

The mechanism of *n*-butane oxidation. Characterization of titania-supported V-P-O catalysts by pulse-flow experiments and *in-situ* XANES spectroscopy

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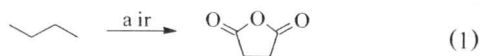
(Received May 22, 1996)

Abstract. Well-dispersed supported V-P-O (Vanadium Phosphorus Oxide) catalysts were prepared and tested in the selective oxidation of *n*-butane to maleic anhydride. Because of their high activity, it was possible to test titania-supported catalysts in a two-step oxidation reduction process at low temperatures. After *n*-butane adsorption and activation in the absence of molecular oxygen, desorption took place after subsequent introduction of molecular oxygen into the gas stream, leading to the selective formation of maleic anhydride.

In-situ XANES spectroscopy was performed under reaction conditions in the two-step oxidation reduction process with a special titania-supported V-P-O catalyst with a high loading. The results of these experiments showed that, after equilibration, no more changes in the valence state of vanadium were observed after reduction or subsequent re-oxidation. This indicates that the generally assumed *Mars-Van-Krevelen* mechanism is not operative for the titania-supported V-P-O catalyst.

Introduction

The selective oxidation of *n*-butane to maleic anhydride (Eqn. 1) over catalysts based on V-P-O (Vanadium Phosphorus Oxide) is a commercially attractive route in view of the availability of *n*-butane and the carbon efficiency of the reaction. However, the *n*-butane content in the gasflow, containing oxygen, being passed over the catalyst, is restricted due to explosion danger.



The mechanism mostly assumed to be operative for selective catalytic oxidation over solid oxides is the *Mars-Van-Krevelen* mechanism, in which the catalyst is alternatively reduced by the compound to be oxidized and oxidized by gaseous molecular oxygen. It is important to assess whether the oxidation of *n*-butane over the selective V-P-O catalyst also proceeds via a *Mars-Van-Krevelen* mechanism. When this mechanism is operative with the V-P-O catalyst, recirculation of the catalyst between a gasflow in which the catalyst is exposed exclusively to *n*-butane and one in which the catalyst is re-oxidized by gaseous oxygen, is viable. Recovery of the more concentrated maleic anhydride from the gas flow can be performed more easily and the risk of explosions is lower. Moreover, *Gleaves* et al.¹ have shown that passing a flow of ¹⁸O₂ and *n*-butane over the catalyst resulted in C¹⁸O¹⁸O, which indicates that oxygen, chemisorbed from the gas phase, leads to a rapid non-selective oxidation. The authors used TAP (Temporal Analysis of Products) in their investigations. This rapid oxidation to carbon dioxide by oxygen, chemisorbed from the gas phase, suggests that, in the absence of gaseous oxygen, a higher selectivity can be achieved.

It is desirable that catalysts, to be used in assessing the

mechanism of the oxidation of *n*-butane, exhibit a high surface-to-volume ratio of the active component, since the reduction of the catalyst may involve only (part of) the surface layer. Furthermore, the catalyst should preferably be active at low temperatures. *Centi* et al.² have observed that exposure of the usual bulk V-P-O catalyst to *n*-butane at more elevated temperatures leads exclusively to desorption of carbon oxides. Reaction of *n*-butane with the surface in the absence of oxygen, or with an oxygen content too low to achieve oxidation of *n*-butane, causes carbon-containing species to be deposited on the surface of the catalyst. Exposure of the thus covered catalyst surface to molecular oxygen at temperatures of 400 to 450°C, results in gaseous carbon oxides only. To investigate whether the adsorbed carbon-containing species can react with molecular oxygen to maleic anhydride calls for operation at lower temperature and, hence, for a catalyst being active at lower temperatures.

