In-situ surface analysis in selective oxidation catalysis:
n-butane conversion over VPP

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Abstract

In-situ analysis of the surface of a working selective oxidation catalyst is an essential yet rarely conducted experiment in attempts to derive structure-function relationships. The case study of n-butane oxidation over vanadyl pyrophosphate (VPP) is used to develop a general working hypothesis and to illustrate that the molecular properties of the substrate set boundary conditions on the surface chemical properties of the catalyst. Experiments using in-situ X-ray photoelectron spectroscopy (XPS) and in-situ low energy X-ray absorption spectroscopy are used to derive compositional, electronic, and geometric structural information of the surface of the working VPP. These data allow the conclusion that a surface phase different from VPP must be present covering at least part of the active material. The recent data together with literature observations are used to derive a scenario explaining the function of VPP as a unique catalytic system.

Keywords: n-butane oxidation; VPP; VPO; in situ XPS; in situ VL-edge NEXAFS; TEM.

Introduction

The quest for performing in-situ analysis in heterogeneous catalysis is now over 30 years old. Yet, there is only a small minority of experiments available standing up to the definition of in-situ analysis. Only experiments that combine on-line catalytic functional analysis and spectroscopic/structural characterisation allow understanding the working catalyst. The value of such non-trivial experiments lies in the experimental derivation of structure-function relationships[1] based on quantitative correlations of performance and spectral properties.

The successes in developing selective oxidation processes working with gas phase oxygen as oxidant and weakly or non functionalised substrates resides to a great extent on a set of heuristic rules known in the field as the "pillars of selective oxidation catalysis"[2]. The intrinsic complexity in catalyst material science and in kinetic demand for observing selective oxidation performance under model reaction conditions has limited the application of in-situ methods in this field to play its leading role in finding the physical underpinnings for the pillars and to validate them versus atomistic understanding.

The present work limits the discussion to one of the most studied systems in the area, namely the selective oxidation of n-butane to maleic anhydride (MA) over vanadyl pyrophosphate (VPP)[3-7]. This system is with its Daltonid formula $(VO)_2P_2O_7$ chemically simple and homogeneous in contrast to many other selective oxidation systems. Yet little solid facts are known about the surface properties, beginning with its surface termination[8-14]. Structural studies done under reaction conditions are despite of their designation "in-situ" not up to the definition, as no catalytic activity was measured of the samples under study[8].

The harsh reaction conditions usually applied in selective gas phase oxidation (700 K, excess of oxygen, addition of steam) are not determined by the organic chemistry of the substrates, as biological systems can activate small alkane molecules under very mild conditions with complete selectivity to partial oxidation. It is noted that this statement is in contrast to an exhaustive analysis of selective oxidation reactions that run against a universal barrier in the selectiv-

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ity-conversion plots. This barrier was explained by the C-H bonding properties[15]. Homogeneous partial oxidation systems [16] also work under mild conditions and use complex reaction sequences to separately activate the oxidant (as reactive additive) and the substrate and to handle the oxidation process with spatio-temporal separation. In heterogeneous gas-surface reactions the same complexity of the chemical tasks for the organic substrate augmented by the problem of molecular oxygen activation has to be handled with a nominally uniform catalyst and no well-understood spatio-temporal separation (all happens on one surface). In addition, the catalytic material in its as-prepared form exists in a poorly active near-equilibrium state not well suited for performing the complex and manifold reaction steps required for the target transformations. This is deduced from the activation behaviour required to arrive, for the present example system, at an "equilibrated" catalyst[14;17].

The hypothesis of the work presented here is that the reaction conditions may be imposed by the material properties of the catalysts requiring transformation of the synthesised pre-catalyst into a highly specific structural and chemical derivative performing the catalytic act: in other words, it is the material science of the system determining the reaction conditions and not the substrate chemistry. This hypothesis is considered to be the generalised form of the often referred "Mars-van-Krevelen" (MvK) mechanism that in its original form contained no atomistic assumptions for the justification of a modification of the Langmuir-Hinshelwood formal kinetic *ansatz*. Concepts of "cus-sites" and "lattice oxygen" were attached later to this formal kinetic approach derived originally from fitting kinetic data of SO$_2$ oxidation over a vanadium-oxide based catalyst. Despite of claims in the literature[18;19], few in-situ experiments controlling the catalytic chemistry simultaneously with the structural chemistry were put forward to prove the attachment of these heuristic atomistic concepts to the MvK mechanism. In the model VPP system there are conflicting interpretations about the undisputed fact that solid-state transformations occur during operation[20-22], with the target of dispute being the role of minority phases and of amorphous surface layers[23;24]. The hypothesis is also compatible with the finding that a MvK mechanism is not essential for the butane oxidation if the VPP is supported into high dispersion[25].

