing. Tech. 84 (2012) 1766–1779.
- [9] M.-J. Cheng, W.A. Goddard, J. Am. Chem. Soc. 135 (2013) 4600–4603.
- [10] F. Ghelfi, G. Mazzoni, C. Fumagalli, F. Cavani, F. Pierelli, EP Patent (2004) EP1663482 (A1).
- [11] V.A. Zazhigalov, J. Haber, J. Stoch, A.I. Pyatnitzkaya, G.A. Komashko, V.M. Belousov, Appl. Catal.A: Gen. 96 (1993) 135–150.
- [12] C. Dobner, M. Duda, A. Raichle, H. Wilmer, F. Rosowski, M. Hoelzle, EP Patent (2006) EP1915210 (A1).
- [13] H.-Y. Wu, H.-B. Wang, X.-H. Liu, J.-H. Li, M.-H. Yang, C.-J. Huang, W.-Z. Weng, H.-L. Wan, Appl. Surf.
 Sci. 351 (2015) 243–249.
- [14] H.-Y. Wu, P. Jin, Y.-f. Sun, M.-H. Yang, C.-J. Huang, W.-Z. Weng, H.-L. Wan, J. Mol. Catal. A: Chem.
 414 (2016) 1–8.
- [15] B. Jordan, C. Calvo, Can. J. Chem. 51 (1973) 2621–2625.
- [16] B.D. Jordan, C. Calvo, Acta Crystallogr. B Struct. Crystallogr. Cryst. Chem. 32 (1976) 2899–2900.
- [17] R. Gopal, C. Calvo, J. Solid State Chem. 5 (1972) 432–435.
- [18] D. Ballutaud, E. Bordes, P. Courtine, Mater. Res. Bull. 17 (1982) 519–526.
- [19] M. Tachez, F. Theobald, E. Bordes, J. Solid State Chem. 40 (1981) 280–283.
- [20] G. Ladwig, Z. Anorg. Allg. Chem. 338 (1965) 266–278.
- [21] R.N. Bhargava, R.A. Condrate, Appl. Spectrosc. 31 (1977) 230–236.
- [22] E. Bordes, Catal. Today 1 (1987) 499–526.
- [23] T. Shimoda, T. Okuhara, M. Misono, Bull. Chem. Soc. Japan 58 (1985) 2163–2171.
- [24] Z.-Y. Xue, G.L. Schrader, J. Phys. Chem. B 103 (1999) 9459–9467.
- [25] M. Abon, J. Catal. 156 (1995) 28–36.

- [26] V.V. Guliants, J.B. Benziger, S. Sundaresan, I.E. Wachs, J.-M. Jehng, J.E. Roberts, Catal. Today 28 (1996) 275–295.
- [27] F. Benabdelouahab, J. Catal. 134 (1992) 151–167.
- [28] S. Geupel, K. Pilz, S. van Smaalen, F. Büllesfeld, A. Prokofiev, W. Assmus, Acta Crystallogr. C Cryst. Struct. Commun. 58 (2002) i9-i13.
- [29] S.C. Roy, R. Glaum, D. Abdullin, O. Schiemann, N. Quang Bac, K.-H. Lii, Z. Anorg. Allg. Chem. 640
 (2014) 1876–1885.
- [30] M.S. Hegde, G. Madras, K.C. Patil, Acc. Chem. Res. 42 (2009) 704–712.
- [31] A. Varma, A.S. Mukasyan, A.S. Rogachev, K.V. Manukyan, Chem. Rev. 116 (2016) 14493–14586.
- [32] C. Heine, M. Hävecker, E. Stotz, F. Rosowski, A. Knop-Gericke, A. Trunschke, M. Eichelbaum, R. Schlögl, J. Phys. Chem. C 118 (2014) 20405–20412.
- [33] G.W. Coulston, Science 275 (1997) 191–193.
- [34] E. Mannei, F. Ayari, C. Petitto, E. Asedegbega–Nieto, A.R. Guerrero–Ruiz, G. Delahay, M. Mhamdi,
 A. Ghorbel, Micropor. Mesopor. Mater. 241 (2017) 246–257.
- [35] K. Amakawa, Y.V. Kolen'ko, A. Villa, M.E. Schuster, L.-I. Csepei, G. Weinberg, S. Wrabetz, R. Naumann d'Alnoncourt, F. Girgsdies, L. Prati, R. Schlögl, A. Trunschke, ACS Catal. 3 (2013) 1103–1113.
- [36] S.C. Roy, B. Raguž, W. Assenmacher, R. Glaum, Solid State Sci. 49 (2015) 18–28.
- [37] Subrata Chandra Roy, Thermodynamically stable and metastable solids: New approaches to the synthesis of anhydrous phosphates containing vanadium, molybdenum, and/or tungsten. PhD Thesis, Bonn, 2015.
- [38] S.L. Wang, C.C. Wang, K.H. Lii, J. Solid State Chem. 82 (1989) 298–302.
- [39] S. Fischer, H. Fischer, S. Diele, G. Pelzl, K. Jankowski, R.R. Schmidt, V. Vill, Liq. Cryst. 17 (1994) 855–
 861.

