Unraveling Property-Performance Relationships by Surface Tailoring of Oxidation Catalysts via ALD

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Atomic layer deposition (ALD) of PO₄ on V₂O₅ powder was applied as a tool to tailor active and selective sites of a bulk catalyst. ALD leads to homogeneous P deposition on the V₂O₅ surface with linear increase of P content with each ALD cycle. The catalyst performance was evaluated and correlated to structural motifs identified by detailed characterization methods. The catalytic conversion of butane to maleic anhydride (MAN) was chosen as proof-of-concept reaction. The selectivity towards MAN increases with ALD cycle number from 1–3 ALD cycles and remains constant at higher ALD cycles. Restructuring of the catalyst surface is induced by steam during reaction conditions at elevated temperatures. Excessive P is migrating away from the catalyst surface to form various VO₆PO₄ polymorphs revealing partially but homogeneously covered V₂O₅ by P. The formed VO₆PO₄ species barely contribute to the yield to MAN. Solid-state 31P-NMR was used to identify fingerprints relevant for selectivity and activity. This work shows that synthesizing model catalysts by atomic layer deposition combined with detailed analytics can reveal property-performance relationships.

Introduction

Vanadium phosphates (VPO) exhibit the best performance in the selective oxidation of n-butane to maleic anhydride (MAN), specifically vanadyl pyrophosphate (VOHPO₄, VPP).1–3 This catalyst is commercially produced by synthesizing the catalyst precursor VOHPO₄·0.5 H₂O in either aqueous or alcoholic media.4 Subsequent activation in N₂ or reaction feed at 400 °C leads to crystalline VPP.6 During the activation period transitions over various phases of VPO type catalysts can be observed until VPP is formed, either phase pure or with traces of VO₆PO₄ polymorphs.5–9 This shows the dynamic properties of vanadium phosphates under the influence of various atmospheres and the importance of controlled activation.5,10–13 The activated catalyst is then considered as the stable catalytic component. Despite intensive research over the last 40 years, the maximum molar yield of commercially applied VPP is 65%, thus revealing potential for improvements.14–17 However, the structural motif of this component is still to be identified and led to heavy discussions in the past. There is a broad agreement in literature that crystalline vanadyl pyrophosphate plays an important role in the oxidation.1,18,19 Researchers state that the fully crystalline VPP is solely responsible for the conversion of butane to MAN.10 Others state that a combination of vanadium (+ V) phosphates and vanadium(+ IV) phosphates are needed for the selective conversion.4,5,11,12,20–23 For that, crystalline VPP and VO₆PO₄ polymorphs are suggested to improve the catalytic performance.4,5,11,12,20 Further research also indicates that amorphous layers are formed on any kind of VPO catalyst, which is then accounted for the catalytic performance.4,5,9,24 However, many studies report amorphous vanadium phosphate species to be responsible for the selective oxidation.4,5,9,13,25,26 Schoepl et al. performed in-situ surface analytics during catalysis to find amorphous V–P–O on the catalyst surface being the active phase.27 Hutchings et al. synthesized fully amorphous vanadium pyrophosphate and subsequent catalytic testing revealed not only that the catalyst is highly performing but also that the catalyst does not need any formation period, in contrast to crystalline VPO.24 Also supported VPO on SiO₂ hint for amorphous phases to be the relevant phase.26 There are even hints for a combination of binary V₂O₅ and phosphoric acid to be responsible for this reaction.25,27 Despite contrary findings between research groups, almost all agree that vanadium phosphates are very flexible materials which can form various polymorphs during reaction.4,5,7,9,11–13,21,22,24,27–29 Furthermore, studies find that the surface of any VPO catalyst under reaction condition is drastically different than suggested by the bulk structure. XPS shows P/V ratios of up to 2.4,7,9,11,12 or even O/V ratios above 4.511,20 which cannot be accounted by the VPP...
bulk structure. Therefore, the exact structural motif which is responsible for the MAN production still remains unclear. Many factors influence the catalyst structure and P/V surface ratio, such as hydrocarbons[4,10–12,27] or water[4,5,10,27,30] during reaction. Therefore, ex situ correlations must be found and carefully interpreted. In this regard, a catalyst which is precisely synthesized by ALD might support either side of the discussion. Depositing phosphorus as foreign element exclusively on the surface of vanadium pentoxide with different P/V ratios might reveal the influence of P and its loading on the catalytic performance. Atomic layer deposition is a promising thin film deposition technique for catalyst synthesis and catalyst modification. The self-limiting sequential reactions lead to precise control over film thickness with high reproducibility.[25] Even highly porous supports can be homogeneously coated with almost any given element, resulting in catalysts with larger active surface area than the respective bulk catalysts.[26] Bottom-up synthesis of supported metal nanoparticles was already successfully conducted for monometallic and multi-metallic systems.[33–38] Also, catalyst modifications by ALD are already developed, e.g. deposition of a functional metal oxide overcoat on supported metal nanoparticles to prevent sintering or coke formation.[39–42] Despite recent developments of ALD in the field of catalysis, modifications of bulk catalysts are barely investigated yet. Review articles about ALD for catalysis highlight significant advances but they deal with catalytically almost inert supports, such as SiO$_2$ or Al$_2$O$_3$.[31,43–46] Strempel et al. investigated the deposition of P on vanadium pentoxide by ALD to prepare a model catalyst related to the vanadyl pyrophosphate.[47] In order to prepare a series of catalysts with a variation of P loading, mechanistic investigations of P-ALD on V$_2$O$_5$ were carried out and allowed a variation of P loading by changing ALD cycle numbers from 1 to 10.[48] Therefore, we consider ALD as the right approach to precisely modify the surface of bulk catalysts and thus reveal property-performance relationships.

