

Investigation of vanadium oxide based catalysts by a combined DFT/TEM approach

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Vanadium phosphorous oxides (VPO) are used in the selective oxidation of n-butane to maleic anhydride. Despite extensive research and contributions to the literature, the understanding of the mode of operation of VPO catalysts remains incomplete. In order to study the interplay and the role of the various VPO phases related to the catalytically active phase, a micro reactor with a transfer system attached was developed. This setup allows the study of microscopic amounts of sample in the catalytic reaction and to transfer the sample at any time into the electron microscope and back to the reactor without exposing the sample to ambient air [1]. Single phase model catalysts, i.e. model systems with a simplified structure but relevant catalytic properties, and 'real world' VPO catalysts can now be characterized by electron energy loss spectrometry (EELS) and high resolution transmission electron microscopy (HRTEM) at any stage of the reaction. In this way, a suitable characterization of a sample and the evolution of the electronic and geometric structure of the material can be achieved while its catalytic function is verified. In order to enable a detailed interpretation of the recorded EELS spectra, ab-initio band structure calculations based on DFT were performed for a number of VPO phases (α_I -, α_{II} - and β -VOPO₄, VO(PO₃)₂, VO(H₂PO₄)₂ and VPO₄). The simulated phases serve as a basis set as they cover a variety of differently linked VO₆ and PO₄ structural units that are common to most of the catalytically relevant VPO phases. The calculated partial density of states provide valuable information about the electronic structure and makes it possible to relate the observed spectral features to the underlying transitions. The goal of the present project is to work out micro structural and electronic structural details that can be used to identify the presence of a particular phase and to investigate the role of the identified phases in the catalytic performance of the catalyst.

References

- [1] M. Hävecker, N. Pinna, K. Weiss, H. Sack-Kongehl, R.E. Jentoft, D. Wang, M. Swoboda, U. Wild, M. Niederberger, J. Urban, D.S. Su and R. Schlögl, J. Catal., 236 221-232, 2005.