Considerations about n-butane activation

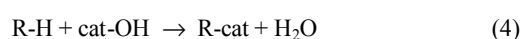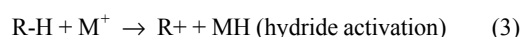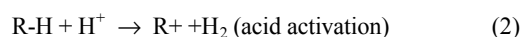The puzzle about the reaction pathway of this truly complex reaction[19]

$$2C_4H_{10} + 7 O_2 \rightarrow 2 C_4H_2O_3 + 8 H_2O \qquad (1)$$
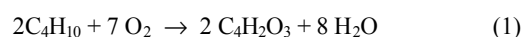
has been the subject of numerous studies[26-31]. There is agreement that a number of stable intermediates of olefins and oxygenates should occur during the reaction path[3;5;32;33]. Agreement seems also to exist that the successful catalyst is non-stoichiometric both with respect to the elemental composition (phosphate enrichment) and to its redox chemistry (presence of V^{5+} sites[34;35]). These findings contradict the notion that well-ordered surface terminations of VPP should be the actives sites. The practically derived non-stoichiometry is seen as an expression of the above-mentioned requirement that a good catalyst is a non-equilibrium solid.

Initial dehydrogenation of the butane molecule is viewed as the most difficult reaction step in terms of activation barrier and/or success rate (ratio of surface coverage of butane and of its first dehydrogenation product). None of these kinetic constants is known for relevant reaction conditions. It is a major puzzle[26] of the system that it is able to activate the consecutive products which are all more reactive, in such a way that the total oxidation reaction remains an unlikely process. Various explanations, ranging from co-existence of several specialised sites (as in biological systems) with unknown structures and unknown transfer processes, to a modification of the reactivity of the same site by its existence in several electronic states (vanadium in several oxidation states) have been taken into consideration. These concepts neglect the fact that various electronic states of a solid surface require also several geometric structures and are difficult to reconcile with a highly defined surface site being part of a translational symmetric lattice.

The electronic properties of the butane molecule have rarely been explicitly taken into consideration. From homogeneous activation of butane in atmospheric chemistry we know that the initial OH radical activation leads to massive internal rearrangements of the electronic structure of butane, facilitating its reaction with less activated oxygen sources[28]. An important piece of evidence is the fact that a kinetic isotope effect was established[36] for centrally deuterated versus terminal deuterated butane molecules. This proves that in heterogeneous activation the attack of a methylene hydrogen is the first step to occur. For this step a variety of reactions have been proposed, all of which are incomplete in their atomistic representation:

$$R\text{-}H + H^+ \rightarrow R+ +H_2 \text{ (acid activation)} \qquad (2)$$

$$R\text{-}H + M^+ \rightarrow R+ + MH \text{ (hydride activation)} \qquad (3)$$

$$R\text{-}H + cat\text{-}OH \rightarrow R\text{-}cat + H_2O \qquad (4)$$

$$R\text{-}H + cat\text{-}OH \rightarrow cat\text{-}O\text{-}R + H_2O \text{ (alkoxide)} \qquad (5)$$

$$R\text{-}H + cat\text{-}OH \rightarrow cat\text{-}O\text{-}R + H_2 \text{ (redox)} \qquad (6)$$

Reactions 2,3, and 6 require a *homo* structure of n-butane with finite electron density at the methylene positions to occur in a facile manner. Reactions 4 and 5 (identical nucleophilic attacks) require a well-developed *lumo* at the methylene hydrogen positions. If the concept of frontier orbital reactivity[37] as the energy-efficient alternative is assumed to hold here, then a comparison of the *homo-lumo* structure of butane should allow to select the likely reaction path and thus to decide if the catalyst requires high acidity (electrophilic) or basicity (nucleophilic) as initial surface reactivity. Figure 1 compares the *homo-lumo* structure and reveals that the methylene positions are clearly susceptible

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for nucleophilic activation, whereas the terminal positions are more reactive towards electrophilic activation.
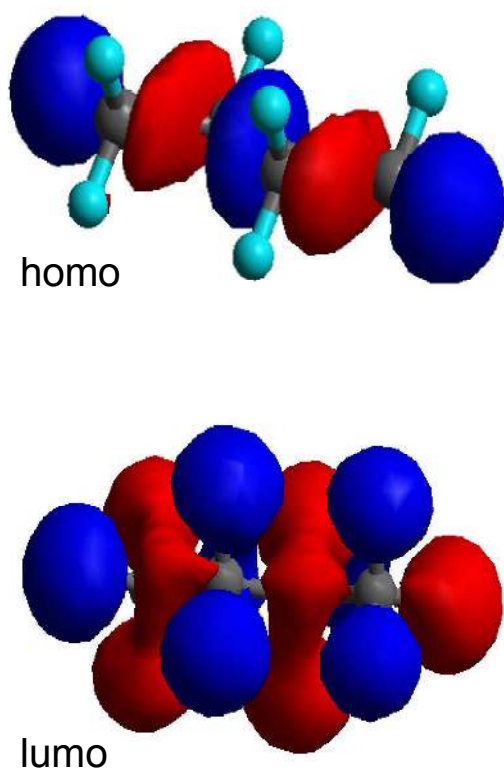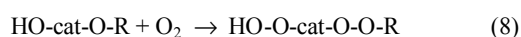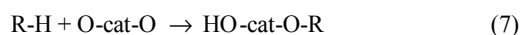

homo

lumo

Figure 1: Molecular orbitals of n-butane as calculated from the minimum energy structure obtained from AM 1semiempirical calculations. All methylene carbon-hydrogen bonds do not belong to the highest occupied molecular orbital (homo) of the molecule. They are, however the centres of the lowest unoccupied molecular orbital (lumo).