The goal of this work is to highlight a useful synthesis approach to modify the elemental composition and understand these properties in terms of catalysis. Therefore, a series of catalysts with varying P surface loading on vanadium pentoxide is prepared via ALD to investigate its influence on butane oxidation. As P is an element absent in vanadium oxide, the change in catalytic performance can be directly correlated to the presence of P and its interaction with V surface species. Catalytic evaluation combined with detailed chemical and physical characterizations will reveal property-performance relations.

Results and Discussion

Vanadium phosphates are dynamic materials which undergo structural changes depending on the exposure to inert atmosphere, hydrocarbons, water or a combination thereof.[4,5,10–12,27,30] The structural change during catalysis is called activation period in which the catalyst is transformed to its most active and selective state.[49] In general, this is visible in the change in conversion and selectivity towards MAN in the first hours of TOS. The change in conversion and selectivity with TOS can be correlated by in-situ analytics such as Raman, XPS or XRD. The change in structure and composition should be observable by ex-situ investigations of the catalysts before and after catalytic reaction with suitable analytics. For that, vanadium phosphate polymorphs of known composition (VOPO$_4$·2H$_2$O, α-VPO$_4$, β-VPO$_4$, γ-VPO$_4$, and (VO)$_2$P$_2$O$_7$) before and after catalysis (Figure 1) were investigated. Synthesis, full characterization, reaction conditions and catalytic performance of these catalysts were conducted and reported elsewhere.[40]

Extensive investigations of the local P environment were conducted by solid state $^{31}$P-NMR. The challenge of $^{31}$P-NMR for VPO is that only V$^{5+}$ is a diamagnetic nucleus, which leads to clear signals, whereas reduced vanadium species, such as V$^{4+}$ or V$^{3+}$ lead to line broadening or drastic chemical shifts due to paramagnetism. Depending on the desired information two NMR techniques can be exploited. The so-called spin echo mapping in $^{31}$P-NMR allows to distinguish between P environments which contain V$^{5+}$ and V$^{4+}$. The V$^{4+}$ nucleus leads to very broad peaks with a maximum at 2500 ppm.[35,50,51] V$^{5+}$ environments all lead to chemical shifts similar to phosphoric
acid, at 0 ppm.\textsuperscript{15,20,50} The downside of this technique is that differentiations between various VOPO\textsubscript{4} polymorphs are impossible, as they all contain similar signal at 0 ppm.\textsuperscript{19} Magic angle spinning \textsuperscript{31}P-NMR allows to distinguish V\textsuperscript{IV} phosphates but identifying V\textsuperscript{V} phosphates is challenging here. \textsuperscript{31}P-MAS-NMR was used in this study to distinguish the VOPO\textsubscript{4} phases. In general, a more ordered environment around the \textsuperscript{31}P-nuclei results in a narrower line width of the NMR signal. Vice versa, the broader the obtained NMR signal is, the more flexible the direct P environment is. In other words, broader peaks relate most likely to P atoms within a less ordered, e.g. an amorphous environment.