- [40] I. Tanaka, M. Yao, M. Suzuki, K. Hikichi, T. Matsumoto, M. Kozasa, C. Katayama, J. Appl. Crystallogr.
 23 (1990) 334–339.
- [41] G. Meyer, SOS. Staatsexamenarbeit, Gießen, 1980.
- [42] 11th International Congress On Catalysis 40th Anniversary, Proceedings of the 11th ICC, Elsevier, 1996.
- [43] J.W. Johnson, D.C. Johnston, A.J. Jacobson, J.F. Brody, J. Am. Chem. Soc. 106 (1984) 8123–8128.
- [44] G. BUSCA, J. Catal. 99 (1986) 400–414.
- [45] H. E. Bergna (1988) US 4769477 A.
- [46] E. Bordes, Catal. Today 16 (1993) 27–38.
- [47] H. Morishige, J. Tamaki, N. Miura, N. Yamazoe, Chem. Lett. 19 (1990) 1513–1516.
- [48] E.A. Lombardo, C.A. Sánchez, L.M. Cornaglia, Catal. Today 15 (1992) 407–418.
- [49] G. Poli, I. Resta, O. Ruggeri, F. Trifirò, Appl. Catal. 1 (1981) 395–404.
- [50] G.J. Hutchings, M.T. Sananes, S. Sajip, C.J. Kiely, A. Burrows, I.J. Ellison, J.C. Volta, Catal. Today 33
 (1997) 161–171.
- [51] L.M. Cornaglia, C.A. Sa'nchez, E.A. Lombardo, Appl. Catal. A: Gen. 95 (1993) 117–130.
- [52] N. Batis, J. Catalysis 128 (1991) 248–263.
- [53] F. Cavani, G. Centi, F. Trifiro, Appl. Catal. 9 (1984) 191–202.
- [54] M. O'Connor, F. Dason, B.K. Hodnett, Appl. Catal. 64 (1990) 161–171.
- [55] R.I. Bergman, N.W. Frisch, Production of maleic anhydride by oxidation of n-butane, Google Patents, 1966.
- [56] A. Celayasanfiz, T. Hansen, A. Sakthivel, A. Trunschke, R. Schlögl, A. Knoester, H. Brongersma, M. Looi, S. Hamid, J. Catal. 258 (2008) 35–43.
- [57] R. Naumann d'Alnoncourt, Y. V. Kolen'ko, R. Schlögl, A. Trunschke, Comb. Chem. High Throughput Screening 15 (2012) 161–169.

- [58] A.C. Sanfiz, T.W. Hansen, D. Teschner, P. Schnörch, F. Girgsdies, A. Trunschke, R. Schlögl, M.H.
 Looi, S.B.A. Hamid, J. Phys. Chem. C 114 (2010) 1912–1921.
- [59] J.S. Valente, R. Quintana-Solórzano, H. Armendáriz-Herrera, G. Barragán-Rodríguez, J.M. López-Nieto, Ind. Eng. Chem. Res. 53 (2014) 1775–1786.
- [60] R.K. Grasselli, J.D. Burrington, D.J. Buttrey, P. DeSanto Jr., C.G. Lugmair, A.F. Volpe Jr., T. Weingand, Top. Catal. 23 (2003) 5–22.
- [61] A. Raminosona, E. Bordes, P. Courtine, J. Solid State Chem. 68 (1987) 1–10.
- [62] G.J. Hutchings, R. Higgins, J. Catal. 162 (1996) 153–168.
- [63] B.Y. Jo, S.S. Kum, S.H. Moon, Appl. Catal. A: Gen. 378 (2010) 76–82.



Figure 1 – Crystal structure of VPP (left) and α_{ll} -type VOPO₄ (right) with VO₆ units (green) and PO₄ units (blue)[28,29]. Oxygen atoms from phosphate groups are given as \circ , vanadyl oxygen atoms as \bullet .



Figure 2 – Flow scheme of the laboratory scale test setup (hte GmbH) with 8 parallel fixed-bed reactors and 1 blank reactor, gas and liquid dosing unit and on-line gas chromatograph for product analysis.



Figure 3 – Guinier photographs of VPO₄-m1 before (top) and after catalytic testing (bottom). Reflections of Al_2O_3 assigned to corundum, which was used as inert material and could not be separated from the catalyst.



