Evolution of oxidation states in vanadium-based catalysts under conventional XPS conditions

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Abstract

The stability of different vanadium-based catalysts for the selective oxidation of small hydrocarbons under the ultra-high vacuum (UHV) conditions of standard X-ray photoelectron spectroscopy (XPS) was studied by using a multi-purpose surface analysis apparatus which allows time spans of only a few minutes between the sample transfer into vacuum and the first photoelectron spectrum. For vanadium phosphorus oxide catalysts a significant dependence of the average vanadium oxidation state on the time of exposure to the UHV was observed, with a substantial decrease of the V^{+5}/V^{+4} ratio within only a few minutes. A much less pronounced reduction was found for alumina-supported VO_x catalysts. The observed changes are predominantly due to the vacuum environment with a rather minor (if at all) contribution of the X-ray excitation.
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1. Introduction

Vanadium oxides (VO_x) and vanadium phosphorus oxides (VPO) are known to be efficient catalysts for the selective oxidation of short-chain alkanes to olefins and oxygenates. An example for the commer-

cial use of these catalysts is the conversion of *n*-butane to maleic anhydride (MA) with VPO, with a total world production of MA well above 1 million tonnes [1]. A lot of effort has been spent to study the respective catalysts with a variety of methods, with the goal of a detailed understanding of the structure-property correlations, and in particular the nature of the "active sites". In case of the MA formation vanadium in its oxidation state +4 is generally accepted to be active in the reaction, but the kinetic significance of V^{+5} species has also been detected with

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time-resolved in situ X-ray absorption spectroscopy [2]. These studies are in accord with previous in situ laser Raman observations [3] and confirm earlier suppositions about the role of V^{+5} centers in the formation of maleic anhydride [4]. However, although a general reaction mechanism which takes into account the role of both V^{+4} and V^{+5} phases has been proposed [5], additional reliable experimental information about the microscopic nature of the active surface, including the determination of the surface composition and the surface oxidation state, is still needed to reveal the quantitative details of the reaction scenario.

Despite of the progress of a novel in situ X-ray photoelectron spectroscopy (XPS) under reactive atmosphere conditions at pressures in the millibar regime [6], the vast majority of our knowledge on the elemental surface stoichiometry of vanadium-based catalysts still relies on the standard technique, i.e. XPS under high or ultra high vacuum (UHV) conditions. Here, different studies of comparable materials showed some discrepancies in particular for the vanadium oxidation states (see e.g. [7–11]), which may mainly be due to different pretreatment and test conditions of the catalysts prior to their analysis. Additional reasons can be the convoluted oxidation states in the V $2p_{3/2}$ peak which cause some ambiguity in their separation, as well as problems caused by the XPS method itself, such as sample charging [12], Fermi level shifting due to variations in the oxygen vacancy defect concentration [13], and the background contribution. However, another essential prerequisite for the reliable interpretation of the data acquired under UHV conditions has not been taken into account so far: the stability of the sample composition during the XPS experiments. In the present study, we investigated the stability of VPO and alumina-supported VO_x catalysts in a multi-purpose UHV apparatus, which allows time spans of only a few minutes between the sample transfer into vacuum and the first photoelectron spectrum. The studied VPO catalysts, when exposed to the vacuum environment, exhibit a fast decrease (on the time scale of minutes) of the vanadium oxidation state ratio V^{+5}/V^{+4} which is followed by the slow formation (on the time scale of hours) of additional oxidation states in the sample, which are attributed to V^{+x} ($x < 3$). In comparison to the VPO material, the supported VO_x catalysts are comparably stable and change their average oxidation state significantly less.

2. Experimental

2.1. Preparation of the catalysts

All catalyst samples were prepared using standard techniques. The $VOHPO_4 \cdot 0.5H_2O$ precursor for the VPO catalyst was obtained by reduction of $VOPO_4 \cdot 2H_2O$ and was subsequently activated in a butane/air mixture at 400–450 °C as described by Kiely et al. [14]. This catalyst was used in an electrochemical membrane reactor for the butane oxidation to maleic anhydride [15]. Supported VO_x catalysts for the oxidative dehydrogenation of ethane in fixed-bed and membrane reactors [16,17] were prepared via the same route as described in detail in Ref. [18] by impregnation of γ-alumina spheres with vanadyl acetylacetonate dissolved in acetone followed by drying overnight and calcination in air.

