Variation of the vanadium oxidation state within a VPO catalyst layer in a membrane reactor: XPS mapping and modelling

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Abstract

Recently, the feasibility of butane oxidation in an electrochemical membrane reactor (EMR) using a vanadium phosphorus oxide (VPO) catalyst layer on a tubular anodic electrode has been reported. This novel application of EMR gives rise to questions about the vanadium oxidation state ($V_{ox}$) under working conditions and about its spatial distribution in the catalyst layer. It has now been determined by means of position-resolved XPS measurements. In addition, model calculations on the spatial $V_{ox}$ distribution have been performed for the first time. The simulations reveal a non-uniform 3D distribution of $V_{ox}$ due to the relative rate of reduction and re-oxidation processes in the catalyst layer, in good agreement with the experimental XPS data.

Keywords: VPO catalysts; Electrochemical membrane reactor; XPS; Modelling

1. Introduction

After discovery of their catalytic properties in 1966 [1], vanadium phosphorus oxides (VPOs) became exceptional catalysts, which actually dominate the industrial oxidation of $n$-butane to maleic anhydride (MA), an intermediate in the production of unsaturated polyester resins, maleic and fumaric acids, maleic copolymers and others [2,3]. Nowadays, three different industrial processes are used for the VPO-catalysed $n$-butane oxidation: the fixed bed, the fluidised bed and the recirculating solids process where oxidation of $n$-butane and regeneration of the catalyst are spatially separated [2–4]. Recently, the feasibility of butane oxidation in an electrochemical membrane reactor (EMR) using a VPO catalyst layer on a tubular anodic electrode (Fig. 1) has been reported [5,6]. Here, oxygen is reduced at the cathode and oxygen ions are transferred through an ion-conducting solid electrolyte membrane to the anode, where they can react with hydrocarbons.

Similarly to the fixed-bed reactor, the catalytic performance of the VPO catalyst in a membrane reactor depends on its morphology, its elemental composition and its redox properties. Despite the abundance of experimental studies by XRD, IR, UV–vis, XPS, NEXAFS, Raman and NMR spectroscopies, a wide range of opinions about existence and role of various VPO phases such as $(\text{VO})_2\text{P}_2\text{O}_7$ ($V^{4+}$ species) or VOPO$_4$ ($V^{5+}$ species) is found in literature. Recent publications stress the importance of the presence of both $V^{5+}$ and $V^{4+}$ in the active catalyst, whereas the concepts regarding the prime role of particular species in the catalytic process itself differ [7–9].

In our opinion, the diversity of assumptions supported by various experimental facts has its main origin in the distribution of the catalytically active species in a thin surface layer (<5 nm). Different techniques exploit different information depths which depend, in turn, on the physical properties of the probing particles: electrons of different energies, X-ray and IR photons, etc. In addition, as shown recently, the ex situ studies in UHV do not always reflect the real state and the composition of the VPO samples because of self-reduction in UHV and X-ray induced damage [10,11]. Thus, measurements performed under real reaction conditions, such as the recently developed in situ NEXAFS and XPS techniques [12,13], could contribute

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Fig. 1. Schematic view of the tubular EMR. During the EMR operation, butane (diluted in N₂) is fed to the outer side at the reactor entrance while the oxygen is fed across the oxygen-ion-conducting solid electrolyte membrane (see cut along A–A’).

essentially to a better understanding of these catalysts. However, despite promising first results, even these novel approaches and especially in situ XPS are difficult to apply under the varying reaction conditions which lead naturally to changes of the X-ray intensity and, consequently, to a varying sample charging [14]. In addition, the (pressure-dependent) scattering of emitted photoelectrons by gas phase molecules modifies the shape of the spectrum background and changes the transmission of the spectrometer.

In the case of a membrane reactor, already the peculiarities of the EMR construction hinder the application of in situ methods: the studied object consists of a few hundred micrometer thin catalyst layer that experiences strongly different conditions at its outer side (butane-contacting) and its inner side which is in mechanical contact with the solid-state electrolyte serving as an oxygen reservoir. On the other hand, this gradient of the conditions is expected to create a highly inhomogeneous distribution of the catalytically active species across the VPO layer. If one succeeds in the conservation of this gradient, e.g., with an inert medium immediately after reaction, it can be studied in conventional ex situ XPS, especially by using a “fast-transfer” mode [10].