Before catalysis, all investigated vanadium phosphates contain sharp peaks, which can be assigned to their respective crystal structure in agreement with literature, except for VPP in which no \textsuperscript{31}P-Signal is obtained.\textsuperscript{19} This is due to line broadening and chemical shifts obtained by the presence of paramagnetic nuclei, in this case vanadium(\textsuperscript{II}).\textsuperscript{31} After catalysis, the vanadium phosphates reveal that initially phase pure materials lead to mixed vanadium phosphates during catalysis, as NMR signals of various vanadium phosphates develop. For example, after catalysis the VOPO\textsubscript{4}·2H\textsubscript{2}O shows signals similar to that of β-VOPO\textsubscript{4} and α\textsubscript{V}-VOPO\textsubscript{4}. This proves that vanadium phosphates are dynamic materials capable of changing local geometric structures under reaction conditions. Surprisingly, VPP reveals \textsuperscript{31}P-NMR signals after catalysis indicating the presence of vanadium(\textsuperscript{II}), although stoichiometry suggests exclusively vanadium(\textsuperscript{IV}) in the crystal structure. The obtained signals in VPP after catalysis are a sharp signal at −1 ppm, representing ordered environments, in addition to a broad signal at 35 ppm indicating disordered structures. As VPP is the best performing catalyst in the butane oxidation to MAN, these signals might be of high importance for the catalytic performance. Literature ascribes importance to these slightly disordered or even fully amorphous structures, which leads to the idea to directly synthesize these.\textsuperscript{1,13,24,29}

Synthesis of such an amorphous vanadium phosphate layer can be realized by atomic layer deposition of phosphorus oxide on vanadium pentoxide, which then can serve as model catalyst for vanadyl pyrophosphate. ALD of PO\textsubscript{2} was conducted on V\textsubscript{2}O\textsubscript{5} with varying ALD cycle number and resulted in a series of catalysts with a linearly increasing P loading, as shown by XRF (SI, Figure 1). Assuming P deposition to exclusively occur on the V\textsubscript{2}O\textsubscript{5} surface, the P/V ratio is below one for up to 3 ALD cycle, almost equal to one after the 3rd ALD cycle and above one for further ALD cycles. The ALD process itself is described in more detail elsewhere.\textsuperscript{48} For clarification, catalysts prepared by ALD are labelled based on the conducted ALD cycles and their catalytic status. For example, the catalyst with one conducted ALD cycle before catalytic reaction is referred to as “1c fresh”. Selected ALD catalysts (0c, 1c, 2c, 3c, 7c and 10c) were investigated in their catalytic performance to convert n-butane to maleic anhydride at different temperatures ramping down from 450–350 °C with constant GHSV of 2000 h\textsuperscript{−1} and constant feed of C\textsubscript{4}H\textsubscript{10}/O\textsubscript{2}/H\textsubscript{2}O = 2/20/3 % balanced with nitrogen. Before discussing the effect of P-deposition on catalysis we want to focus on structural changes induced by catalysis.

Similar to the VOPO\textsubscript{4} polymorphs, changes in \textsuperscript{31}P-NMR signals of the ALD samples before and after catalysis can be observed. The fresh catalysts show broad peaks, indicating amorphous phases being formed on the surface during ALD synthesis (Figure 2) with chemical shifts comparable to α\textsubscript{V}-VOPO\textsubscript{4} and β-VOPO\textsubscript{4}. However, those signals completely diminish after catalysis and new signals appear.