For both types of catalysts, samples from different batches and "fresh" as well as "used" materials were investigated. In order to preserve the oxidation states as much as possible, the VPO samples were rapidly cooled to room temperature in a nitrogen atmosphere after the activation procedure (fresh samples) or catalytic reaction (used samples), respectively. In case of the supported VO_x catalysts, the fresh samples were analyzed directly after calcination while the used samples were quenched after the catalytic tests in a nitrogen atmosphere. As far as possible all further sample handling was done in a glove bag under a flow of nitrogen in order to minimize water adsorption from air. The catalysts were fixed on molybdenum sample holder plates through a double-sided conducting adhesive polymer tape typically used in electron microscopy. The tape was previously XPS analyzed in order to avoid a misinterpretation of the peaks characteristic for the VPO and VO_x samples.

2.2. XPS measurements

The possibility to transfer a sample from ambient pressure into the vacuum required for XPS experiments within the shortest possible time is of crucial importance for the investigation of the stability of its

surface composition and oxidation state. The present study was carried out in a stainless steel multi-chamber UHV system, which allows sample transfer times of less than only 5 min between the start of the evacuation of the load lock and the first XPS spectrum at a pressure better than 5×10^{-9} mbar in the analysis chamber. The latter is equipped with a hemispherical electron energy analyzer (PHOIBOS 150, SPECS) which provides the possibility of simultaneous photo-electron detection on nine channels, and allows fast data acquisition times. A standard high-intensity Al/Mg twin anode X-ray source (XR-50, SPECS) has been used, mainly in a "stop-and-go" mode in order to reduce sample irradiation (Mg Kα, excitation energy 1253.6 eV, 150 W) to the time of data acquisition only. During the time-dependent measurements presented herein, neither the sample nor the X-ray source was moved, thus ensuring that the same sample regions were probed in all cases.

Except for photo-electron spectroscopy (XPS, UPS), the multi-chamber UHV system contains instrumental facilities for scanning probe microscopy (STM, AFM), surface infrared spectroscopy, low-energy electron diffraction (LEED) and others.

High-resolution spectra (pass energy 10 eV) of the V 2p, Al 2p, O 1s, and C 1s lines as well as survey spectra were measured with the largest possible aperture in order to obtain maximum signal intensity from a rectangular sample area of approximately 9 mm × 12 mm. A satisfactory signal-to-noise ratio was obtained with 0.5 s per data point. No charge compensation was used in our experiments. In case of the VPO materials, correction for static charging effects was performed by assigning a value of 284.5 eV to the C 1s peak of adventitious carbon which was always found in the catalysts due to their activation in butane/air or the catalytic reaction [12]. Here the C 1s line was measured directly before or after the region of interest. For the alumina-supported VO$_x$ catalysts, the Al 2p line (74.5 eV) was used as a reference [19]. The work function of the analyzer was calibrated using the Au 4f$_{7/2}$ (E_b = 84.0 eV) signal from a clean gold foil.

The percentage of V^{+5} and V^{+4} was determined by deconvolution of the V 2p$_{3/2}$ peak as described in Refs. [8,9] by using Voigt functions and a Shirley back-ground subtraction (software: CasaXPS package). The average absolute error in the V^{+x} evaluation is estimated to be less than 10% as a result of the precision of the determination of reference binding energies and of the used deconvolution procedure [8,9]. However, the relative error between photo-electron spectra evaluated in the same way is expected to be significantly smaller.

3. Results and discussion

Relative changes in a sample composition under UHV conditions can be evaluated quite reliably since this does not require the determination of the absolute binding energy with maximum precision. However, for the quantitative comparison of our results to those of others an experimental check of the V 2p$_{3/2}$ electron binding energy in a well-defined substance is recommended and was performed using vanadyl acetylacetonate, the precursor material for the VO$_x$ catalyst. For this material of oxidation state +4, the V 2p$_{3/2}$ peak (based on the 284.5 eV C 1s reference) was found at 516.9 eV and is in a good agreement with the previously reported binding energies of 516.5–517.1 eV for V^{+4}, while for V^{+5} values between 517.5 and 518.2 eV are given in the literature [7–9,19–22]. It is worth noting that although the absolute V 2p$_{3/2}$ peak positions for vanadium phosphorus oxides differ slightly from those measured for vanadium oxides [23,24], the relative differences between different oxidation states are very similar and do not influence the results of our observations.

Since the energy splitting between the V^{+5} and V^{+4} oxidation states is about 1 eV, it is possible to distinguish between the two by using the procedure described in Refs. [8,9], that is by peak deconvolution of the V 2p$_{3/2}$ core level with binding energies of 518 eV for V^{+5} and 516.9 eV for the V^{+4} species, respectively. The same binding energies have also been used in other XPS studies of VPO catalysts [5,8,9,20]. Provided that the curve fitting and the deconvolution are performed in the same way for all samples under study, this technique allows to monitor the changes in the relative ratio of V^{+5} and V^{+4}.