In our first attempts to detect reaction-induced variations of the vanadium oxidation state in EMR, indeed significant differences in the distribution of V⁵⁺ and V⁴⁺ species on the inner and outer sides of the tubular VPO layer were observed [15]. In addition, these first measurements revealed deviations from a uniform average vanadium oxidation state (V_{av}) distribution along the reactor coordinate that is along the reactor tube. In the present contribution, we extend our earlier XPS investigation to the mapping of the radial as well as azimuthal distributions, creating thus a 3D picture of V_{av} in the VPO layer. We improved significantly the performance of our XPS apparatus by using monochromatic X-ray excitation, and will also present the first model calculations of the spatial distribution of the vanadium oxidation state, as well as comparison to XPS data.

2. Experimental

The precursor for the VPO catalyst was prepared from V₂O₅ and H₃PO₄ with isobutanol by the one-step organic synthesis route published by Johnson et al. [16], and described in detail in Ref. [6]. The three-step conversion of the precursor material VOHPO₄·0.5H₂O to activated VPO was performed by treatment in nitrogen at 823 K for about 40 h, calcination in air at 673 K for 1 h and subsequent activation in a laboratory microreactor with 1.0 vol% butane in air at 673 K for 2 h. Before and after operation in EMR, the VPO samples were characterised by the BET surface area measurements, X-ray diffraction and conductivity measurements [15]. For the XPS analysis, the VPO samples were collected from the membrane surface under dry nitrogen atmosphere in a glove box, fixed to the sample holder (see below), and transferred under nitrogen to a multipurpose UHV surface analysis apparatus (SPECS). A possible vacuum-induced reduction of the VPO samples was minimized by fast sample transfer times of less than 5 min between the start of the evacuation of the load lock and the first XPS spectrum at a pressure less than 5 × 10⁻⁹ mbar [10]. As already mentioned, a monochromatic X-ray source (FOCUS-500, SPECS, excitation energy 1253.64 eV, Al Kα, line-width < 0.3 eV) was used in the present study providing the dual benefit of enhanced energy resolution due to the narrow excitation line and of low background contribution. Both factors are especially important in the case of vanadium oxides due to the known problems with the unknown background contribution and uncertainties with multiplet splittings, as will be discussed in more detail below. The X-ray source was used in a “stop-and-go” mode in order to reduce possible damage due to sample irradiation. High-resolution spectra (pass energy 10 eV, step size 0.1–0.2 eV) were recorded at room temperature with a hemispherical energy analyzer (PHOIBOS-150, SPECS), which provides the possibility of simultaneous photoelectron detection on nine channels, and allows fast data acquisition times (0.5 s per data point) with a satisfactory signal-to-noise ratio.

Particular care was directed towards the minimization of differential charging of the VPO powder probes, since this effect, which causes the dispersion of the individual XPS-peaks (and may lead to apparent V⁵⁺ contributions with n ≤ 3), can hardly be reduced by commonly used techniques as flood-gun application [17]. In the present study, the VPO motes were compression-moulded as an almost optically dense “powder monolayer” on a thin indium foil which was pressed on a molybdenum sample holder. Those regions of the In foil between the moulded VPO particles and directly accessible by the X-rays functioned as local photoelectron sources, i.e., a kind of “embedded flood-guns”. Locally enhanced electrostatic
fields over the protruding VPO particles distribute the photomitted electrons in a self-regulating way that the charged particles are to a large extent neutralized. No additional charge compensation was used in the present experiments. This sample preparation allowed us to achieve a FWHM of less than 1.3 eV for the V 2p3/2 peak of the V2O5 powder reference, a value comparable to that measured in the synchrotron-based experiments for nm-thin V2O5 layers on metal substrates [18]. The binding energies reported here are referenced to the carbon impurities (C 1s peak at 284.5 eV), which could always be found in the VPO catalyst.