In this paper, we investigate the mechanism of *n*-butane oxidation using a titania-supported V-P-O catalyst. A newly developed procedure for the application of hydrated vanadia on the surface of supports involving V^{III} was used to prepare titania-supported V-P-O catalysts of high activity³. V^{III} was produced via a scaled-up electrochemical reduction procedure of V^V salts. Using on-line mass spectrometry, the composition of effluent gas from the catalysts after reaction with consecutive pulses of *n*-butane and oxygen was analyzed. To establish the reduction of the active component, XANES (X-ray Absorption Near-Edge Structure) spectroscopy was used. This technique provides information about the oxidation state of the vanadium. Furthermore, the characterization can be performed *in-situ*, and under well-defined reaction conditions. Since the titania-supported catalysts are well-dispersed, the contribution of the (active) surface to the total spectrum is large. Therefore, the surface reactivity of the titania-supported V-P-O catalyst can be assessed with this technique.

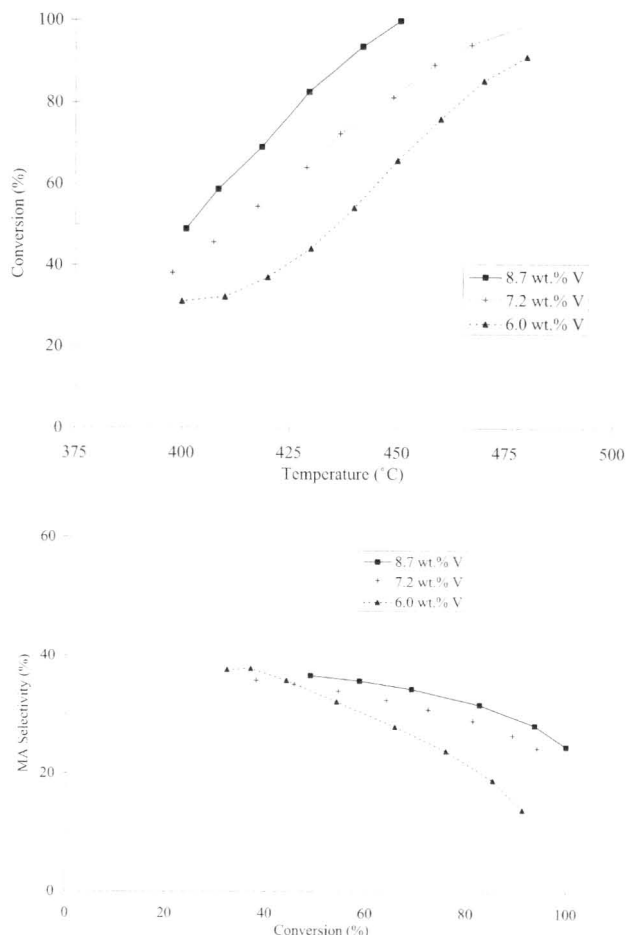


Figure 1. Conversion as a function of temperature (top), and selectivity to maleic anhydride (MA) as a function of conversion (bottom) of a number of silica-supported V-P-O catalysts with different loadings of V-P-O, and with a P/V ratio of 1.1.

Experimental

Preparation of supported V-P-O catalysts

Supported V-P-O catalysts have been prepared on TiO₂ (Degussa P25) and SiO₂ (Degussa P200) according to a newly developed procedure described by Overbeek et al.^{3,4}. In brief, the method comprises an electrochemical reduction of V^V species V^{III} ions in diluted hydrochloric acid solution, followed by homogeneous precipitation (HDP) of the V^{III} species in the presence of NH₄H₂PO₄ (P/V ratio 1.1). For the preparation of silica-supported catalysts this method was slightly adapted⁴, because of the poor interaction of the V-P-O with silica. First an amount of vanadium oxide was precipitated, which was subsequently impregnated with diluted phosphoric acid to create silica-supported V-P-O. Catalyst precursors were calcined in N₂ at 450°C for 16 h prior to testing.

For XANES measurements, a titania-supported V-P-O catalyst precursor was prepared with a high loading of active phase (8.2 wt.% on the basis of vanadium, P/V ratio 1.1) to reduce the impact of absorptions of titanium on the vanadium K edge, and to obtain a sufficiently high signal to noise ratio. Moreover, electrochemical reduction of V^V species was executed in formic acid 1/1 diluted to avoid interference of chlorine in the spectra.

