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## In situ characterisation of vanadium-phosphorus-oxide (VPO) catalysts for n-butane oxidation by applying X-ray absorption spectroscopy

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### Introduction

Vanadium phosphorus oxides (VPO) are well known to be efficient catalysts in the selective oxidation of n-butane to maleic anhydride [1]. It is believed that vanadyl pyrophosphate  $(VO)_2P_2O_7$  is the active phase in this process [2]. Structural nuances of the catalyst seem to be of great importance for the catalytic performance. The material undergoes strong structural rearrangements during the activation process from the precursor to the equilibrated catalyst. The preparation conditions have a strong influence on the performance of the catalyst. The specific structure of vanadyl pyrophosphate with its chains of  $V_2O_8$  octahedra linked by tetrahedra of pyrophosphate  $P_2O_7$  units was found to be uniquely active and selective for the reaction. This catalyst is especially interesting since there exists no other direct oxidative activation for n-alkane molecules.

### Experimental

We used high-pressure X-ray absorption spectroscopy (XAS) in the soft energy range [3,4] to study the electronic structure of VPO catalysts. In combination with mass spectrometry this method allows to obtain spectroscopic information from the catalyst's surface and to measure the conversion of the gas phase by the catalytic reaction simultaneously.

The XAS experiments were performed with a special reactor cell designed for in situ X-ray absorption investigation.

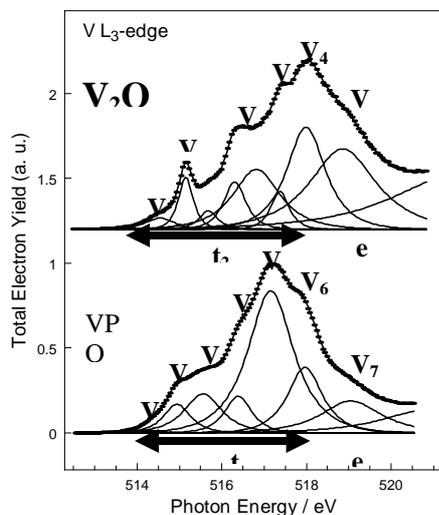


Fig.1:  $V L_3$ -NEXAFS of  $V_2O_5$  and VPO

Details about the set-up and the data processing can be found in the literature [3,4]. The experiments were carried out at the undulator beamline U49/1. In our experiments we analysed the near edge X-ray absorption fine structure (NEXAFS), i. e. the strong variations of the absorption coefficient just at the absorption edge.

Spectra were taken ex situ under high vacuum as well as under reaction conditions in a stream of 1.2vol% n-butane, 20vol% oxygen and 78.8vol% helium at temperatures from 300 K up to 673 K at a total pressure of 2 mbar. The activity of the catalyst was monitored by on-line mass spectrometry. The VPO powder sample was prepared by subsequent transformation of the precursor compound  $VOHPO_4 \cdot 0.5H_2O$  under n-butane oxidation conditions (feed gas: 1.5vol% butane in air for 200 h).

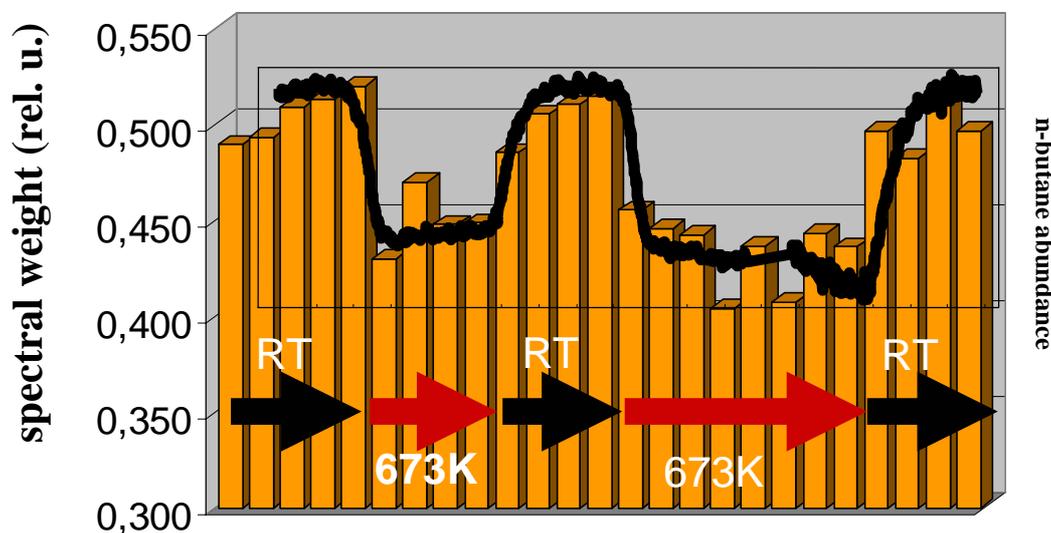
### Results

Fig. 1 shows the  $V L_3$ -NEXAFS of the VPO catalyst. For comparison the spectrum of the reference compound  $V_2O_5$  which possesses a similar local geometric structure is also shown. The spectra are related to the  $V 3d-O 2p$  hybridised unoccupied states. The overall peak position at the  $V L_3$ -absorption edge is

determined by the formal oxidation state of the absorbing vanadium atom. Details of the absorption fine structure are influenced by the geometric structure of the compound. Empirically, we found a linear relationship between the energy position of several absorption resonances and the V-O bond length of the participating atoms [5]. This allows to identify the contribution of specific V-O bonds to the V  $L_3$ -near edge X-ray absorption fine structure. Our analysis points to a deviation of the geometric surface structure of the VPO catalyst from the crystalline bulk structure of  $(VO)_2P_2O_7$ . This deviation could be caused by disorder or an amorphous layer at the catalyst's surface, an interpretation which is supported by HRTEM.

A detailed analysis of the V  $L_3$ -absorption edge by a least square fit showed defined reversible changes depending on the reaction conditions. An example for the observed dynamic behaviour of the VPO surface is shown in Fig. 2. The spectral weight of a particular resonance ( $V_5^*$ ) is decreasing from 50% of the total intensity at the V  $L_3$ -edge at 300 K to 43% under n-butane oxidation conditions at 673 K. While cooling down to room temperature the initial state is almost recovered. A decrease in intensity and therefore a change in the electronic structure could be caused by a modification of the geometric structure or the presence of adsorbats on the surface. Simultaneously, the energy position of this resonance shifts by about 90 meV to lower photon energies, an effect which is partially reversible if returning to 300 K. The catalytic activity of the sample under the applied conditions could be proven by using simultaneously on-line mass spectrometry which showed a decrease of the n-butane abundance in the reactant stream of around 5% at 673 K.

In summary our observations show a significant difference of the electronic structure of the catalyst surface under reaction conditions and its ability to react dynamically on the reaction conditions.



**Fig.2:** The relative spectral weight of resonance  $V_5^*$  (compare to Fig. 1) while changing temperature from 300 K to 673 K in a stream of n-butane, oxygen and helium is displayed as a bargraph. Additionally, the abundance of n-butane in the gas phase is shown.

## Acknowledgement

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