In order to determine the spatial distribution of the vanadium oxidation states in the catalytic VPO layer in EMR, position-resolved XPS measurements were carried out. For this purpose, several catalyst samples were taken along the axial reactor coordinate. In order to investigate the radial distribution of oxidation states, the outer side of the VPO layer was carefully mechanically ablated and XPS measurements were performed after each ablating procedure. The same has been done for the inner side of the catalyst layer.

3. Results and discussion

3.1. Distribution of the vanadium oxidation states in the VPO layer: XPS results

The evaluation of the vanadium oxidation state in the vanadium-containing catalysts still remains a challenge for XPS, since despite of intensive studies even the interpretation of the XPS spectra of reference compounds, namely various stoichiometric oxides, is still under discussion [19–22]. The main problem results from the multiplet splitting caused by lifting of degeneracy of the sublevels in the 2p component due to interaction of the core-holes created by the photoemission process with the valence-holes due to partial filling [23]. This leads to different lineshapes of the V5+, 4+, 3+, 2+ components and makes it very difficult to develop a set of fitting parameters for each valence state. Fortunately, the changes in the lineshapes do not influence the first momenta of the O 1s and V 2p3/2 peaks, which allowed Coulston et al. to elaborate a criterion independent of particular lineshapes [24]. This criterion for the average vanadium oxidation state (Vox) is based on the difference of the first momenta of the O 1s and V 2p3/2 peaks, and is independent of peak broadening since this does not change the position of the centroids. Unfortunately, in the case of the VPO catalysts used, the position of the O 1s peak may be strongly influenced by potential adsorbates. Other alternatives such as the difference spectrum method which subtracts the “known” spectrum of a standard compound from the data of the studied material [25] provides at present no real advantage in comparison to the peak fitting procedure.

The problems listed above led to the controversial values for V5+, 4+, 3+ contributions which are reported in literature [26]. We note that a lot of published data for the V 2p3/2 peak are referenced not to the C 1s but to the O 1s peak, for which an energy of 530 eV is usually taken to be fixed [26]. The position of the O 1s peak is, however, known to vary strongly for the VPO compounds, and to be a function of the experimental conditions (e.g., temperature-dependent variations up to a few electron volt are reported [27]).

In the present work, we used the peak deconvolution procedure where VOPO₄ (oxidation state, +5) with phase structure confirmed by XRD provided the reference value for the binding energy of the V 2p3/2 peak. The measured V 2p3/2 peak (FWHM < 1.3 eV) could be well fitted with a single Gaussian with a maximum at 518 eV, in good agreement with literature data [26,28,29]. The position of the V4+ component obtained independently lies at 516.9 eV [10,15], well separated from the V5+ contribution. V3+ contributions, which would be shifted to lower energies and would exhibit a bigger FWHM than the V4+ peak, thus creating an asymmetric low energy shoulder, were not observed.

Fig. 2a shows a high-resolution XPS spectrum containing the O 1s, V 2p1/2 and V 2p3/2 photoelectron peaks for a fresh, activated VPO sample. The deconvolution of the V 2p3/2 peak shown in the insert yields 76% and 24% for the V5+ and V4+ contributions, respectively, revealing a formal effective vanadium oxidation state of 4.76 for this sample. This value

![Fig. 2. High-resolution XPS spectra obtained with monochromatic Al Kα (1486.74 eV) excitation. (a) O 1s, V 2p1/2 and V 2p3/2 photoelectron peaks for a fresh VPO sample. (b) The same for the sample locally used extracted from the catalytic layer of the EMR.](image-url)
is only marginally lower than our previous result (4.82 [10]) obtained with a non-monochromatic Mg Kα source (possibly due to a slightly different information depth) but again significantly higher than those previously reported in literature (due to a slightly different information depth) but again time scale under the reducing UHV conditions.

