



XPS investigations of VPO catalysts under reaction conditions

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Abstract

The surface of vanadium phosphorus oxide (VPO) catalysts was investigated by (in situ) X-ray photoelectron spectroscopy (XPS) under reaction conditions. Two differently prepared VPO samples with similar catalytic activities showed different spectral behaviour while the catalytic conditions were changed. The vanadium surface oxidation state of both catalysts was found to have the same value close to 4 under reaction conditions, while the oxidation state of vanadium in deeper layers differed significantly. The experimental results suggest that in VPO the catalytically active species located in the topmost surface layers (up to 1 nm depth) are only weakly related to the structure of deeper layers. Based on our results we suggest that the deeper layers act as a substrate material only and can be different from the surface.

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1. Introduction

For the last three decades vanadium phosphorous oxides (VPO) have been the only catalysts

that were used for the industrial production of maleic anhydride (MA) from *n*-butane. These catalysts have been a subject of numerous studies since their invention. The complexity of the chemical reaction and the multiphase composition of the catalyst, however, still leave open questions about the nature of the active surface and the reaction mechanism. Different models of the active phase were presented in the literature [1–8]. Some authors suggest a V⁴⁺ phase to be catalytically

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active and the presence of V^{5+} phases to be detrimental for the catalytic performance. Others in the contrary stating the positive role of the V^{5+} and the negative one of the V^{4+} phases.

It is generally accepted that well crystallized $(VO)_2P_2O_7$ (which is a V^{4+} phase) is the major phase that is present in an industrial VPO catalyst after long operation time. Several groups suggested that the (100) crystal plane of $(VO)_2P_2O_7$ is the catalytically most active VPO surface while other VPO phases are thought to be much less catalytically active or even detrimental for the catalytic activity of the sample [1–3]. Other investigations, however, indicate the participation of V^{5+} species in the form of $VOPO_4$ phases, dispersed on the surface V^{4+}/V^{5+} couples or surface and bulk crystalline defects in the catalytic process [4–7]. In Refs. [4–7] the importance of the presence of both V^{4+} and V^{5+} in active catalysts is stressed. Furthermore, Coulston et al. [8] argued about the central role of V^{5+} in the reaction and the responsibility of V^{4+} for by-product formation. Such a wide range of opinions supported by experimental facts might well be explained by the location of the active material in the topmost (1–2 nm) surface layer, which can hardly be investigated by XRD, Raman, NMR and V K-edge XAS used in the works mentioned above. The participation of the first four layers in the gas-lattice oxygen exchange during the reaction was concluded from studies based on ^{18}O isotopic labeling experiments [9]. Recent TEM investigations showed the existence of a thin (about 1 nm) amorphous layer on top of $(VO)_2P_2O_7$ for VPO catalysts [10]. Some other observations [7,11,12] could be viewed as indirect prove for the presence of a thin active layer on top of a bulk phase. Bulk VPO and VPO supported on SiO_2 substrate were found to have equal catalytic properties [11]. The supported VPO, however, had an amorphous nature, while the bulk VPO was crystalline. Furthermore, a completely amorphous VPO catalyst was synthesized using supercritical CO_2 [12]. For this catalyst no activation time was necessary to reach full catalytic performance. In addition, no crystallization of the material was observed during the reaction, which is in contradiction to modern methods of industrial catalyst preparation. Earlier observations [7]

of similar intrinsic activity to MA (i.e. activity divided by the surface area) for catalysts prepared by different methods and having different bulk phase compositions also indicate that bulk and surface layers do not necessarily consist of the same phases.

The goal of our study is to investigate the relationship between catalytic activity of an VPO catalyst and its bulk and surface composition under reaction conditions. If the active layer is found to have indeed a different structure than the bulk, this could be an important finding for the improvement of the performance of VPO catalysts. While the modern preparation methods are designed to produce catalysts with a $(VO)_2P_2O_7$ bulk phase, it might be more important to optimize the preparation process towards the formation of an active surface layer. The long activation time of the industrial catalyst could be related to structural rearrangement and a water desorption process, which disturb the active layer. A substrate different from $(VO)_2P_2O_7$ can be chosen for the active layer. A new substrate may cause a decrease of the activation time and an improvement of catalytic performance [13]. Therefore the investigation of the nature of the surface layer and its interaction with deeper layers are extremely important. As it was demonstrated by our previous in situ XAS studies, the VPO surface electronic structure is very sensitive to the reaction conditions [14,15]. In this work we report the first observation of the active VPO catalyst surface by XPS under reaction conditions.

