



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

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Abstract

Vanadium phosphorus oxides (VPO) are well known to be efficient catalysts in the selective oxidation of n-butane to maleic anhydride [1, 2]. 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. This observations highlight the importance of dynamic processes which occur in the case of the oxidation of n-butane on VPO. Vanadium phosphorus oxides can be considered as reference materials for mild oxidation of light alkanes and the basis for the development of a new catalytic formulation for the mild oxidation within the chemical industry of other alkanes than n-butane.

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 online 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. 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. Additionally, first results obtained by applying in situ photoelectron spectroscopy (XPS) will be reported. Spectra were taken ex situ under high vacuum as well as under reaction conditions (butane ox) 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.

Fig. 1 shows the V L₃-NEXAFS of the VPO catalyst. For comparison the spectrum of the reference compound V₂O₅ which possesses a similar local geometric structure is also shown. The overall peak position at the V L₃-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

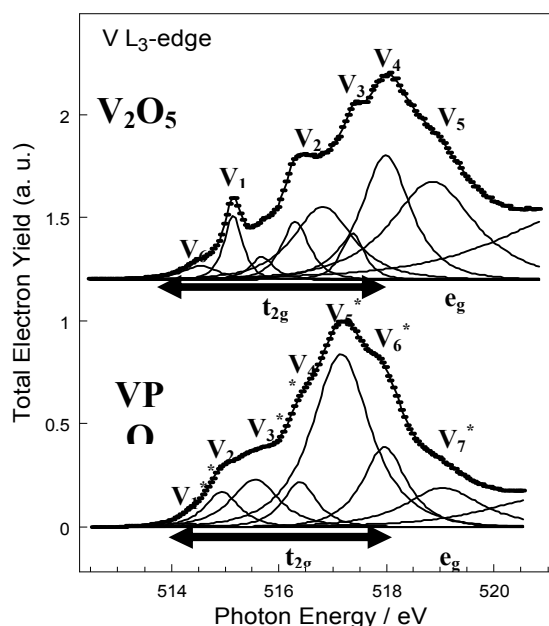


Fig. 1: V L₃-NEXAFS of V₂O₅ and VPO

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.

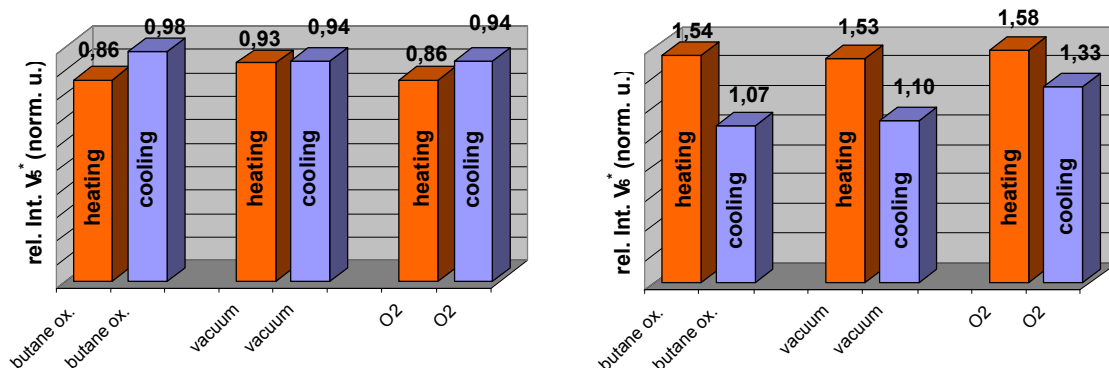


Fig.2: The change of spectral weight of resonance V_5^* and V_6^* (compare to Fig. 1) while changing temperature from 300 K to 673 K (heating) and back from 673 K to 300 K (cooling) under different conditions (butane ox: stream of n-butane, oxygen and helium; O_2 : stream of oxygen) is displayed as a bargraph. The value at the beginning of the temperature cycle is taken as 1.00.

A detailed analysis of the V L_3 -absorption edge by a least square fit showed defined partially 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 particular resonances (V_5^* , V_6^*) is significantly changing when applying different reaction conditions. The catalytic activity of the sample under

butane oxidation conditions (butane ox) could be proven by using simultaneously online mass spectrometry.

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

References

- [1] R. L. Bergman, and N. W. Frisch, U.S. Patent, 3,393,368 (1968) assigned to Princeton Chemical Res.
- [2] G. Centi, Catal. Today, 16 (1993) 5
- [3] M. Hävecker, A. Knop-Gericke, Th. Schedel-Niedrig, and R. Schlögl, Angew. Chem., 110 (1998) 2049; Int. Ed. 37 (1998) 206
- [4] A. Knop-Gericke, M. Hävecker, Th. Schedel-Niedrig, and R. Schlögl, Topics Catal., 15 (2001) 27
- [5] M. Hävecker, A. Knop-Gericke, R. W. Mayer, M. Fait, H. Bluhm, and R. Schlögl, J. Electron Spectrosc. Rel. Phenom. (2002), accepted