Figure 4 – Guinier photographs of single phase $V_{0.8}W_{0.2}OPO_4$ after catalytic testing and simulated XRPD pattern of $V_{0.8}W_{0.2}OPO_4$.[37]







Figure 6 – Selectivity for MAN dependent on conversion of *n*-butane under GHSV = 2000 h^{-1} c(C₄)/c(O₂)/c(H₂O)=2 %/20 %/3 %.

Table 1

Catalyst characterization by XRPD and BET measurements and surface before catalytic testing

Catalyst	$S_{\text{BET,fresh}}$	Structure	Space	Scherrer	
	(m²/g)	Type ^a	Group	Diameter (nm)	
VOPO ₄	3.5	β	Pnma	>200	
V _{0.99} W _{0.01} OPO ₄	1.3	β	Pnma	103	
V _{0.94} W _{0.06} OPO ₄	2.4	<i>C</i> II	P4/n	>200	
V _{0.9} W _{0.1} OPO ₄	4.9	Øli	P4/n	165	
V _{0.8} W _{0.2} OPO ₄	3.4	Øli	P4/n	84	
WOPO ₄	3.9	WOPO ₄	P2 ₁ /m	78	
V _{0.8} Mo _{0.2} OPO ₄	0.8	β	Pnma	52	
V _{0.8} Mo _{0.2} OPO ₄	1.1	γ	Pbam	192	
W _{0.67} Fe _{0.33} OPO ₄	6.2	WOPO ₄	P2 ₁ /m	68	
VPO4-m1	6	VPO ₄	C2/c	53	
(VO) ₂ P ₂ O _{7^b}	80	VPP	Pca2₁	31	
(VO) ₂ P ₂ O ₇ ^c	14	VPP	Pca2₁	>200	
(V _{0.95} Mo _{0.05} O) ₂ P ₂ O ₇	15	VPP	Pca2 ₁	>200	
Fe(WO ₂) ₂ (P ₂ O ₇)(PO ₄)	3	VPO ₄	C2/c	>200	

^a Greek letters refer to the various polymorphs of VOPO_{4;} ^b from organic synthesis route; ^c from SCS

Table 2

Catalyst performance data, stability, specific surface before and after catalytic testing.

Catalyst	X(n-butane) ^f	S(MAN) ^f	S(CO _x)	$S_{\text{BET,fresh}}$	$S_{\text{BET,used}}$	Structure
	(%)	(%)	(%)	(m²/g)	(m²/g)	Stability
VPO4-m1 ª	6	21	72	1.9	-	
VPO4-m1 ^b	14	49	54	-	4.7	Noc
(VO) ₂ P ₂ O ₇ ^d	80	70	29	26	26	Yes
(VO) ₂ P ₂ O7 ^e	14	43	45	2.1	1.8	Yes
(V _{0.95} Mo _{0.05} O) ₂ P ₂ O ₇	15	30	34	1.5	1.3	Yes
Fe(WO ₂) ₂ (P ₂ O ₇)(PO ₄)	3	0	68	1.1	0.8	Yes

^aTOS = 254 h; ^bTOS = 480 h; ^c Formation of (VO)₂P₂O₇ and β-VOPO₄; ^d from organic synthesis route; ^e

material from SCS; ^f temperature for catalytic testing at 400 °C

Table 3

Catalyst stability, specific surface before and after catalytic testing, and activation energy

	Structure	$S_{\text{BET,fresh}}$	$S_{\text{BET,used}}$	Structure	E _a ^b (kJ
	Type ^a	(m²/g)	(m²/g)	Stability	mol ⁻¹)
VOPO ₄	β	3.5	2.6	Yes	74
V _{0.99} W _{0.01} OPO ₄	β	1.3	1.2	Yes	93
V _{0.94} W _{0.06} OPO ₄	alı	2.4	3.9	Yes	93
V _{0.9} W _{0.1} OPO ₄	alı	4.9	6.5	Yes	108
V _{0.8} W _{0.2} OPO ₄	alı	3.4	6.3	Yes	115
WOPO ₄	WOPO ₄	3.9	5.5	No ^c	24
V _{0.8} Mo _{0.2} OPO ₄	β	0.8	0.5	Yes	98
V _{0.8} Mo _{0.2} OPO ₄	γ	1.1	1.3	Yes	111
W _{0.67} Fe _{0.33} OPO ₄	WOPO ₄	6.2	6.1	No ^d	n.a.

^aGreek letters refer to the various polymorphs of VOPO₄; ^bActivation energies derived from Arrhenius

plots; ^cBy-phase related to MPTB. ^dAfter catalytic testing one additional reflection occures