In Fig. 1a section displaying the O 1s, V 2p$_{1/2}$ and V 2p$_{3/2}$ lines in the photoelectron spectra of a fresh VPO sample are shown: (a) 5 min, (b) 13.5 min and (c) about 19 h after the sample had been brought into the vacuum. Since the interference of the oxygen satellite
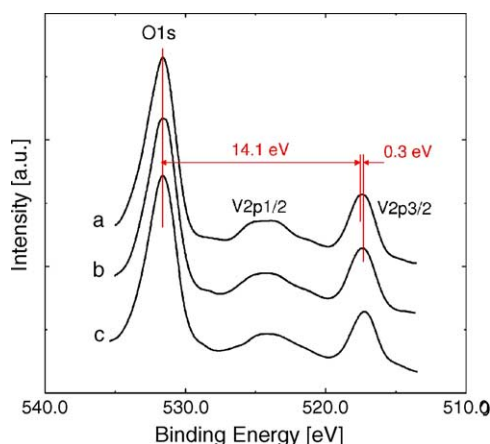
Fig. 1. O 1s, V $2p_{1/2}$ and V $2p_{3/2}$ photoelectron peaks of a fresh VPO catalyst: (a) 5 min (b) 13.5 min and (c) 19 h after the transfer of the sample into vacuum. Already within the first few minutes a shift in the V $2p_{3/2}$ mean binding energy is observable. Within the following hours, and without further exposure to X-rays, a shoulder at even lower binding energies is developed (for a detailed evaluation of the V $2p_{3/2}$ region see Fig. 2).

peaks resulting from the Mg Kα_3 and Kα_4 radiation with the V $2p_{1/2}$ feature makes its quantitative analysis difficult, we will discuss only the V $2p_{3/2}$ data here. As can be seen by comparison of the spectra (a) and (b), already a short exposition of the VPO sample to UHV leads to a shift in the vanadium $2p_{3/2}$ peak by 0.3 eV to lower values within the only 8.5 min between their recording, thus suggesting a decrease of the average oxidation state in the sample [13,25]. More changes are observed after prolonged exposure of the sample to the vacuum conditions, as can be seen from spectrum (c). Here, the formation of a low-energy shoulder in the V $2p_{3/2}$ peak is noticeable, suggesting a continuing

reduction of the sample. This observation will be addressed below.

As suggested by Coulston et al. [13], the energy difference between the O 1s and V $2p_{3/2}$ lines can be used as a measure for an (effective) "average oxidation state" V_{eff}^{ox}. For well-defined VO$_x$ samples, a linear relation $V_{eff}^{ox} = 13.82 - 0.68\,[E_b(O1s) - E_b(V2p_{3/2})]$ has been reported, which would yield a value of $V_{eff}^{ox} \approx$ 4.2 for our VPO sample after 5 min and $V_{eff}^{ox} \approx 4$ after 13.5 min in vacuum, respectively. However, it has to be taken into account that the above linear relation has been obtained for vanadium oxides and is also somewhat dependent on the used photoelectron spectrometer [26]. It should thus be applied with caution to the vanadium phosphorus oxides in our experiments. For a reliable evaluation of the V^{+5}/V^{+4} changes, a peak deconvolution is the more appropriate approach. The latter is shown in Fig. 2 for the V $2p_{3/2}$ region in the above spectra of Fig. 1. Spectra (a) and (b) can be described by contributions of V^{+5} and V^{+4} only, the ratios of these oxidation states being 28:72 and 14:86, respectively. In spectrum (c), a third peak is clearly evident with a contribution of about 10% to the total integrated intensity. Its corresponding binding energy is found at ∼515.1 eV, suggesting an oxidation state of less than +3.

The time evolution of the percentage of the vanadium oxidation state +5 in the fresh VPO catalyst is shown in Fig. 3, together with that obtained for a used catalyst. In both cases, a significant decrease of the V^{+5}/V^{+4} ratio is observed within the first 15–20 min after the samples were transferred into the vacuum environment, after which it apparently becomes constant even for extended periods of time. The experimentally determined V^{+5}/V^{+4} ratios
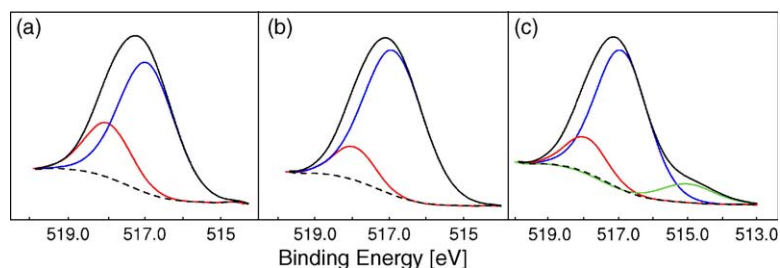