TEM (Transmission Electron Microscopy) investigations showed that the active phase was well dispersed at the titania surface³. XPS (X-ray Photoelectron Spectroscopy) measurements revealed that both phosphorus and vanadium were present at the surface³. The dispersion calculated from XPS results amounted to 50%^{5,6}.

Testing of catalyst performance

After calcination, both silica and titania-supported V-P-O catalysts were tested in the selective oxidation of *n*-butane using a 1.5% *n*-butane, 20.5% O₂, 78.5% Ar flow (GHSV, General Hourly Space Velocity, 2000

h⁻¹). Evolved gaseous products, as well as unconverted reactants were analyzed using an on-line Balzers QMA-420 mass spectrometer, operating at 150 °C to avoid condensation of products. Carbon mass balances were in the range of 0.98 to 1.02. A detailed description of the experimental conditions is given in earlier publications^{3,4}.

Equilibrated titania-supported V-P-O catalysts have also been tested in a two-step oxidation reduction process. After *n*-butane adsorption (2% *n*-butane in Ar, GHSV 2000 h⁻¹, 5 min) at 280°C, the catalyst was re-oxidized with different amounts of oxygen in argon at 280°C for 2 min (GHSV 2000 h⁻¹). Subsequently, the catalyst was equilibrated again for 15 min at a chosen temperature under 'normal' steady state conditions, followed by a new oxidation reduction cycle. A complete overview of the performed pulse-flow experiments will be published elsewhere⁷.

XANES (X-ray Absorption Near-Edge Structure) measurements

XANES experiments were performed at the Synchrotron Radiation Source at Daresbury Laboratories (Station 8.1) in England. The energy of the electron beam amounts to 2 GeV. Further details will be published elsewhere⁷. A vanadium metal foil of 5 μm was used for calibration. Absorption spectra were calibrated at the position of the main-edge jump of vanadium at 5465 eV according to Wong et al.^{8,9}. The main indication of the oxidation state of the vanadium atoms is the position of the K-edge in the spectrum. A higher valence state implies a lower energy of the core electron levels and, consequently, the presence of the K-edge at a higher energy⁸⁻¹⁰. Also the pre-edge of the spectrum, which reflects transitions from the K-shell to empty bound d-levels, provides information about the oxidation state of vanadium. Oxidation generally brings about an increase in the intensity of the pre-edge peak, though an effect of the surroundings of the vanadium ions also has to be taken into consideration^{9,11}. In this paper, the position and intensity of the vanadium pre-edge will be used to determine changes in the oxidation state of vanadium in a titania-supported V-P-O catalyst.