2. Experimental

2.1. Sample preparation and characterization

Two VPO samples (called VPO_{P4} and VPO_{P9} in the following) were prepared and characterized as described in detail in [16]. (The sample annotation is the same as in Ref. [16].) The precursor for VPO_{P9} was prepared from V_2O_4 , H_3PO_4 and water. The mixture was heated in an autoclave (145 °C, 72 h), then washed with cold water and dried in air (120 °C, 16 h). The VPO_{P4} precursor was prepared using V_2O_5 , $H_4P_2O_7$, H_3PO_3 and water in the same way like VPO_{P9} , with a subse-

quent reflux in water for 2 h. The activation was performed in a laboratory microreactor in a mixture of 1.7% *n*-butane in air at 400 °C.

For the in situ XPS measurements the catalyst powder (50 mg) after the test of catalytic performance was pressed into pellets with a diameter of 13 mm, using a pressure of 10 MPa. During the XPS experiments the catalytic activity of the samples towards MA was measured using proton transfer reaction mass spectrometry (PTRMS) at outlet of the gas flow through the experimental chamber.

2.2. Experimental conditions

The samples were investigated in a constant gas flow. The mixture of 1.5% *n*-butane in He (partial pressure 1.6 mbar) and oxygen (partial pressure 0.4 mbar) had a total pressure of 2 mbar in the reaction cell. Spectroscopic measurements were done at temperatures of 150–200 °C, where the MA yield was negligible, and at 400 °C, which is the usual reaction temperature. Additionally the catalysts were reduced in the absence of oxygen (in 1.6 mbar of 1.5% *n*-butane in He) at 400 °C.

2.3. In situ XPS

The experiments were performed at beamline U49/2-PGM1 at the synchrotron source BESSY-II in Berlin [17]. The in situ XPS system is a modified standard XPS spectrometer [18]. Three differential pumping stages keep the hemispherical analyzer at high vacuum while the pressure in the sample cell is in the mbar range. The reaction cell is separated from the synchrotron beam line by a 100 nm thick SiN_x X-ray window. The main limiting factor for the maximum pressure in the reaction chamber is the scattering of photoelectrons by gas molecules. The pressure limit in our experiments was estimated to be approximately 2 mbar for the reaction gas mixture. At this pressure it is still possible to get spectra with good signal to noise ratio. A discussion of the general principles of an in situ XPS system can be found in [19]. The overall spectral resolution of the system was evaluated from a measurement of the Ar 2p_{3/2} gas phase peak and found to be better than 0.3 eV at

a photon energy of 700 eV. We have recorded the O 1s/V 2p, C 1s, P 2p and valence band regions in our experiments. The incident photon energy was varied such that the kinetic energy of the photoelectrons was constant for all recorded XPS regions, thus providing for a uniform information depth, a constant analyzer transmission function contribution as well as a constant gas phase scattering contribution. In addition we have performed depth-profiling by varying the excitation photon energy applied to the same core-level, which leads to a change of the photoelectron kinetic energy, and as a consequence to a change in the information depth. The values for the excitation energies and corresponding information depths taken from the “universal curve” [20] are presented in Table 1.

3. Results and discussion

3.1. Sample activity during spectroscopic measurements

The catalytic reactivity (Fig. 1) was measured using PTRMS. Protonated MA molecules produce a signal at *m/e* = 99 amu/e. The mass spectra were recorded simultaneously with the XPS measurements, which allowed us to correlate the XPS results with the catalytic activity of the material. No significant increase in the MA signal was observed after heating the samples to 150 or 200 °C (Fig. 1a and b). Therefore, the samples can be considered as practically inactive under these conditions. The XPS measurements of the inactive surface were performed at 150–200 °C (and not

Table 1
Excitation energy and information depth

Photoelectron kinetic energy, eV	Excitation energy, eV		Information depth [20], nm
	O 1s–V 2p	P 2p	
200	730	335	1
720	1254 ^a	854	3

^a The 1254 eV photon energy corresponds to MgK_α line, which is in common use in laboratory XPS systems for chemical analysis (ESCA).