Fig. 2. Deconvolution of the V $2p_{3/2}$ peaks (see the corresponding spectra in Fig. 1). The first two spectra (a) and (b) contain only contributions from V^{+5} and V^{+4} at 518 and 516.9 eV, respectively. After several hours, however, a third peak with $E_b \approx 515.1$ eV can clearly be identified and is attributed to V^{+x} with $x < 3$ (c).
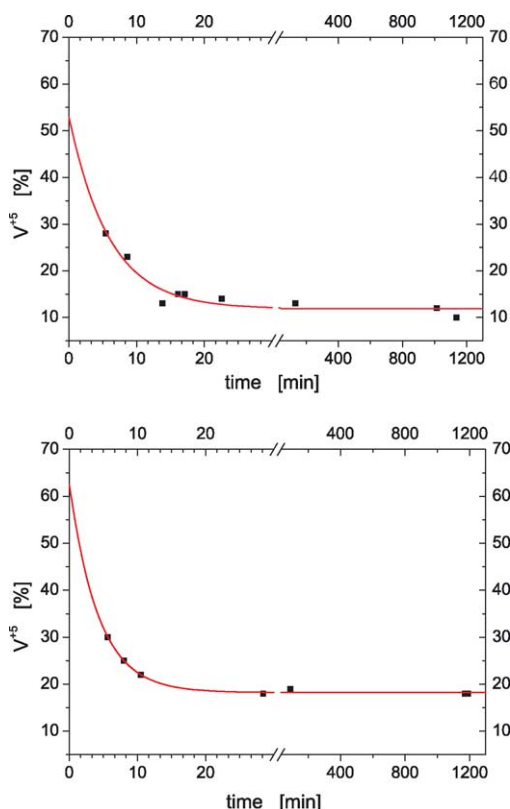
Fig. 3. Time evolution of the V^{+5} content in a fresh (top) and a used (bottom) VPO catalyst, as obtained by deconcolution of the V $2p_{3/2}$ peak. (■): Results of the deconvolution. The solid lines are single exponential decays which were fitted to the data.

decreased by at least a factor of $\sim$2, and stabilized between 11 and 15% V^{+5} for the fresh and between 15 and 18% V^{+5} for the used VPO. These values are close to others reported in the literature [10,11], and suggest that the latter may not reflect the original oxidation state of the active catalysts but rather that of samples which are significantly reduced under the experimental vacuum conditions. The fit of a single exponential decay to the measured data, corresponding to a first-order kinetics, suggests that the initial V^{+5}/V^{+4} ratios may have been as high as 50–60% for our samples.

As mentioned above, prolonged exposure of the samples to vacuum for 15–20 h leads to the appearance of a low-energy shoulder on the low-energy side of the V $2p_{3/2}$ peak which indicates the formation of a third component with a contribution of

about 10% to the total peak intensity (see Fig. 2c). Long-term studies in which samples were held for 250 h in vacuum show that this contribution with its peak maximum at $\sim$515.1 eV gains in intensity before it seems to saturate around 15%. The nature of this species is not yet clear. However, the relation given by Coulston et al. [13] as well as our own calibration data for various vanadium oxides [26] suggest a vanadium oxidation state of +2 rather than +3.

It can be concluded from a careful set of experiments in a ''stop-and-go'' mode in which the X-ray source was switched on only during data acquisition for 10–20 s, that all changes described above are predominantly due to the vacuum environment with a very minor (if at all) contribution of the X-ray excitation. This is also supported by the fact that the background pressure rose only slightly during operation of the X-ray source. No specific mass patterns indicative of a decomposition of the sample due to the X-rays were found in the mass spectra of the gas phase.

It is worth noting that an effect of water adsorption as a contribution to the measured data can be neglected in the present study, since it is known to cause a shoulder on the high binding energy side of the O 1s peak [13]. Its desorption in the vacuum environment would modify the O 1s line shape, which was not observed. The same holds true for a possible influence of the carbon contamination which could influence the scattering of the V 2p photoelectrons [13], since the C 1s signal was of similar magnitude and independent of the time under vacuum for all samples.

The stability of fresh as well as used VO_x catalysts on a γ-Al_2O_3 support was studied under the same conditions as in the case of the VPO samples (see Fig. 4). Although a decreasing V^{+5}/V^{+4} ratio could be observed as a function of the time of exposure to vacuum for this material, too, the observed changes are much less pronounced and of about the same magnitude as the (absolute) accuracy of the deconvolution itself ($\sim$10%). At the present stage, they are therefore regarded as less significant on the time scale of a typical XPS experiment.