The likely configuration of the activated butane is then a 2-butyl alkoxide resulting from a nucleophilic attack that occurs from a strongly bound oxygen site with high local electron density[35;38]. Such a site requires vanadium centres being present in at least V^{4+} (or lower) oxidation states. The proton and electron resulting from the activation reside with neighbouring oxygen and vanadium centres of the active ensemble. The primary alkoxide product (reaction 7) is an ether structure that could activate an oxygen molecule (reaction 8) forming a peroxide structure[37], and an electrophilic oxygen anion residing on another centre of the active site.

$$R\text{-}H + O\text{-}cat\text{-}O \rightarrow HO\text{-}cat\text{-}O\text{-}R \qquad (7)$$

$$HO\text{-}cat\text{-}O\text{-}R + O_2 \rightarrow HO\text{-}O\text{-}cat\text{-}O\text{-}O\text{-}R \qquad (8)$$

Such structures allow further dehydrogenation steps leading to the postulated olefinic intermediates. A reduction of the metal sites to formally V^{3+} that is the consequence of further dehydrogenation of the C4 substrate, is beneficial to accommodate electrophilic oxygen and the olefinic interme-

diate and to reduce the stability of intermediate –OH groups, allowing their desorption as water.

The strongly activating effect of attaching a formally charged oxygen atom (alkoxide) to the butane molecule can be seen from the substantial redistribution of partial charges displayed in Figure 2 and from the equally drastic changes
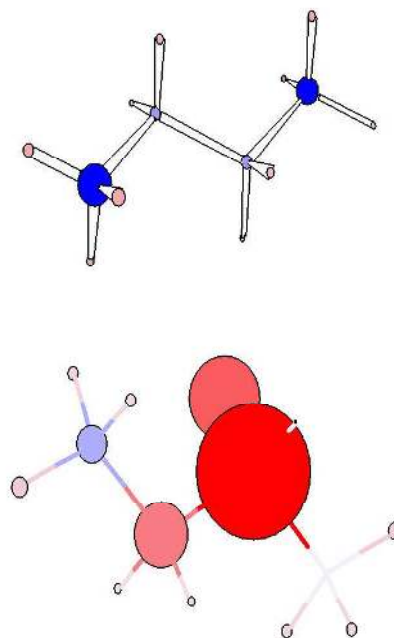

Figure 2: Partial charges residing on n-butane and on a model of butyl alkoxide. Positive signs are in red, negative signs in blue, relative atom sizes represent charge magnitude. A calculation on the AM 1 level allowing for open shell configuration was used for energy minimisation.

in predicted carbon-carbon bond lengths listed in Table 1. It occurs that C-C bond cleavage that is clearly undesired becomes a likely alternative if the activating oxygen bonding is too strongly charged: the moderating effect of the oxide surface that would reduce the partial charge on the oxygen atom is critical for keeping the molecular backbone intact.

Table 1: Carbon-carbon bond lengths in pm of activated and non-activated butane. The energy-minimised structures were obtained from AM 1 calculations assuming a formal charge of −1.0 at the alkoxide oxygen.

Bond	Non-activated	Activated
C1-C2	152	150
C2-C3	152	156
C3-C4	152	155

Consequences for the catalytic material

The above considerations highlight some consequences for an active catalytic material: The catalytic process of which only the beginning is considered in section 2 requires a substantial flexibility of the reaction centres in

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their electronic structure. It seems further advantageous to consider oxygen-terminated sites as reaction centres[37], with the underlying metal-oxygen bonds[35] controlling the specific function. This specificity requires a significant flexibility in the metal-oxygen coordination in the absence of non-oxygen ligands. In summary, a rigid and complex structure as existing on the hypothetical basal plane of VPP is, in contrast to literature models[39;40], not a likely candidate for the required flexibility. As the metal centres contain only vanadium-oxygen bonds it is the hybridisation of these bonds that has to provide the desired electronic structural flexibility[41].