All spent ALD catalysts develop a similar broad peak at around 35 ppm, which is the only remaining peak for 1c, 2c and 3c catalyst. Based on chemical shift and shape this peak fits to the broad one found in the spent vanadyl pyrophosphate catalyst. Furthermore, catalysts with high ALD cycle number (7c and 10c) show additionally two distinct peaks (−0.6 ppm, −14.7 ppm) which cannot be directly attributed to any known vanadium phosphate polymorph. The mismatch of structures in spent VPO catalysts compared to phase pure VPO structures was already reported by Vedrine et al.\textsuperscript{28} The signal at −0.6 ppm lies in between the signals for the α\textsubscript{V}-VOPO\textsubscript{4} and β-VOPO\textsubscript{4} but...
could also be attributed to phosphoric acid, which serves as internal NMR reference at 0 ppm.

XRD was conducted to investigate the morphology and shows for the fresh catalysts exclusively reflections attributed to vanadium pentoxide up to 10 ALD cycles (SI, Figure 2).[49] Neither were there any indications for crystalline VOPO$_4$ phases nor for vanadyl pyrophosphate. However, after catalysis (Figure 3), additional reflections (12.5° and 29.3°) are observed for catalysts with higher ALD cycles (7c, 10c). The reflections at 12.5° and 29.3° could be assigned to H$_n$(VO)$_3$(PO$_4$)$_3$(H$_2$O)$_3$*4H$_2$O,[52] which is comparable to a partially reduced and hydrated VOPO$_4$. Therefore, XRD reveals a difference between low ALD cycle and high ALD cycle samples, as reconstruction of the surface must occur during reaction, especially for higher ALD cycle catalysts. This finding matches the $^{31}$P-NMR perfectly. Apparently, P/V ratios above one lead to the formation of VOPO$_4$ polymorphs.

The absence of both additional reflections in the lower ALD cycle samples does not directly mean that the crystallites are not present. They might be formed but are below the size of the XRD detection limit. Although NMR signals similar to that of VPP are found, we want to highlight that XRD does not hint to any VPP crystallites.

Electron microscopy was conducted to investigate the distribution of phosphorus among the vanadium pentoxide particles. STEM-EDX revealed for the fresh ALD catalysts homogeneously distributed P on the V$_2$O$_5$ surface. Neither particles without phosphorus nor particles with P agglomerates could be found up to 10 ALD cycles.[44] This observation is in line with $^{31}$P-NMR results of the fresh catalysts, as mostly broad peaks are observed, indicating amorphous structures. Lamella were prepared by focused ion beam (FIB) from the 1c, 3c and 7c catalysts after reaction and investigated with STEM-EDX. There, P enriched regions are already visible in the 1c catalyst while still containing finely dispersed P on the vanadium surface (Figure 4). The higher the ALD cycle number was the more P agglomerates were found. This must be carefully interpreted as electron microscopy is a local analytical method and extrapolating local findings to the entire sample might lead to misjudgments. However, a relation between the area of detected P agglomerates (A(P)) and the area of finely covered V$_2$O$_5$.

Figure 3. XRD pattern of PO$_x$/V$_2$O$_5$ catalysts by ALD after catalysis. No change of V$_2$O$_5$ bulk structure is visible except for 7c and 10c catalysts and 1c wet treated catalyst with additional reflections at 12.5° and 29.3°.

Figure 4. STEM-EDX of (a) 1c catalyst (b) 3c catalyst and (c) 7c catalyst, all in the state after catalysis investigated as FIB lamella. Shown are the respective HAADF micrographs and their respective elemental distribution mappings (V, P, V + P).
(A(V₂O₉)) was measured and calculated within each lamella FIB lamella. For the 1c catalyst and 3c catalyst the ratio is very low and almost similar with A(P)/A(V₂O₉) = 0.13% and 0.42% respectively. For the 7c catalyst the ratio increases drastically to 10.65%, as more and bigger P agglomerates can be found.