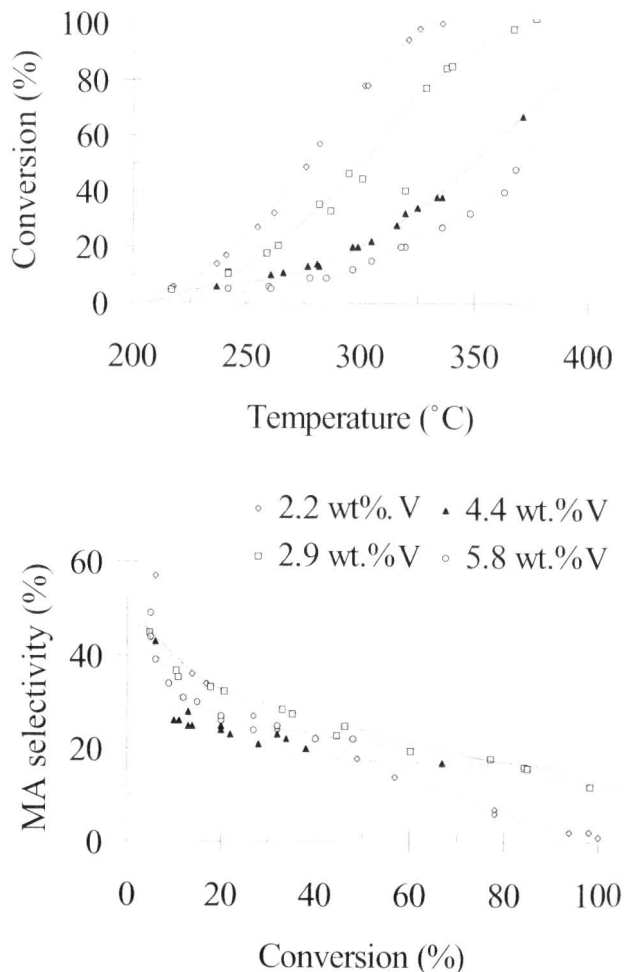


Figure 2. Conversion as a function of temperature (top), and selectivity to maleic anhydride (MA) as a function of conversion (bottom) of a number of titania-supported V-P-O catalysts with different loadings of V-P-O, and with a P/V ratio of 1.1.

A specially developed high-temperature *in-situ* cell was used, adapted to operate both in vacuum or under flow conditions¹². Samples were characterized *ex situ* in He at -196°C after calcination of the fresh

precursor in nitrogen at 450°C for 16 h, after subsequent oxidation in air at 380°C for 1 h, and after a number of oxidation reduction cycles. *In-situ* spectra were recorded at 280°C after exposure to concentrated *n*-butane

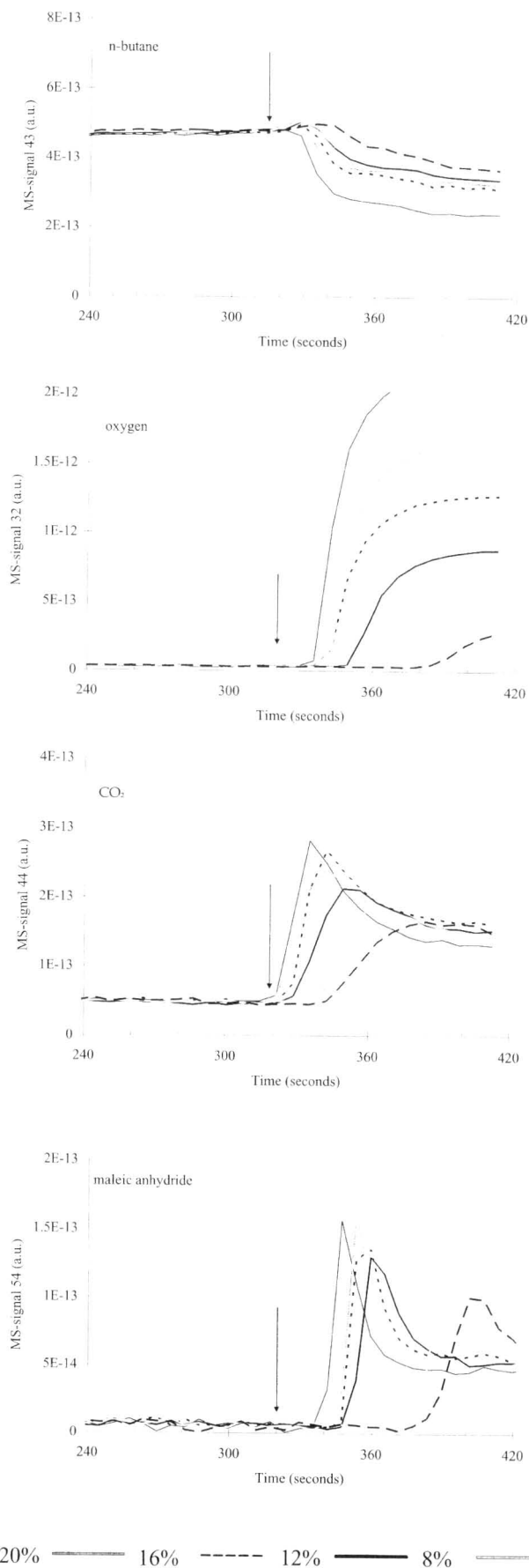


Figure 3. Product evolution expressed as a function of oxygen concentration in mass intensities for the reoxidation step in the reduction-oxidation process ($GHSV$ 2000 h^{-1} , $T = 300^\circ C$). The arrows indicate the moment of introduction of oxygen in the gas stream (catalyst: 2.9 wt.% V / TiO_2 , P / V ratio 1.1).