The connectivity of the V-O bonding network requires changes during each complete turnover of one butane molecule. High barriers of activation energies for such changes will result if the active site is part of a three-dimensional translational symmetric solid structure as that of VPP. These barriers translate into high reaction temperatures and this might be one reason for the level of reaction temperatures mentioned in the introduction. The temperature level of 700 K is a typical value for the onset of oxygen anion mobility in (defective) oxides and could explain the notion from environmental electron microscopy that lattice point defects should be of particular relevance in catalytic function of VPP[42]. Recent studies on binary vanadium oxides and its non-chemical reduction pathways[43], and studies on chemical reduction scenarios of MoO_3 confirm that this temperature level is typical for reductive processes controlled by oxygen transport[44;45].

The modification of the solid-state reactivity of VPP should affect the catalytic reaction temperature if the oxygen transport were indeed rate controlling as suggested in variants of the MvK concept[18]. Literature results reporting an improved productivity in butane oxidation by milling VPP or their precursors[46;47] and the pronounced effect of fully amorphous VPP samples[24] requiring no equilibration time for full performance do indicate that solid state reactivity is an important factor, but these results showed no clear reduction in the temperature required for full performance. It has to be assumed that with the geometric structural modifications also the local electronic structure of the material was modified. In this way two factors affecting the performance were altered without allowing independent observation. Comparative studies on the nature of active sites of VPP in different catalytic reactions concluded that different active sites should form in different reactions despite the same bulk VPP phase being present[48;49]. These findings all point to the existence of a dynamical active catalyst without identifying structural details or even a single controlling factor for the formation of the active site. In this situation attempts were made to apply in-situ structural methods looking at the geometric and electronic structure of the working catalyst to corroborate the dynamic nature of the VPP system.

Localisation of the active material

There is overwhelming evidence that the bulk active phase of the butane oxidation catalyst is indeed VPP with, however, minority phases of amorphous or crystalline materials being present without clear correlations to the catalytic performance[50-52]. The "six rules" of a good catalyst[40] indicate for a successful catalyst a systematic deviation from stoichiometric VPP. Experiments presented in Figure 3a and b with non-chemical reduction of VPP in the electron microscope clearly reveal that the pyrophosphate part of the material is stable against reduction, whereas the vanadium-oxygen part is quite susceptible to reduction, as can be seen from the strong changes in line shape of the *O K edge*-V-O structure compared to almost unchanged structures of the *V L2,3 edge* and *O K edge*-P-O features. High resolution TEM images presented in Figure 3c-e taken under strict exclusion of beam damage artifacts reveal also that the bulk of all well-ordered VPP crystals[51;53;54] complies with the standard VPP crystal structure. The pattern in the basal plane view arises from the interchange between double-polyhedra of vanadium oxide and the pyrophosphate units and can be simulated using the atomic coordinates from X-ray diffraction. It is pointed out, however that structural variants of the vanadium-oxygen polyhedra within the double polyhedra motif would be difficult to detect by TEM, as tests have shown with simulated structures of $VO(PO_4)$. The prism view reveals layers composed of the two-dimensional networks between phosphates and vanadium oxide. The defect structures for the bulk catalysts discussed as being essential[55] were not seen in samples not excessively reduced, such as those observed in the unsteady state operation of a riser reactor concept.

The prismatic edges, and frequently also the basal planes are, however covered with a thin (ca. 1-3 nm) adlayer of a non-crystalline material. This can be seen from the representative images in Figure 3. Frequent variations in bulk ordering and in thickness of the adlayer were found in about 50 equilibrated catalyst samples from different sources without any clear correlation of the micromorphological features to catalytic performance. Observing the temporal evolution of the beam damage of VPP starting from the surface indicates that at zero time the adlayer is about 1 nm thick. It is assumed that this thin adlayer is intrinsic to equilibrated samples (not visible in every projection due to focussing/contrast formation problems) as it may be the termination of VPP under reactive conditions (water from oxidation, reduction from organics of feed or from catalyst synthesis). This layer is a suitable candidate for the localisation of the active phase. It seems to be metastable with respect to chemical and electron beam reduction. It may further be present as a patchy structure without forming a dense shell around each VPP crystal. The failure to correlate activity with the visual detection of the adlayer indicates, however, that an additional parameter, such as the local electronic structure of the V-sites, is also essential for the catalytic function[39;56].

The experimental strategy was to select surface-sensitive tools that can provide insight about the following points:

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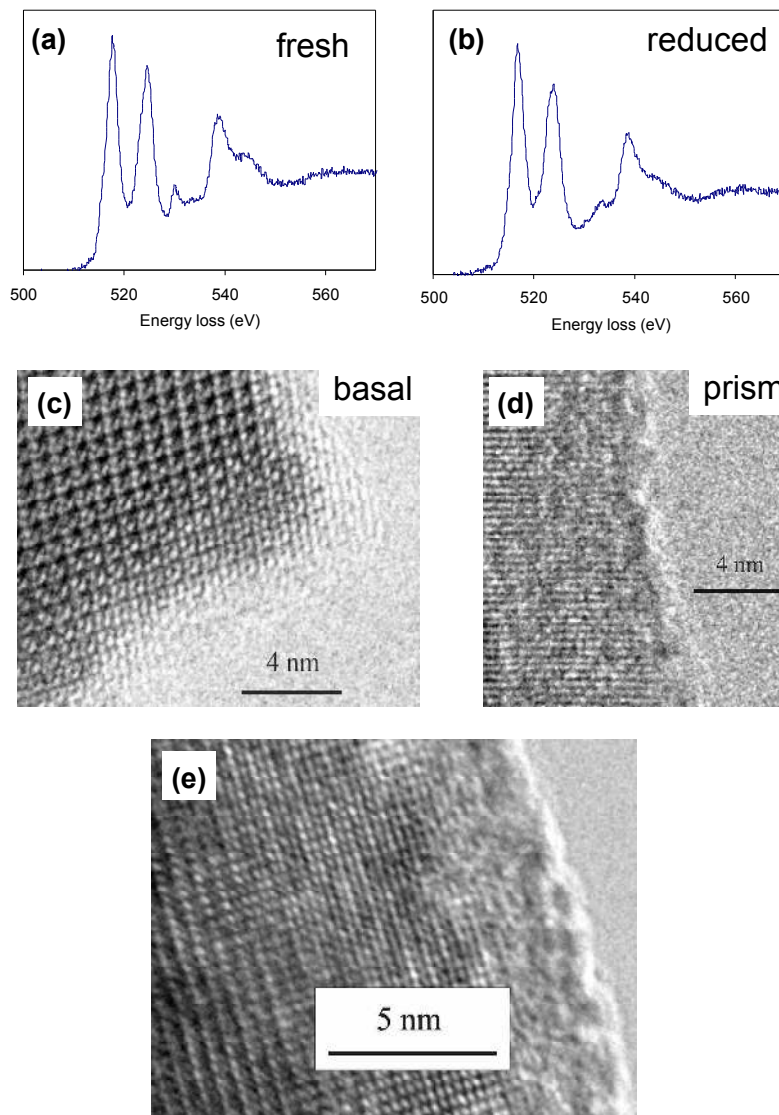
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Figure 3: ELNES spectra of the V L 2,3 and O K edge region of VPP: **(a)** fresh without any beam damage, and **(b)** reduced, after amorphisation by the electron beam. The arrows indicate the spectral range with strong modifications of the O K edge structures (see text). HRTEM top view images of the **(c)** basal and **(d)** prism edges of individual VPP platelets. The images were recorded at 400 keV to minimise the beam damage. **(e)** Non-crystalline adlayer on the surface of a VPP particle.

- There is a chemical non-stoichiometry at the working surface with a possibly variable V:P:O ratio that would prove the presence of more than one Daltonid compound (VPP).
- There are structural parameters (bond distances) that are characteristic for the VPP structure (known from bulk X-ray investigations) or identify another surface structure. The corresponding V-O fragments must be active in the catalytic cycle.
- In the active state there is a defined electronic structure of the V sites that can be related to the chemical concept of oxidation state (around 4+ according to empirical determinations).

In this way a signature of the active site might emerge that can either be used for retro-synthesizing such sites or can go into theoretical modelling efforts with starting conditions more realistic than those of the VPP bulk structure.

These considerations do not exclude that the source of the active material becoming operational at the surface may actually be located in volume defects, such as impurity phases or grain boundaries of the VPP host material. Also the intrinsic and not catalyst material-related defect structure of VPP[57] may play an important role in forming the surface phase. The differentiation of various materials in catalytic performance according to their chemical history does reflect their varying ability to transform their surface into the active state and keep it active during operation times.

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In-situ surface composition

XPS is a very valuable method to determine the atomic surface composition of a catalyst. Its cross section values and depth of information characteristics[58] are well evaluated and can directly be applied. For synchrotron-based experiments a complex correction procedure of the experimental intensities accounting for the non-constant primary intensity, for the transmission function of the high-pressure window and for the energy-dependence of the elemental cross section has to be applied. For VPP several ex-situ studies have identified an excessive enrichment[12;13;40;59;60] of P over the stoichiometric value of V:P:O of 1:1:4.5 for VPP. The data in Figure 4 were taken such that the same kinetic
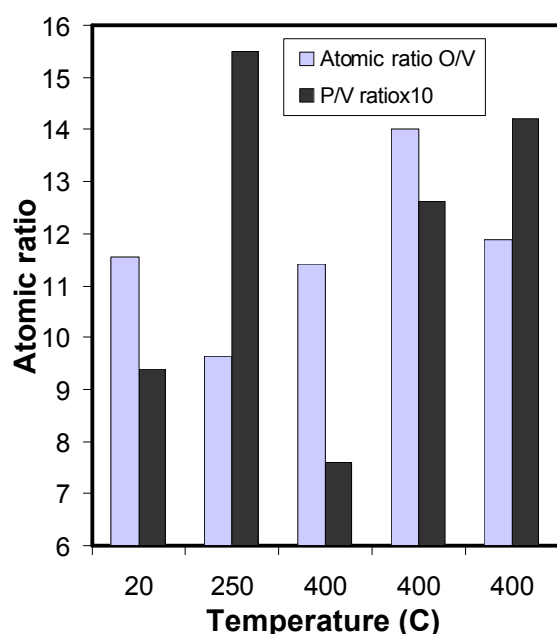