This is in good agreement with XRD and NMR, as NMR shows hints for ordered structures and XRD reveals additional reflections indicating additional crystalline phases. Coming back to XRF analysis, it shows that a theoretical P/V ratio of below 1 leads to barely any P-agglomerates, whereas a P/V ratio above 1 leads to formation of new VPO phases. Analyzing the agglomerates by integrated STEM-EDX shows a P/V ratio of 1 : 1 in the formed VPO phases (Figure 5). Purely based on the stoichiometry of V:P:O, the phase may be assigned to any form of VOPO₄ or even (VO)₂P₂O₇. There were no areas found in which the P/V ratio was above one. Unfortunately, vanadium phosphates are very beam sensitive and thus high resolution electron microscopy or selected area electron diffraction (SAED) could not be conducted to further investigate the crystallinity of the agglomerates. Even though SAED is missing, XRD and especially NMR showed that various VOPO₄ polymorphs are formed during catalysis and therefore matching the electron microscopy. Apart from the agglomerates, all investigated samples show a similar P loading of homogeneously distributed P on vanadium pentoxide of \( \sim 0.05 \) : \(-0.01\) atomic\%. (SI, Figure 3–5) This strongly indicates that an excess of P on the surface leads to vanadium phosphate species, which migrate and agglomerate in interparticle space between the P coated vanadium oxide particles, resulting in almost similar surface compositions for all spent catalysts. The similar surface structure is supported by catalytic studies in which various VPO catalysts show similar catalytic performance and therefore hints for similar surfaces. \(^{[4,24,25]}\) Migration of vanadium phosphates could be induced by steam\(^{[13,30]}\) as some vanadium phosphates are even soluble in water. \(^{[4,11,25]}\) With the previously discussed analytics the catalysis can now be correlated, and fingerprints for certain catalytic performances can be revealed. The catalytic performance (SI, Table S5) is displayed and interpreted as relative performance to vanadium pentoxide to better visualize the effect of P addition (Figure 6). Until up to three ALD cycles the catalysts reveal an almost constant conversion of butane compared to V₂O₅. For higher ALD cycle catalysts the conversion drops relatively by 38% (compared at a temperature of 425 °C) indicating a difference between low ALD cycle catalysts (1–3c) and high ALD cycle catalysts (7c, 10c). The addition of PO₄ in the first three cycles does not decrease the conversion, although the surface coverage increases linearly over the whole range of cycles. In the first two ALD cycles the P/V ratio is below one and approaches \( \sim 1 : 1\) with the 3rd ALD cycle. A theoretical P/V ratio above one apparently leads to a decreased conversion, as observed in the 7c catalyst and 10c catalyst. The reduced activity could be rationalized by blocked active sites which are formed on top of the V–P–O surface with P/V = 1. The decreased conversion cannot be explained by phosphorus loss during reaction or decreased specific surface area. \(^{[6]}\) XRF not only reveals the linear growth of phosphorus content with ALD cycle number but also shows that none of the deposited phosphorus is lost during the reaction over the course of 200 h TOS (SI Figure 1). In contrast to P deposited by ALD, P added by incipient wetness impregnation can be lost during reaction \(^{[47]}\) which is also found for the vanadyl pyrophosphate on industrial level. \(^{[34]}\) As 200 h time on stream is relatively short compared to a continuous industrial process, P loss might occur over a longer time frame for these catalysts but a loss was not detected in this study. This indicates a non-volatile water resistant phosphorus species. Furthermore, the specific surface

![Figure 5. STEM-EDX of 7c catalyst in the state after catalysis investigated as FIB lamella. Shown are the is the elemental distribution of P (green) and V (red). Area 1 shows a P/V of around 1:1, whereas area 2 shows low P loadings of 0.05 atomic%.](image_url)

![Figure 6. Catalytic performance of PO₄/V₂O₅ catalysts with varying P loading prepared by P-ALD in the conversion of n-butane to maleic anhydride at 425 °C. Shown is the conversion of n-butane (blue) and the selectivity towards maleic anhydride over ALD cycle number and P/V ratio. The GHSV was constant at 2000 h⁻¹ with a constant feed of C₆H₁₃O/O₂/H₂O = 2/20/3% balanced with nitrogen. Raw data is provided in the supplemental information (SI, Table S5).](image_url)
area of 4.4 ± 0.6 m²/g does neither change during ALD nor during catalysis (SI, Table 4). The difference between low ALD cycle catalysts and high ALD cycle catalysts was confirmed by 31P-NMR, XRD and STEM-EDX. With higher ALD cycle number P enriched phases are formed which were identified by XRD and NMR to some form of VOPO₄.