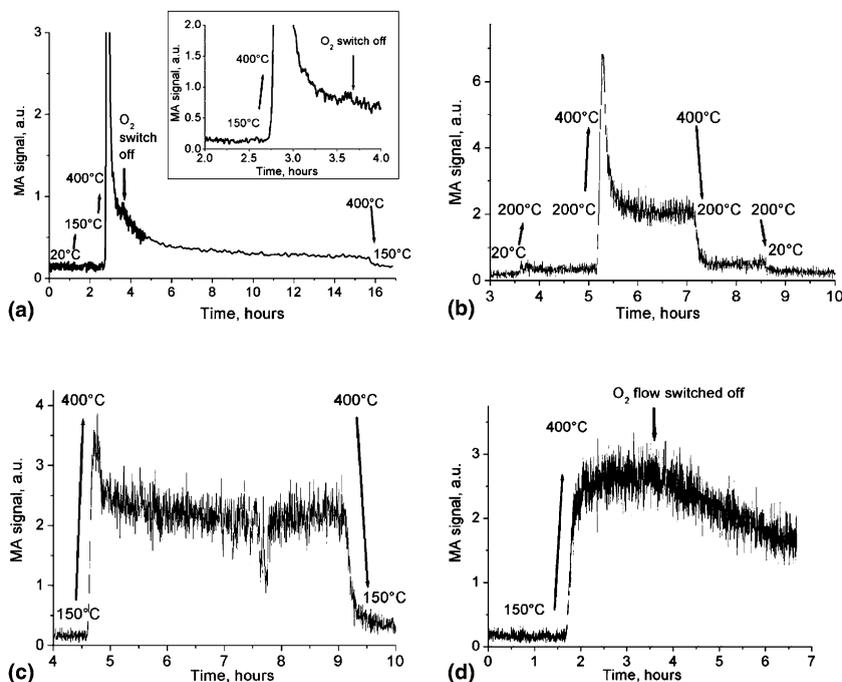


Fig. 1. Catalytic reactivity towards MA registered by PTRMS (signal on $m/e = 99$ amu/e). (a) VPO_{P9} in reaction mixture and in *n*-butane/He atmosphere, (b) VPO_{P4} in reaction mixture—first heating, (c) second heating, (d) third heating and in *n*-butane/He atmosphere.

at room temperature) because it was found that at 200 °C differential charging effects are reduced [14].

When the samples were heated to 400 °C with 20 °C/min heating ramp (Fig. 1a and b), a peak in the MA signal followed by a decrease to a constant MA signal level after less than 1 h was observed. It can be clearly seen that MA could be detected for both catalysts at 400 °C and practically no MA was detectable after cooling down to temperatures lower than 200 °C. The temperature was cycled three times between 150–200 °C and 400 °C for the VPO_{P4} sample (see Fig. 1b–d). The steady-state level of the MA yield at 400 °C was found to be the same in all three cycles, which indicates that the MA is a product of the catalytic process and not an artefact from an unsteady-state process. The amplitude of the initial peak of the PTRMS MA signal significantly decreased during the second heating cycle (see Fig. 1b), and no peak was visible during the third cycle (Fig. 1c). The behaviour of this peak clearly shows

that it is caused by the desorption of MA that was produced in the prior activation of the catalyst in a microreactor, before our XPS experiments. The same behaviour was observed in our previous experiments [14]. The absence of the desorption peak during the third heating cycle does not indicate the absence of adsorbed MA molecules but rather the lack of sensitivity of our system to register the desorption of the small amount of MA attached to the surface at the low-pressure conditions. The observed steady-state MA yield in the reaction gas mixture at 400 °C was 2.6 times higher for VPO_{P4} compared to VPO_{P9}. After normalisation to the BET surface area (23 and 11 m²g⁻¹ for VPO_{P4} and VPO_{P9}, respectively) the ratio of the normalized yields is 1.2, which indicates that both samples have nearly the same intrinsic activity to MA. The reduction of the samples in a *n*-butane/He atmosphere (see Fig. 1a and d) led to a significantly different deactivation time behaviour. A fit of the MA yield versus time in *n*-butane/He with a first order exponential decay

function gave time constants of 6.4 and 0.9 h for VPO_{P4} and VPO_{P9} , respectively. Such a different response on reducing conditions can mean a different composition of a bulk material of the catalysts while the same intrinsic activity suggests the same nature of active surface. This hypothesis will be supported below by spectroscopic data.