The results presented herein demonstrate unambiguously that conventional X-ray photoelectron spectroscopy of vanadium-based catalysts under UHV conditions does not necessarily reflect the original surface stoichiometry and in particular the
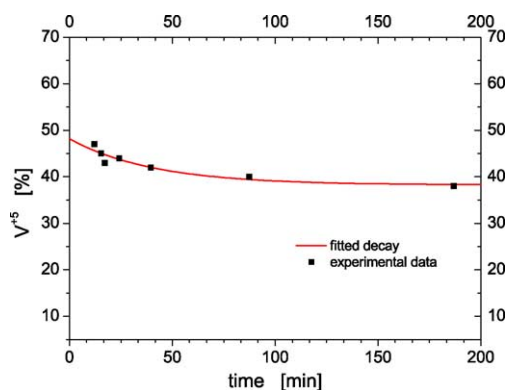
Fig. 4. Time evolution of the V^{+5} content in a VO_x catalyst supported on γ-Al_2O_3. The solid line represents an exponential decay which was fitted to the data.

initial oxidation states of the active material. In this class of catalysts a wide variety of different preparation and reaction conditions have been reported, only two of which were used in our study. For this reason it can not be concluded that all vanadium-based catalysts necessarily behave in the same way as observed here. However, the reduction under vacuum conditions is not surprising, and can be understood by means of thermodynamics. While e.g. in case of vanadium oxides at standard pressure and moderate temperatures, V_2O_5 is thermodynamically more stable than lower oxides, the change of the oxygen chemical potential in a vacuum environment can modify the V–O stoichiometry. In a recent calculation, an oxygen partial pressure below about 4×10^{-10} mbar at 800 K was predicted to be necessary for the reduction of bulk V_2O_5 to VO_2 [27]. Reactive evaporation of vanadium metal in an oxygen atmosphere of 2×10^{-7} mbar on a Rh(1 1 1) substrate led to the formation of high-quality V_2O_3 films, and no oxidation state +5 [28]. In an in situ XPS study of the V_2O_5(0 0 1) single crystal surface under equilibrium conditions a significant dependence of the V^{+4}/V^{+5} oxidation state ratio on the oxygen partial pressure was found at 800 K in the pressure range from 10^{-5} to 0.6 mbar [29]. Also for VPO catalysts under reactive and non-reactive gas compositions, a quick dynamic response of the catalyst surface to the applied conditions has been reported [30].

A surface reduction in a XPS vacuum chamber, possibly enhanced by X-ray radiation, has also been observed for ceria nanoparticles, which were investigated with XPS and X-ray absorption near edge spectroscopy (XANES) [31]. A comparison of the results showed that XPS yields a higher concentration of Ce^{+3} ions than XANES, and suggests that high-vacuum studies overestimate the Ce^{3+} content under ambient conditions.

At present it is not possible to distinguish between thermodynamic and kinetic contributions to the effect observed here for vanadium-based catalysts. In addition, in case of the VO_x catalysts the γ-Al_2O_3 support may play a role. The latter supposition is supported by first experiments with a titania support, where a remarkably faster reduction of the VO_x was observed. A systematic study is under way.

4. Summary and conclusions

By using a multi-purpose surface analysis apparatus with XPS and a fast sample transfer from ambient conditions into UHV, the vanadium oxidation state in VPO and alumina-supported VO_x catalysts has been investigated as a function of the time of exposure against vacuum. All samples were found to be remarkably reduced on a time scale as short as only 15–20 min, after which V^{+5}/V^{+4} ratios comparable to those previously reported in the literature were found. In case of VPO, the extrapolation of the observed time dependence suggests that the initial ratios might be up to three to four times larger, and XPS results obtained under standard vacuum conditions do not necessarily reflect the surface stoichiometry under reaction conditions. After prolonged exposure to vacuum even the slow (on the time scale of hours) formation of an additional oxidation state was observed in significant amounts. Due to its peak position, this species is tentatively attributed to V^{+2}. In all experiments, the exposure of the samples to X-rays was reduced to a minimum. This indicates that the vacuum environment is responsible for the observed changes, and that the X-rays have an (if at all) very minor contribution.

For VO_x on γ-Al_2O_3 support, the vacuum-induced changes were found to be significantly smaller than for the VPO samples and within the accuracy of the determination of the absolute V^{+5}/V^{+4} ratio, and can thus be regarded as minor important for standard XPS measurements.

Acknowledgments

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