Correlating the butane conversion with NMR indicates that the sharp peaks at −0.6 ppm and/or at −14.4 ppm might be highly relevant. Every spent catalyst which contains these peaks showed lower conversion levels than all catalysts that do not exhibit these signals. These signals at −0.6 ppm and −14.4 ppm could in theory be assigned to vanadium phosphate poly-morphs, such as α₃-VOPO₄, VOPO₄-2H₂O, β-VOPO₄ or α₅-VOPO₄. In terms of catalysis, they should be spectator species, as their catalytic performance is worse than that of all ALD catalysts. The conversions of mentioned vanadium phosphates at 425 °C are all below 5% with selectivities to MAN not higher than 12.5%. (SI, Table 5). Furthermore, literature showed that the conversion of various VOPO₄ are almost similar indicating that additional P-species must be present here. Please try to avoid repeated use of the same references. Despite their poor catalytic performance, they are not expected to account for the drastic loss in conversion. A linear decrease of conversion with ALD cycle number would be expected, as more VPO polymorphs should be formed with more ALD cycles.

The NMR signal at −0.6 ppm may also correspond to phosphoric acid. The formation of strong phosphoric acid sites under reaction conditions is known from literature. Please try to avoid repeated use of the same references. Phosphoric acid is also partially co-fed under industrial conditions to decrease the conversion at “hot-spots”, thus remaining the stable catalytic performance. Please try to avoid repeated use of the same references. Considering that phosphoric acid is formed during catalysis for the ALD catalysts, it might spread on the surface blocking active sites. The presence of phosphoric acid cannot be confirmed but in the context of decreased conversion the assumption is justified.

Although exact structural assignment of the P environment in the region of −0.6 ppm was not possible yet, the species giving rise to this peak, is most likely responsible for decreased butane conversion and therefore serves as fingerprint. The 1–3c spent catalysts do not contain this NMR signal and show superior conversion. One could think of phosphoric acid to be formed by the steam during reaction conditions, as phosphates show affinity towards water to form phosphoric acid... Please try to avoid repeated use of the same references. However, XRD can confirm the evolution of crystalline VOPO₄ species also for the spent catalysts (SI, Figure 7). The broad NMR signal at 35 ppm, which was found in the spent dry ALD catalysts and the spent VPP catalyst was also found in the 1 cycle wet spent catalysts.

Correlating the S(MAN) to 31P-NMR signals it becomes clear that all catalysts with the broad peak at 35 ppm show higher yields than catalysts which do not contain any signal at 35 ppm. The selectivity to maleic anhydride increases up to the 3c catalyst. With higher ALD cycles the S(MAN) does not further increase but rather remains in the same range as the 3c catalyst. This indicates the formation of selective species up to the P/V ratio of 1 above which no additional selective sites are formed but rather structures which result in decreased conversion. As the 35 ppm signal is the only obtained one for the 1–3c spent catalyst, it strongly indicates its responsibility for the selectivity towards MAN and can serve as fingerprint for increased S(MAN).

Furthermore, the vanadyl pyrophosphate catalyst as best performing catalyst in this study also contains this fingerprint at 35 ppm. As the peak is significantly broadened and therefore assigned to a very flexible and most likely amorphous environment, a defined molecular structure around the P-nuclei cannot be determined. As previously discussed, literature supports the idea of amorphous P environments being responsible for the selectivity to maleic anhydride.

Out of all investigated vanadium phosphates, the spent vanadyl pyrophosphate catalyst revealed the broad NMR signal at around 35 ppm. As the shift to 35 ppm is expected to be induced by paramagnetic nuclei, such as vanadium(+VI), one could propose that a mixture of V⁴⁺/V⁵⁺ is needed for the selective oxidation of butane to MAN, which is in agreement with the vast majority of literature. Please try to avoid repeated use of the same references. In addition, DFT calculations proposed a “Reduction-Coupled Oxido Activation mechanism” in which mixed valent vanadium is needed for the C–H activation. Please try to avoid repeated use of the same references. This leads to the conclusion that PO₄/ALD results in homogeneous distributed P on vanadium pentoxide surface before catalysis without forming agglomerates or additional phases. Under reaction conditions and even in steam at 450 °C restructuring of the catalyst surface occurs as the vanadium phosphate system is very flexible. The PO₄/V₅O₄ system adjusts itself to a certain but low P/V ratio on the surface during catalysis. Excess P is forming agglomerates of different vanadium phosphates, which migrate away from the vanadium oxide particle, revealing the amorphous P on vanadium oxide. The formed agglomerates can be attributed to some form of VOPO₄ which are barely participating in the selective oxidation. The amorphous V–P–O on the vanadium oxide is responsible for the selectivity towards maleic anhydride. However, the amorphous environment should contain V⁴⁺ and V⁵⁺ simulta...
neously for selectivity towards MAN. As long as an excess of P or V is present, restructuring and phase formation of VOPO₄ will occur. Once the vanadium oxide surface is saturated with phosphorus one might expect the formation of phosphoric acid on top which results in decreased conversion.