3.2. XPS data

The $V2p_{3/2}$ XPS peak was used to follow the changes in the vanadium oxidation state under the different experimental conditions. A Shirley-type background was subtracted. The energy scale was calibrated by assuming a BE of 530 eV for the O 1s peak, which is the value found in the literature for vanadium oxides [21]. At room temperature a strong distortion of the peak shape was found due to differential charging. To minimize the charging effect we increased the sample temperature to 150–200 °C as was discussed before.

Fig. 2 shows $V2p_{3/2}$ spectra of sample VPO_{P4} for two different incident photon energies: 860 eV (top) with an information depth of about 1 nm,

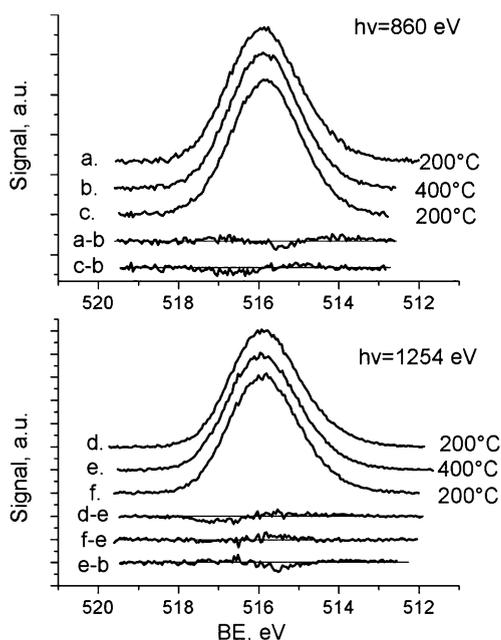


Fig. 2. $V2p_{3/2}$ spectra of VPO_{P4} in heating-cooling experiment. (a)–(c) $h\nu = 860$ eV, (d)–(f) $h\nu = 1254$ eV.

and 1254 eV (bottom) with an information depth of about 3 nm. (We will in the following refer to the 860 eV spectra as “surface”, and the 1254 eV spectra as “bulk” spectra.) In each case $V2p_{3/2}$ spectra were taken at 200 °C, then at 400 °C, and at the end of the experiment again at 200 °C in the reaction mixture. Fig. 2 shows also the difference spectra between 400 °C and 200 °C data for each incident photon energy. One has to be careful when evaluating the difference spectra, since they are influenced by such factors as charging effects and BE shifts [22]. They are, however, useful to get an impression about qualitative changes in the spectra. The difference spectra in Fig. 2 show only small features with amplitudes on the order of the noise level, which implies that within the uncertainty of our experiments no changes are observed in the spectra. This leads us to the conclusions that the vanadium oxidation state in the VPO_{P4} sample is uniform with depth and does not change with temperature.

For the VPO_{P9} sample a different behaviour was observed. Fig. 3 shows $V2p_{3/2}$ spectra of VPO_{P9} with the more surface-sensitive spectra displayed in the top part of the figure and the more bulk sensitive spectra in the bottom part. Sample VPO_{P9} shows strong changes of the vanadium oxidation state with temperature. A peak at 517 eV is clearly visible in the 400–150 °C difference spectra for both bulk and surface sensitive measurements. This peak has a BE difference of about –13 eV relative to O 1s, which is a typical value for V^{5+} species [23].

Fig. 4 shows a comparison of the spectra taken under reaction conditions (400 °C) for the two different samples. Also shown in Fig. 4 are the differences between the bulk spectra and the surface spectra of the two samples. It is obvious from a comparison of the spectra of the two catalysts at 400 °C in the reaction mixture that the oxidation state of the surface is more similar than that of the bulk.