Most of the published data were presumably collected on this allowed us to construct a 3D map of the V resolution (see above). These position-resolved measurements allowed us to construct a 3D map of the V⁴⁺ species in the VPO layer. The corresponding results are summarized in Fig. 3a, where the effective oxidation state along the reactor coordinate z (axial distribution) as well as along the coordinate r across the VPO layer (radial distribution) is plotted. The graph shows a remarkable reaction-induced variation in V₂ox across the VPO layer as well as slight variations of the oxidation state in the axial direction along the reactor coordinate. Only negligible deviations of the oxidation state in the azimuthal distribution were observed, as expected for cylindrical geometry. The lowest oxidation state (4.5) is measured for the outer sample surface, facing the anodic gas compartment, the highest (4.85) for the inner (electrolyte membrane) side. The latter is comparable to the initial oxidation state of the fresh catalyst. It can also not be excluded that the contribution of the V⁴⁺ phase in the catalytically active topmost layer on the outer side is even somewhat higher than deduced from our XPS experiments, because the XPS data average over the attenuation length of the emitted photoelectrons (2.5 nm in the present case). This would be in agreement with recent XPS results obtained in situ during n-butane conversion over VPO, which show significant deviations in the surface composition as compared to the bulk [32]. It should be noted that no V⁵⁺ formation in the VPO layer used has been observed in our experiments. Apparently the V⁴⁺ phase formed during the EMR operation is stable under the reducing conditions, as was also observed for other reactor types [33]. This suggests the presence of the crystalline (VO)₂P₂O₇ phase in the reaction-equilibrated VPO layer which is known to be stable against changes from reaction temperature to room temperature.

3.2. Model simulation

Recently, a reactor model realistically describing the conversion and selectivity behaviour of the EMR under varying steady-state operation conditions was developed [34]. The model contains balance equations for all gas phase components and the local catalyst oxidation state as well as electrochemical relations for the local oxygen feed to the catalytic layer. Temperature gradients across the catalytic layer can be neglected as shown in Ref. [34]. In the present work, we apply this model to explain the experimentally observed spatial V₂ox distribution within the catalytic layer.

Taking the cylindrical symmetry of the EMR used into account, a 2D description is sufficient for the evaluation of the local concentration distributions within the VPO layer. For geometrical reasons (layer thickness ≪ reactor length) mass transport within the catalytic layer occurs preferably in radial direction. Thus, the balance equations for all gas phase species (C₄H₁₀, MA, CO, and O₂) reduce to 1D differential equations in radial direction and overall a 1D + 1D model for the VPO layer is obtained. The VPO oxidation state is included in the model as dimensionless oxygen loading of the catalyst lattice where ξ = 1.0 refers to the maximum oxygen load (equivalent to V⁴⁺) and ξ = 0 to the minimal stable oxygen content to which the catalyst might be reduced under reaction conditions in EMR. Additionally, adsorbed surface oxygen species are considered and transport of oxygen via surface diffusion on the catalyst surface is included in the model, besides the gas phase diffusion.

In the reactor gas channels, plug flow without axial dispersion is assumed. Further assumptions are ideal gas phase behaviour and isobaric conditions.

Fig. 3. Spatial distribution of the vanadium oxidation state in a VPO layer after operation in a tubular EMR: (a) laterally resolved XPS measurements; (b) simulation results for typical EMR operation conditions (understoichiometric oxygen feed and moderate butane conversion of 15%). The direct electrochemical re-oxidation of VPO is neglected and a high diffusion resistance is assumed; (c) the same as in (b) but with the full kinetic scheme and fast diffusion. The meaning of the reactor coordinates r and z as well as of the dimensionless oxygen loading of the catalyst lattice ξ is explained in text.
To describe the mechanism of reactions taking place within the catalytic layer a simple reaction scheme found in literature [35] was adopted with the main reaction steps being oxygen adsorption and catalyst oxidation:

\[
\begin{align*}
O_2 + 2(S) & \leftrightarrow 2O(S) \quad (1) \\
O(S) + (L) & \leftrightarrow O(L) + (S) \quad (2)
\end{align*}
\]

as well as catalyst reduction or butane oxidation, respectively:

\[
\begin{align*}
C_4H_{10}O + O(L) & \rightarrow C_2H_2O_3 + 4H_2O + (L) \quad (3) \\
C_4H_{10}O + O(S) & \rightarrow 4CO_2 + 5H_2O + (S) \quad (4) \\
C_4H_2O_3 + O(S) & \rightarrow 4CO_2 + H_2O + (S) \quad (5)
\end{align*}
\]

Here, (S) and (L) denote the surface and the lattice sites, respectively. Under steady-state conditions, catalyst reduction and re-oxidation rates are balanced, and a Mars-van Krevelen type reaction mechanism is assumed.