Despite the transformation of the ALD prepared catalyst under reaction conditions, ALD was found to be helpful in understanding the catalytic system. Adding a foreign element to an existing bulk catalyst and subsequent detailed analytics reveal its influence on the performance. Even after the first ALD cycle, a significant improvement of the catalytic performance was observed. As the catalyst improvement exhibits a maximum with 3 ALD cycles being the best performing catalyst, it shows that ALD can enhance catalytic performances with only few ALD cycles already. This opens up further strategies to develop novel catalyst systems and investigate element specific properties during catalysis. Furthermore, solid state ³¹P-NMR can be used as a fingerprint method to reveal selective and/or conversion inhibiting P-species.

Conclusion
Up to 10 ALD cycles of PO₄ atom layer deposition were conducted on vanadium pentoxide powder. The samples were subsequently investigated as catalysts in the reaction of n-butane to maleic anhydride. The selectivity towards MAN increased drastically with the addition of phosphorus already after the first cycle. The catalytic performance increases until up to 3 ALD cycles after which the P/V ratio equals 1. Additional ALD cycles lead to a decrease in conversion. Detailed analytics reveal changes of the catalytic relevant moieties under reaction conditions. During reaction at elevated temperatures the catalyst surface undergoes structural changes. The deposited phosphorus forms agglomerates with the vanadium oxide, resulting in (nano)crystalline vanadium phosphates which were detected by XRD and ³¹P-NMR. However, the formed agglomerates are barely contributing to catalysis. Besides the formed P-rich phases, the vanadium pentoxide is still homogeneously covered by phosphorus in the same degree for all catalysts irrespective of ALD cycle number, as shown by STEM-EDX measurements. The amorphous vanadium phosphorus oxide species formed under reaction conditions is responsible for the increase in selectivity towards maleic anhydride. Decreased conversion might be the result of formed phosphoric acid, which block active sites. This paper shows that ALD on bulk oxidation catalysts is complex and might result in a pre-catalyst, which undergoes changes during reaction. However, it was shown that ALD is a suitable approach to modify bulk catalysts and investigate the influence of the deposited element on catalysis. High numbers of ALD cycles are not necessary, as an improvement of catalytic performance peaks at three ALD cycles.

Experimental Section

Chemicals
Divanadium pentoxide (V₂O₅, 99.9 %, Sigma-Aldrich) was sieved to the fraction of 100–200 μm prior to use as substrate. Trimethoxy phosphine (P(O(CH₃))₃, TMPT, 99.90 %, Sigma-Aldrich) and high purity oxygen (O₂, 99.999 %) served as precursor for phosphorous oxide ALD and were used without further purification. High purity nitrogen, argon and helium (99.999 %) acted as carrier and purging gas.

Atomic layer deposition
Phosphorus oxide ALD was performed in quartz tube fixed bed reactor on divanadium pentoxide. The setup is described in more detail elsewhere [15]. Phosphorus oxide ALD was performed by saturating a constant N₂ stream of 25 mL/min with trimethoxy phosphate at 60 °C, diluting it in additional 25 mL/min of N₂ and then depositing it at 150 °C in the first half cycle until saturation. Oxygen served as reactant in the second half cycle with a flow of 10 mL/min diluted in 40 mL/min of He at 450 °C until saturation. Up to ten ALD cycles of PO₄ were performed. In between all half cycles, the reactor was purged with 50 mL/min of Ar. Before catalytic evaluation, the catalysts were treated in either dry or wet (10 % H₂O) synthetic air at 450 °C for over 4 h.