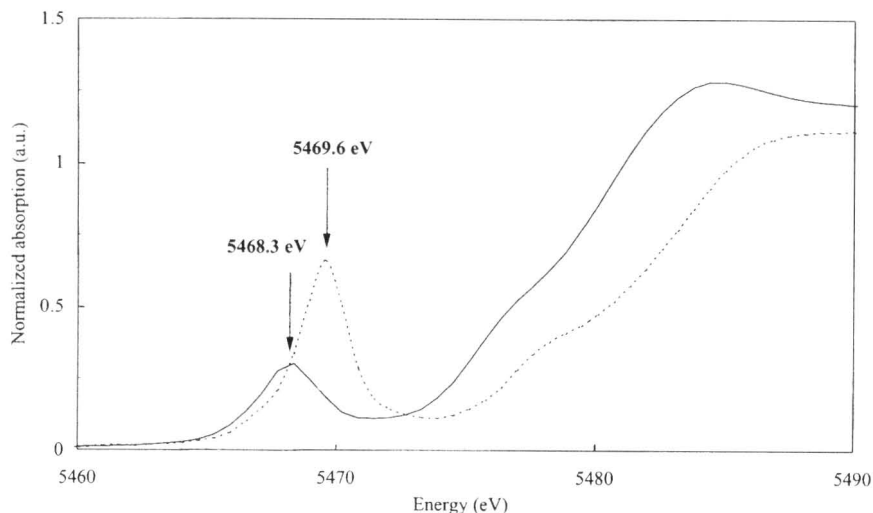


Figure 4. X-ray absorption edge of a titania-supported V-P-O catalyst (8.2 wt.% V, P/V 1.1). The solid line represents the catalyst after calcination of the fresh precursor in N_2 at $450^\circ C$; the dotted line represents the catalyst after subsequent oxidation in air at $380^\circ C$. Spectra were recorded in He at $-196^\circ C$.

for about five min and after subsequent oxidation for at least five min in a flow of synthetic air (He/O_2). After a second exposure to *n*-butane again an *in-situ* spectrum was recorded.

Results and discussion

Figure 1 represents the conversion of *n*-butane as a function of the catalyst temperature and the dependence of the selectivity on the level of the conversion for various silica-supported catalysts with different loadings of active phase. Though the supported catalysts exhibit a stable behaviour much more rapidly than the usual bulk catalysts, the conversions and selectivities are comparable per quantity of V-P-O. In order to have comparable amounts of V-P-O in the reactor, bulk catalysts were diluted with quartz. The bulk catalyst prepared in an organic liquid displayed a conversion of about 20% and a selectivity to maleic anhydride of about 53% at $450^\circ C$, while a bulk catalyst prepared from an aqueous solution showed a conversion of about 12% at a selectivity of 50%, after equilibration at $480^\circ C$ for 16 h. This is considerably lower than with the supported system, which indicates that a

large part of the bulk V-P-O catalysts does not take part in the reaction.

Figure 2 shows the activity and selectivity of titania-supported catalysts with different loadings of the active component. It is interesting that the activity drops at an increased coverage of the support with V-P-O, which indicates the effect of titanium on the activity and selectivity. With all titania-supported catalysts the coverage of the titania with a thin layer of active species is uniform. At lower loadings, the coverage of the surface of the support is incomplete. The presence of titanium at the rim of the active layer is assumed to cause the higher activity⁴. Titania-supported V-P-O catalysts exhibit a much higher activity in comparison with bulk and silica-supported catalysts, which makes them suitable for use in the assessment of the mechanism of *n*-butane oxidation at low temperature. Results of pulse experiments shown were performed over a titania-supported catalyst with a loading of 2.9 wt.% of V and a P/V ratio of 1.1. Catalysts with higher loadings exhibited similar behaviour, although they were less active. The results are represented in Figure 3. It is important to note that no reaction products are detected on exposure to *n*-butane of the titania-supported V-P-O catalysts at the reaction temperatures