Mixed oxide catalysts in contact with a solid electrolyte membrane and an electrically conducting electrode can possibly be directly electrochemically re-oxidized. Lintz [36] used this effect in (solid electrolyte potentiometry aided) catalytic studies. Correspondingly, the following catalyst re-oxidation reaction was added to the kinetic model:

\[
O^{2-} + (S) \leftrightarrow O(S) + 2e^- \quad (6)
\]

which possibly takes place at the interface between the Au electrode and the VPO layer (Fig. 1). In addition, oxygen ions transported through the solid electrolyte membrane, as described above, can combine to form gaseous oxygen at the anode:

\[
2O^{2-} \leftrightarrow O_2 + 4e^- \quad (7)
\]

Both reactions (6) and (7) are described by rate expressions of Butler-Volmer type. Further details of the calculations will be published elsewhere [34].

The described model can be used to simulate the distribution of gas phase concentrations and catalyst oxygen loadings under the applied experimental conditions. Two cases are investigated: (i) the direct electrochemical re-oxidation of VPO according to reaction (6) is neglected and the influence of radial diffusion is studied and (ii) the full kinetic scheme is considered and the effect of reaction (6) is taken into account.

In the first case simulations reveal significant diffusion resistances in the VPO layer, a concentration distribution of gas phase components with the lowest value of the oxygen-to-butane ratio on the outer VPO surface \((r = 1)\) at the reactor entrance \((z = 0)\), while the highest value is located on the inner VPO surface \((r = 0)\) at the reactor outlet \((z = 1)\). The resulting \(V_{ox}\) distribution (Fig. 3b) is determined by the relative rate of the reduction and re-oxidation processes, and is therefore directly related to the local oxygen-to-butane ratio distribution. A high diffusion resistance means that conversion is limited by diffusion which arises when the intrinsic reaction rates are fast compared to the diffusion rates, \(e.g.,\) due to a low voids fraction of the catalyst layer and resulting low effective diffusion coefficients.

In the second case even for fast diffusion and thus negligible radial concentration gradients of the gas phase components and the local oxygen-to-butane ratio a \(V_{ox}\) distribution as experimentally observed is obtained in the simulation (Fig. 3c). Here, the direct electrochemical re-oxidation according to reaction (7) leads to filling of catalyst lattice oxygen sites at the VPO–Au interface. Due to low surface diffusion rates, a steep radial gradient of the catalyst lattice oxygen concentration is obtained close to the VPO–Au interface while away from the interface the lattice concentration is determined by the balance of reactions (1)–(5) as in the first case.

In both cases, the convex shape of the radial \(V_{ox}\) distribution as well as the axial \(V_{ox}\) distribution on the outer side correlate well with the experimental results. On the inner side of the VPO layer, non-uniformity of the oxygen-ion supply may be the reason for the experimentally observed deviation of the axial \(V_{ox}\) distribution from that predicted in the model calculations. In order to differentiate two possible explanations of the observed \(V_{ox}\) distribution or to prove evidently one of them, further experiments are needed. Using the same reactor design and catalyst, but only operating the reactor in the co-feed mode where butane and oxygen are fed premixed at the reactor entrance, would give information on the quantitative contribution of the direct electrochemical VPO re-oxidation. Using thicker catalyst layers, in turn, might validate the influence of diffusion resistances.

4. Conclusions

Summarizing, the experimental XPS results, which reveal a non-uniform 3D distribution of the vanadium oxidation state within a VPO catalyst layer in a membrane reactor are realistically described by a model based on the spatial distributions of the reactants during the reactor operation. The observed variations of \(V_{ox}\) in the VPO layer reflect the resulting steady-state of the system and should be taken into account in predicting the reactor performance in possible technological applications.

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