The exact determination of the oxidation state is quite complicated. The usual approach to fit a spectrum with several peaks [24], each representing a unique oxidation state, is based on the knowledge of the line shape and the BE position of the peaks for each oxidation state, which is often

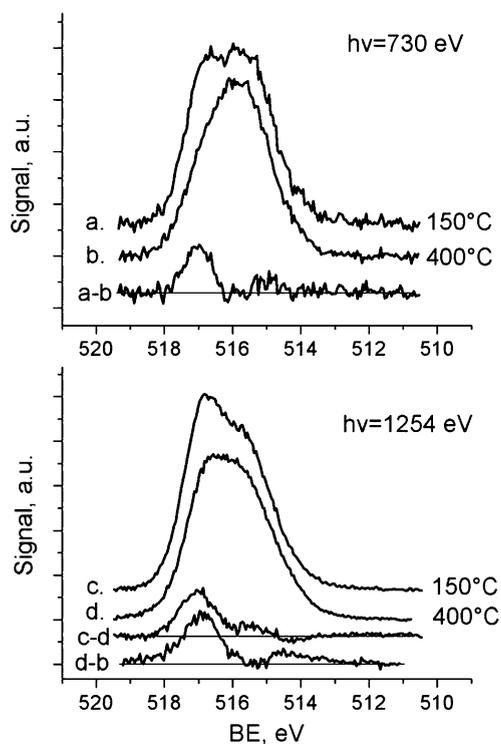


Fig. 3. $V2p_{3/2}$ spectra of VPO_{P9} before and after heating in reaction mixture. (a) and (b) $h\nu = 730$ eV, (c) and (d) $h\nu = 1254$ eV.

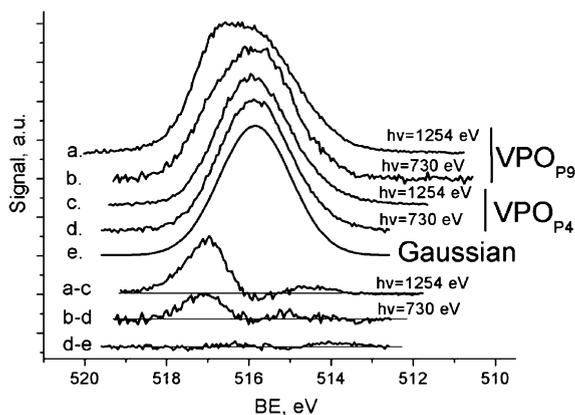


Fig. 4. Comparison of $V2p_{3/2}$ peaks of VPO_{P4} and VPO_{P9} at reaction conditions. (a) and (b) VPO_{P9} , (c) and (d) VPO_{P4} , (e) Gaussian.

difficult to determine experimentally. A wide range of $V2p_{3/2}$ BEs for VPO is reported in the literature

(see Table 1 in Ref. [25]), which makes this fit procedure complicated. Another method to determine the oxidation state was suggested by Coulston et al. [26] This procedure is based on the BE difference between the first momenta of the $O1s$ and $V2p_{3/2}$ peaks. However, the authors mentioned that the results depend on the presence of adsorbates, which distort the overall $O1s$ peak shape.

The shape of the surface $V2p_{3/2}$ peak of VPO_{P4} , (spectrum d in Fig. 4) under reaction conditions can be fit with a single Gaussian. We can therefore conclude that the surface of VPO_{P4} has an oxidation state equal to 4 within the error of our measurement. A small amount of V^{5+} is present in the VPO_{P9} surface spectrum. This V^{5+} species can be related to deeper layers below the surface, since photoelectrons escape from an infinite range of depth with exponentially decreasing probability and therefore the information depth value represents only a mean free path of photoelectrons. Thus it can be deduced that a surface layer with a thickness of about 1 nm for both catalysts has the same oxidation state at the reaction conditions. Taking into account nearly the same intrinsic catalytic performance of the catalysts this leads us to the conclusion that only this layer participates directly in the catalytic cycle while deeper layers (which show quite different XPS spectra for the two samples) act only as a substrate. This conclusion is in agreement with literature data [7,10–12], which suggest that the active surface layer has a different composition than the bulk.