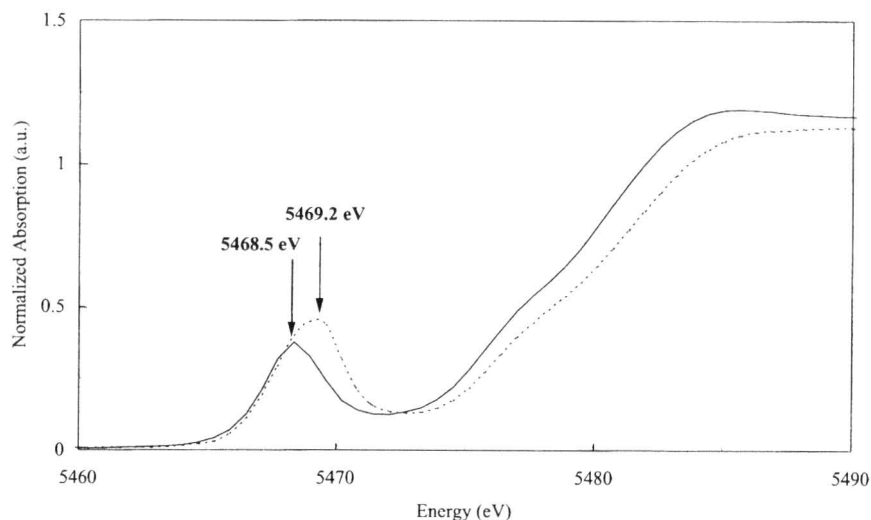


Figure 5. X-ray absorption edge of a titania-supported V-P-O catalyst (8.2 wt.% V, P/V 1.1). The solid line represents the catalyst after the first exposure to *n*-butane at $280^\circ C$; the dotted line represents the catalyst after subsequent exposure to O_2 at $280^\circ C$. Spectra were recorded *in situ* at $280^\circ C$ under reaction conditions.

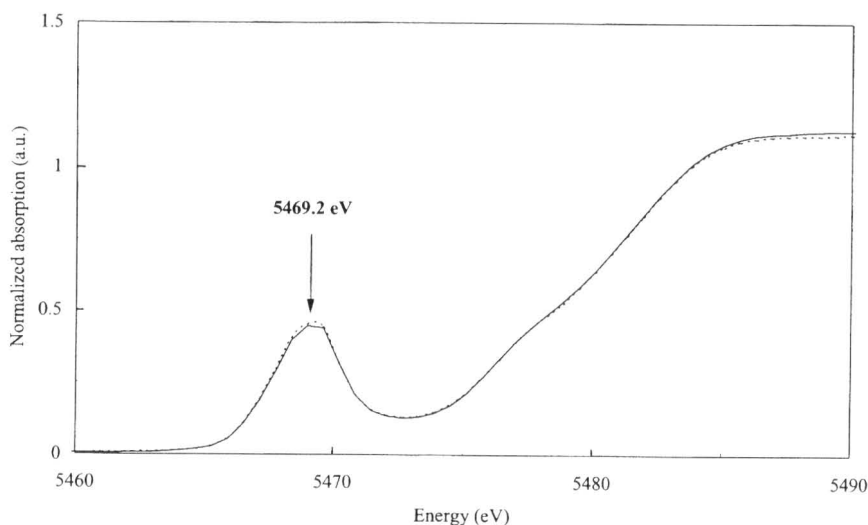


Figure 6. X-ray absorption edge of a titania-supported V-P-O catalyst (8.2 wt.% V, P/V 1.1). The solid line represents the catalysts after exposure to O_2 at $280^\circ C$; the dotted line represents the catalyst after subsequent exposure to *n*-butane at $280^\circ C$. Spectra were recorded *in situ* at $280^\circ C$ under reaction conditions.

