

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

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Vanadium oxide based materials attract attention in various fields related to material science due to their rich structural chemistry. In the field of catalysis, they are used in the oxidative dehydrogenation of lower alkanes. A prominent example are the vanadium phosphorous oxides (VPO), which catalyze 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 vanadium-based oxidation catalysts remains incomplete. Experimental results suggest that the structure of the catalytically active species is only weakly related to the bulk structure and that the bulk basically acts as a support material and reservoir for the constituents of the active phase [1]. For this reason, conventional structural analysis with X-ray diffraction cannot be expected to be adequate.

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 TEM and back to the reactor without exposing the sample to ambient air [2]. The key idea is to minimize the amount of catalyst used for catalytic testing in order to obtain uniform reaction conditions and to approach a situation in which TEM data are representative for the whole catalyst. 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 EELS and TEM 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 interpretation of the recorded EELS spectra, ab-initio band structure calculations based on DFT were performed for a number of VPO phases ( $\alpha_I$ -,  $\alpha_{II}$ -  $\beta$ -,  $\delta$ - and  $\epsilon$ -VOPO<sub>4</sub>, VO(PO<sub>3</sub>)<sub>2</sub>, VO(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> and VPO<sub>4</sub>). The simulated phases serve as a basis set as they cover a variety of differently linked VO<sub>6</sub> and PO<sub>4</sub> 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, such as the degree of covalency of the oxygen-cation bond and makes it possible to relate the observed spectral features in the ELNES 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.

[1] E. Kleimenov, H. Bluhm, M. Hävecker, A. Knopp-Gericke, A. Pestryakov, D. Teschner, J.A. Lopez-Sanchez, J.K. Bartley, G.J. Hutchings, R. Schlögl *Surf. Sci.*, **575** 181, 2005.

[2] M. Hävecker, N. Pinna, K. Wei, 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.