The stability of the active layer was investigated by reducing it in an *n*-butane/He atmosphere. It is clearly visible in Fig. 5 that the VPO_{P9} surface responds much more dynamically to the reducing conditions compared to VPO_{P4} . The MA yield for VPO_{P9} also decreases much faster (see Fig. 1a and d). There could be two reasons for the different response of the two samples to the changing conditions: either differences in the properties of the active layer, or a different interaction with deeper layers (substrate). The latter one is more probable since the oxidation state of the two surfaces was the same for both catalysts under reaction conditions, which suggests the same nature of the surface layer for both catalysts. This implies that the oxygen transport from the substrate to the sur-

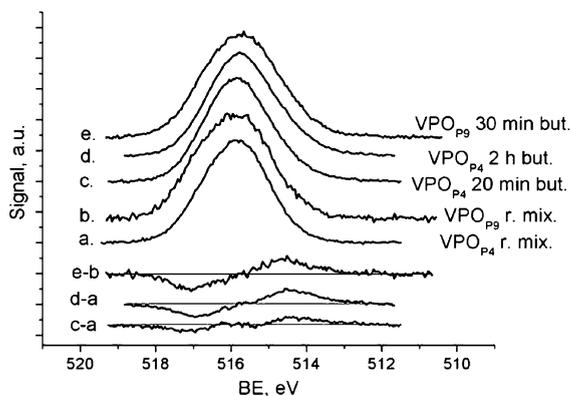


Fig. 5. Changes of surface $V2p_{3/2}$ spectra in *n*-butane at 400 °C. (a) VPO_{P4} in reaction mixture, (b) VPO_{P9} in reaction mixture, (c) VPO_{P4} after 20 min in *n*-butane, (d) VPO_{P4} after 2 h in *n*-butane, (e) VPO_{P9} after 30 min in *n*-butane.

face is higher for VPO_{P4} compared to VPO_{P9} . This obviously does not influence significantly the catalytic performance of the active layer in co-feed of oxygen and *n*-butane, but apparently makes sample VPO_{P4} more stable with respect to conditions changes.

3.3. P/V ratios

The P/V ratio is often considered an important factor for the catalytic properties of VPO [27]. This argument is based mainly on XPS experiments where a phosphorous enrichment at the surface was found. As was reported in [26] the absolute P/V ratio value depends strongly on the assumptions made about the sensitivity factors. The most widely used theoretically calculated photoionisation cross-sections [28,29] lead to higher P/V ratios than estimated from measurements of reference compounds with known P/V ratio [26]. We have also performed measurements on some reference compounds, namely α -, δ -, and γ - $VOPO_4$. Our measurements yielded sensitivity factors that are about 0.5 times that from theoretical calculations [29], in agreement with other experimental measurements where the same factor between measured and calculated values was found [26]. On the base of the experimental data we have calculated the P/V ratios for all the conditions we used

for our catalysts. The ratios did not show any correlation with the experimental conditions, but are rather randomly distributed within a variation of $\pm 10\%$ range of the total value. These variations are comparable to the background subtraction error, which was estimated to be $\pm 10\%$. The average P/V ratio for VPO_{P4} is 1.3 for the surface and 1.2 for the deeper layers, i.e., there is no difference within the experimental error. The values are different from unity, which should be the case according to the preparation. The deviation may be related to an error of the experimental estimation of the absolute value of the sensitivity factors.

4. Conclusions

We investigated two VPO catalysts with nearly the same intrinsic catalytic activities. One catalyst showed a high homogeneity depending on depth and stability of oxidation state towards condition changes. Another catalyst had a gradient of oxidation state and showed flexibility of oxidation state with conditions changes. At the reaction conditions both catalysts had the same surface oxidation state, which was close to 4, while the bulk oxidation state differed significantly. The experimental results suggest that in VPO the catalytically active species located in the topmost surface layers (up to 1 nm depth) are different from the bulk structure. The deeper layers are acting as a substrate material only. The finding indicates that the bulk oxidation state in this case has no direct correlation to the catalytic properties. The concept of a difference in a structure of the active layer and of the bulk can play a central role in the strategy of improvement of a VPO catalyst. While the modern preparation methods are designed to get $(VO)_2P_2O_7$ bulk phase, the optimization of an active surface layer formation could be more important.

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