Figure 4: Atomic abundance of the constituent elements of a VPP catalyst. The data were obtained under various episodes of an extended in-situ XPS experiment. The feed was 1.6 mbar of a 1.5% n-butane/98.5% He-mixture + 0.4 mbar oxygen. The catalyst treatment previous to the series of experiments displayed was an oxidation in 0.27 mbar oxygen at 523 K.

energy of all electrons from the various core levels was obtained to guarantee a uniform depth of information that was minimised to about 2 nm at 200 eV kinetic energy. The P:V ratio varies around unity for the different gas phase compositions and temperatures; during conversion at 673 K the ratio varies between 0.8 and 1.4. A defined value above unity seems not to be a strict condition of an active surface. More critical is the enormous excess of oxygen over vanadium in the state where MA is produced, reaching values above a factor of three, and this in the presence of butane in the gas phase that should consume surface adsorbed and/or lattice oxygen. Even a full chemisorption layer on top of a hypothetical VPP surface would not account for this excess. In addition, varying the kinetic energy of the ejected electrons shows no drastic change of the excess indicating that an adsorbate alone cannot account for the observation. The

atomic ratios between all elements vary for each gas phase composition. This is proof for the presence of more than one chemical compound under working conditions. The data show that there is no lateral homogeneity in the active surface as neither VPP (in any termination) nor a binary V-oxide alone can explain the data. A mixture of a binary V-oxide and hydrated phosphoric acid from hydrolysis of pyrophosphate (two contributions to the oxygen 1s line at 530 eV and at above 532 eV could support this picture and exclude a chemical uniformity) would account best for the large excess of oxygen over vanadium. The allegation about amorphous surfaces that should contain local ordering like in VPP[61;62] stems from the assumption that the system is laterally homogeneous and exhibits only a one-dimensional gradient in P-content from surface to the bulk value. The origin of this gradient was assumed to be in a pyrophosphate termination [40;60] that, however, is not necessarily present under the conditions of the experiments taking into account the massive deviation of the surface composition of V:P:O = 1:1:4.5.

In-situ surface structure

Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy at low-energy absorption edges is a chemically sensitive tool for elucidating electronic structures and, with certain limits, also for deriving bond distances between sufficiently localised metal-ligand bonds. The electron yield detection mode ensures a surface sensitivity of about 4 nm at the conditions of the present experiments. The physical background of the correlation between spectral data and bond distance and the experimental details are reported in detail elsewhere [63-65].

The experiments were conducted at temperatures between 300 K and 673 K in a mixture of 1.2 % n-butane + 20 %oxygen + 78.8 % helium at a total pressure of 2 mbar. A set of catalysts exhibiting different MA yields was compared in their performances under in-situ and atmospheric pressures to validate the in-situ conditions as being representative of normal kinetic experiments. The data in Table 2 indi-

Table 2: Normalised yields of a subset of VPP catalysts prepared via different pathways. The MA yields were measured at 673 K. At atmospheric conditions 1.8% n-butane in air was used at a GHSV of 2477 h^{-1}, whereas at 2 mbar a mixture of 1.2% n-butane + 20 % oxygen + 78.8 % He was passed over a 50 mg catalyst pellet at a total flow of 17.5 ml/min.

Sample	1 bar	2 mbar	ratio
1	1.4	1.7	0.82
3	1.05	1.45	0.73
4	4.25	4.4	0.95
9	3.4	4.6	0.74

cate a reasonable relation between the performances taking into account that plug flow reactors and single pellets in a flow through-cell represent substantially different reaction environments. This rather demanding criterion for the valid-

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ity of an in-situ experiment demonstrates that it should e possible to deduce relevant information for the state of the practically active catalyst.