Catalysis
A series of 7 catalysts with varying ALD cycles and treatments were evaluated in an 8-fold parallel setup in the oxidation of n-butane. The temperature was increased from 350 °C–450 °C with 25 °C per step and then decreased to 350 °C in 25 °C per step. At each temperature level five consecutive gas chromatograms were obtained every 3 h for each reactor. The GHSV was constant at 3500 h⁻¹ with a constant feed of C₄H₁₀/O₂/H₂O = 2/20/3 %v balanced with nitrogen. The conversion (X) of n-butane and the selectivities (S) of the respective products are typically calculated from the concentrations measured with reference to the internal standard Ar [Eqs. (1) and (2)]. The latter are averaged over 5 runs measured at each temperature step, respectively. The selectivities of the (by)products were normalized to the number of carbon atoms (Nc) in the (by)products and n-butane, respectively [Eqs. (3) and (4)]. Possible by-products include butenes, acrylic acid, acetic acid, acrolein, acetaldehyde, propene, propyne, acetylene, ethane, 2,5-dihydrofurane, furane, 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 is preferred. The catalytic performance at 425 °C for each catalyst is shown in the supporting information (SI, Table 5).

\[ X = 1 - \frac{C_{\text{n-butane}}}{C_{\text{n-butane,0}}} \times \frac{C_{\text{P,O}}}{C_{\text{P,O,0}}} \]  

\[ S_i = \frac{C_i \times N_i}{C_{\text{n-butane,0}} \times \frac{N_{\text{n-butane}}}{N_i} - C_{\text{n-butane}}} \]  

\[ X = 1 - \frac{C_{\text{n-butane}}}{C_{\text{n-butane}} + \sum (C_i \times \frac{N_i}{N_{\text{n-butane}}})} \]
Characterization

$N_2$ physisorption

$N_2$ physisorption measurements were performed at liquid $N_2$ temperature on a Quantachrome autosorb-6B analyzer. Prior to the measurement, the samples were degassed in dynamic vacuum at 150°C for 2 h. Full adsorption and desorption isotherms were measured. The specific surface area $S_{BET}$ was calculated according to the multipoint Brunauer-Emmett-Teller method (BET) method.

Nuclear magnetic resonance (NMR)

Solid state – Magic Angle-Spinning (MAS) (Bruker Avance II 400WB spectrometer, Germany) was employed to record the $^1$H pulse solid state NMR spectra. The NMR spectra were collected operating in a magnetic field of 9.4 T, using a Bruker CPMAS probe with ZrO$_2$ rotor (outer diameter (OD) 4 mm). The sample rotation frequency was 12 kHz. The spectra were recorded employing a π/2 pulse of 2 μs on 31P and using a relaxation delay of 10 s. 31P spectra were referenced to an 85% solution of phosphoric acid in water using ammonium dihydrogen phosphate as a secondary reference.

X-ray fluorescence spectroscopy (XRF)

XRF was performed in a Bruker S4 Pioneer X-ray spectrometer. Samples were prepared by melting pellets with a ratio of 100 mg sample with 8.9 g of Li$_2$B$_2$O$_3$.

Electron microscopy

Prior to electron microscopy lamellas were prepared by deposition of tungsten as protective coating and consecutive cutting by a focused ion beam of Ga$^+$ (Thermo-Fisher Helios G4). Transmission electron microscopy was performed on Thermo-Fisher Themis Z3.1 with an XFG field emission gun and an acceleration voltage of 300 kV. STEM-EDX mappings were acquired with the SuperXG2 system of 4 SDD EDX detectors.

Powder X-ray diffraction (XRD)

XRD measurements were performed in Bragg-Brentano geometry on a D8 Advance II theta/theta diffractometer (Bruker AXS), using Ni-filtered Cu K$_{α1,2}$ radiation and a position sensitive energy dispersive LynxEye silicon strip detector. The sample powder was filled into the recess of a cup-shaped sample holder, the surface of the powder bed being flush with the sample holder edge (front loading).

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: electron microscopy · heterogeneous catalysis · NMR spectroscopy · oxidation · surface chemistry

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