investigated. Only adsorbed carbon species result, although *n*-butane is consumed from the gas stream. Using *in-situ* DRIFTS (Diffuse Reflectance Fourier Infrared Transform Spectroscopy) it was found that the converted *n*-butane was adsorbed and activated at the catalyst surface without formation of detectable, desorbed reaction products in the effluent. Subsequent exposure to a gas flow, containing molecular oxygen leads to immediate desorption of carbon dioxide and a small increase of the *n*-butane signal. This increase is due to the fact that the conversion decreases to almost zero level. Oxygen and *n*-butane are probably competing to adsorb at similar active sites. After a slight delay, maleic anhydride is detected, and finally molecular oxygen appears in the effluent. Furthermore, the breakthrough of the oxygen signal shifts to a later period when decreasing the oxygen concentration. This indicates that reaction of the most reactive oxygen species with adsorbed and activated *n*-butane intermediates gives rise to the formation of carbon dioxide. The less reactive species subsequently react with the remainder of the adsorbed and activated *n*-butane, leading selectively to the formation of maleic anhydride. Experiments, not described in this publication, have shown that the mechanism of the selective oxidation over these titania-supported catalysts is analogous with non-supported V-P-O catalysts. The adsorption of the carbon-containing intermediate on the catalyst surface requires a considerably higher temperature than the subsequent reaction with oxygen, which allows maleic anhydride to form and desorb.

It is interesting to establish the mode of adsorption of the carbon-containing intermediate and, especially, whether the reaction to the adsorbed carbon-containing species leads to a reduction of vanadium at the surface of the catalyst. To this end, XANES experiments were carried out with a titania-supported V-P-O catalyst with a loading of 8.2 wt.% of vanadium. Figure 4 shows the vanadium K-edge and the pre-edge of the catalysts at $450^\circ C$ in a flow of nitrogen. Oxidation in air at $380^\circ C$ brings about a shift in the vanadium K-edge of 3.5 eV. The pre-edge also shows an increase in intensity, viz., 0.6 compared with 0.2 of the height of the main edge, while a shift from 5468.3 to 5469.6 eV is exhibited. All these changes indicate a change in the oxidation state of vanadium to a higher value⁸⁻¹¹.

Exposure of the thus oxidized catalyst to *n*-butane at $280^\circ C$ in the absence of molecular oxygen results in the spectrum represented in Figure 5. Although the position of the pre-edge after *n*-butane adsorption is not as low as for the fresh

catalyst, it is obvious that a reduction of vanadium has taken place. It is important to note that subsequent oxidation in air at $280^\circ C$ is much less severe than oxidation at $380^\circ C$; the effect on the spectrum is therefore much smaller, which is visualized by a shift of the pre-edge to 5469.2 eV (5469.6 eV at $380^\circ C$). Finally, Figure 6 shows the spectrum before and after exposure to *n*-butane at $280^\circ C$. It appears that *n*-butane is adsorbed without an observable change of the oxidation state of vanadium. Subsequent oxidation of the catalyst does not lead to a change of the valence state of vanadium. However, the structure of the active site changes during the alternating exposure to *n*-butane and air.

Summarizing, after only a few oxidation reduction cycles, the titania-supported V-P-O catalyst was equilibrated. Neither the position of the vanadium K-edge nor the position and intensity of the pre-edge changed further upon exposure to an atmosphere of O_2/He or *n*-butane. These observations imply that *n*-butane does not react with lattice oxygen from the V-P-O phase and, as a consequence, the valence state of vanadium does not change.

The above observations have important implications. The presence of oxygen on the surface of the catalyst leads to oxidation to carbon oxides. In the absence of molecular oxygen, *n*-butane reacts with the surface to an adsorbed species of which a substantial fraction can react to form maleic anhydride after introduction of gaseous oxygen. The reaction of the oxidized catalyst surface with *n*-butane to adsorbed carbon-containing species does not involve a change in the (average) oxidation state of the vanadium. However, oxygen is required to desorb the adsorbed species as maleic anhydride.

Conclusions

The *Mars-Van-Krevelen* mechanism is not exhibited by titania-supported V-P-O catalysts. Initially, *n*-butane reacts with the active surface without affecting the oxidation state of vanadium. Subsequent reaction with molecular oxygen leads to reaction and desorption of maleic anhydride.

The ability of the titania-supported V-P-O catalyst to activate *n*-butane already at low temperatures yields the formation of stable adsorbed intermediates, which allow the subsequent oxidation with gas-phase oxygen at lower temperatures, generating selective oxidation products.

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