Fig. 5a shows a high resolution NEXAFS spectrum of a VPP catalyst taken at 673 K. The complex shape required 7 resonances in an unconstrained fit as minimum features to account for the complex lineshape that changed slightly with reaction conditions. Only after analysing the spectral parameters of each of the components it became clear that two of the resonances, namely V5 (the largest contribution) and V6, changed systematically with reaction conditions. All other features remained unaffected. In Fig. 5b it is demonstrated that the intensity of V5 decreased sys-
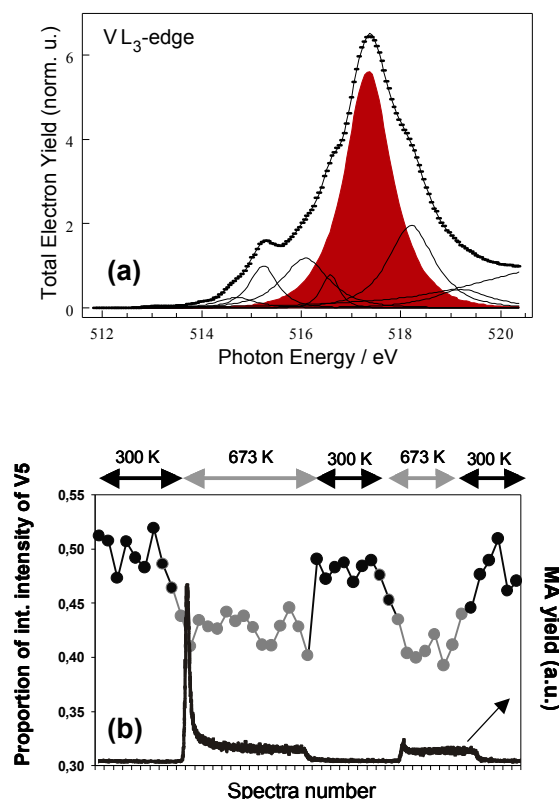

Figure 5: (a) Deconvoluted high resolution V L3 edge NEXAFS of VPP under working conditions (T = 673 K). **(b)** Variation in intensity of the resonance V5 (coloured in the top spectrum) during temperature cycling between 673 K and 523 K. Overlayed is the PTR-MS trace for MA (m/e = 99).

tematically with increasing MA yield and re-gained its initial value by changing the sample temperature from 673 K to 523 K. A possible temperature-only effect was excluded. The initial peak in the MA yield stems from the reaction of pre-adsorbed intermediates that were stored in/on the catalyst[25]. The V6 resonance showed the opposite trend, namely it became more intense with catalytic action and was reversibly reduced to its initial value upon switching off the reaction.

These changing intensities of two resonances indicate that only a fraction of the whole structure is directly involved in the catalytic action. The remaining features de-

scribe a "matrix" holding the active species in place during their operation. The intensity change could either mean a reaction-induced increase in specific V-O abundance, or indicate a change in electronic structure expressing itself in a reaction–induced cross section change for the relevant transitions. The fact that a shift of 100 meV in position follows exactly the intensity change is taken as proof that the electronic structure is changing and not the site density.

These signatures of an active site can be translated into the following chemical information. The V5 transition indicates a V-O-V structure element with a bond distance of ca. 172 pm, being untypical for the VPP structure, whereas the V6 resonance characterises a vanadyl group. The average oxidation state calibrated from the centre of gravity position of the whole resonance is compatible with a V^{4+} oxidation state of the active surface. The fact that during catalytic action strong intensity modulations but only small positional changes and no line splitting occur in the NEXAFS is a strong indication for the average maintenance of the electronic structure of the matrix, but for a local change of electronic structures in some V-O bonds of the surface material during catalytic action. The data show that on a time-averaged basis there is a re-hybridisation of electron density in some chemically active V-O bonds[66], that is, however, much less drastic than expressed by chemical interpretations[67;68] with redox couples $V^{4+/5+}$ or $V^{3+/4+}$. The signs of the intensity changes allow to conclude that during catalytic action the V-O-V bridge site gains d-electron density and the V=O site looses d-electron density as compared to their states without catalytic action. These modifications point to a local geometric displacement of the surface V-oxygen polyhedra with respect to the nominal bulk VPP geometry. A theoretical analysis that is currently underway will allow suggesting a geometric model of the V-O polyhedra under reaction conditions.

Conclusions

The results from sections 5 and 6 strongly suggest that under working conditions the catalyst surface contains a material with more oxygen and/or less integrated phosphorous groups than VPP. The average oxidation state of the probably binary oxide is V^{4+}, and the structure contains vanadyl groups. This is no contradiction to bulk structural chemistry (no vanadyl species in V_2O_4) as the material occurs only as surface phase[69]. In the absence of any knowledge of the real VPP surface termination it has to be stated that the predominance of pyrophosphate pockets at the active surface that was suggested in the literature[60;70] is not compelling in view of the massive excess of oxygen. Rafts of a binary oxide of which only a substructure (cluster) is active in the reaction, supported on VPP and held in a two dimensional state by phosphate growth inhibitors (such as in Ca carbonate growth inhibition or by destabilising the correct oxidation state and thus oxygen coordination of V-centres[35]) would represent one realisation of a metastable catalyst structure. Its formation requires destruction of the VPP material at the surface by hydrolysis that would require the energy provided by the reaction temperature and the time provided during the equilibration period. Amorphisation is

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clearly beneficial for this surface "restructuring"[24;55]. Mobility and desorption of the phosphate growth inhibitor limit the lifetime of the rafts ending up as inactive, e.g. $VOPO_4$, bulk species[71].

The significant confusion in the substantial body of literature [26] and the numerous controversies on selected aspects of the function of VPP may be seen as a consequence of erroneous conclusions following an early picture of a two-phase active state[72]. Despite of claims in the literature[8;52] there were no surface-sensitive *in situ* experiments available addressing the fundamental question about the termination of the VPP under working conditions. The present findings indicate that VPP is metastable under working conditions (enhanced liability by steam addition, milling defects or nanostructuring by preparative measures) and stabilises itself by surface phase segregation that is of limited long-range order. Thick layers of amorphous phases or three-dimensional segregations of $VOPO_4$ or binary oxides are inactive or detrimental[52] for the function. Metastable VPP is a valuable precursor as the kinetics of active phase formation termed "equilibration" is enhanced. Too reactive VPP is detrimental, however, as in this case the redox state of the system cannot be maintained in 20% oxygen.

The co-operation of several kinetic processes is required to explain the apparently confusing situation. A suggestion to unravel it is given in Figure 6. Removal of the crystal water of the hemihydrate precursor leads to a metastable situation with VPP and eventually some minority phases being formed during activation/equilibration. Water from the catalytic cycle drives the system in a surface phase-segregated state of a binary vanadium oxide that cannot crystallise into large crystals, as the growth inhibitor phosphate evaporates only very slowly. Excess oxygen oxidises the V_xO_y compound into V_2O_5 that reacts with phosphoric acid to $VOPO_4$ and opens a second channel besides evaporation to remove the growth inhibitor. This process chain leading to a thermodynamically stable situation for the solid contains with its surface intermediate V_xO_y the catalyst phase. It works according to the site isolation concept only in a two-dimensional form that is suitable to prevent deep oxidation to V_2O_5 and deep reduction to below V^{3+} compounds. As long as the V_xO_y stays two-dimensional it can catalyse the butane conversion. During this process it forms water and hence accelerates hydrolysis of phosphate. Liberating the growth inhibitor and consuming oxygen prevents its own deep oxidation.

This scenario of two coupled sequences of a chain process of solid state reactions and a cycle of catalytic operation is controlled in its kinetics and its thermodynamics by the temperature[54] and by the reactants, and there in particular by the oxygen partial pressure. This variable provides the driving force (together with the reductant butane) for the whole process and controls the rate of butane activation, the rate of formation of selective and total oxidation products, and hence the water partial pressure, the rate of hydrolysis of the VPP, and the oxygen stoichiometry in the surface phase, and therfore in turn the nature and the crystallisation kinetics of the products of VPP decomposition.

It is no surprise that kinetic measurements[73] find a high formal reaction order for oxygen that is not necessarily related to lattice oxygen diffusion. It is concluded that the characteristic timescales for all oxygen-controlled processes are similar giving rise to the convoluted experimental observations obtained with methods looking at certain parts of Figure 6 without showing the whole picture.

The failure to optimise the catalyst performance of VPP [15] lies in the neglect of the optimisation of the oxygen partial pressure taking into account its multiple function. As most studies use air as oxidant, they fix the working point of the kinetic network following from Figure 6 to one particu-
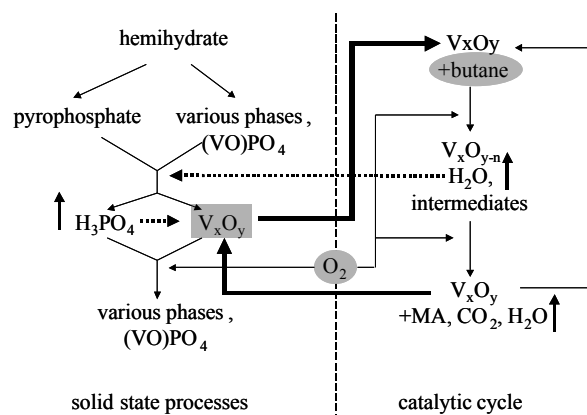

Figure 6: Schematic representation of the kinetic processes that determine the formation of the active catalyst phase from VPP. The dashed separation in solid state and catalytic regimes is artificial and supports only the explaination of the complex interrelations.

lar point that is further determined by the explosion limit of the air/butane mix. Addition of steam, operation in the explosion regime and application of other oxidants will each affect this working point and may thus produce significantly different performances of the system. Optimisation strategies need to take into account that they only work when the solid state kinetics of the catalyst is adjusted such that changing the oxygen partial pressure leads to immediate adaptation of all four interrelated processes named above.

Cluster structures of binary vanadium oxides with partially variable charge density stored in V=O and V-O-V bonding structures [74] should be the active sites with a similarity to such species on grafted vanadia catalysts used for selective oxidation reactions[75-77]. In addition, such clusters should be excellent models to study the selective oxidation reaction and would be much more appropriate than a hypothetical perfect basal plane of authentic VPP that should be an inactive material.

Acknowledgements

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