Micro- and Electronic Structure of the Catalyst and the V^{5+} Phases of Vanadium-Phosphorus Oxides

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Vanadium phosphorus oxides (VPO) are commercially used as catalysts for the synthesis of maleic anhydride (MA) in the partial oxidation of n-butane. The phase constitution and the morphology of the catalyst are found to be dependent on the preparation routes and the applied solvent. The final catalyst consists of the main V^{4+} phase $(VO)_2P_2O_7$ and a mixture of pentavalent phases: α_I-$VOPO_4$, α_{II}-$VOPO_4$, γ-$VOPO_4$ [1]. These phases are crucial for the conversion and selectivity rate of the final catalyst. It is believed that only a specific combination of V^{4+} and V^{5+} phase leads to the high catalytic performance [2]. In this work we present a comprehensive characterisation of the V^{5+} phases α_{II}-$VOPO_4$ and β-$VOPO_4$ and of the real VPO catalyst. A combination of methods are applied: scanning electron microscopy (SEM) for the information about morphology; x-ray diffraction (XRD) for phase analysis; transmission electron microscopy (TEM) for microstructural analysis (low- and high resolution, electron diffraction) and electron energy loss spectrometry (EELS).

Scanning electron images clearly show that the morphology of the α_{II}-$VOPO_4$ (Fig. 1) is dominated by large (ca. 5-10 μm) and flat plates, while the β-$VOPO_4$ (Fig. 2) is composed of a series of square- and rectangular-like particles with the size varying from 0.5 μm to 2 μm. γ-$VOPO_4$ (Fig. 3) is made up of dense agglomerates of plate- and needle-like crystallites (where the size ranges from 0.2 μm to 4 μm). The activated catalyst, (Fig. 4) prepared from V_2O_5 and $H_4P_2O_7$ contains particles of different shapes and sizes. Diversity of the surface morphologies is influenced by the preparation procedure (starting material and its morphology, calcination temperature, environment of the process – oxygen, n-butane/air mixture or air).

Since activated vanadium phosphate catalysts have a widely varying morphology and the various $VOPO_4$ phases have identical chemical compositions and in addition, most of the vanadium phosphate phases are prone to electron beam damage, distinguishing between the various $VOPO_4$ phases using microanalysis techniques such as EELS is very difficult. Ab-initio band structure calculations based on density functional theory (DFT) were performed for α_{II}-$VOPO_4$ and β-$VOPO_4$. The evaluated partial density of states (Fig. 5) does not only provide valuable information about the electronic structure such as the degree of covalency of the oxygen-cation bond, but also allows the simulation of core level absorption spectra like EELS (Fig. 6). This enables to relate spectral features in the ELNES (Energy Loss Near Edge Structure) to the corresponding transitions and the assignment of the measured spectra to the corresponding phase (i.e. α_{II}-$VOPO_4$ or β-$VOPO_4$).

The goal of the present work is to work out microstructural and electronic structural details that can be used to identify the presence of a particular phase and to finally investigate the role of the V^{5+} phases in the catalytic performance of the final catalyst.

Reference:
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[2] C.J. Kiely, A. Burrows, G.J. Hutchings, K.E. Bere, J.C. Volta, A. Tuel, M. Abon, Faraday Discuss., 1996, 105

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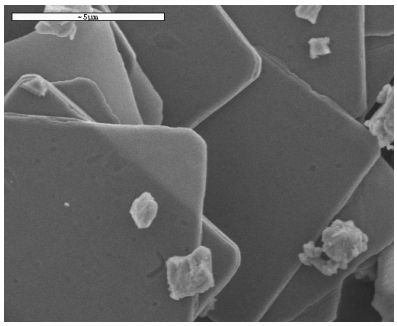

Fig. 1. SEM image of α_{II}-$VOPO_4$

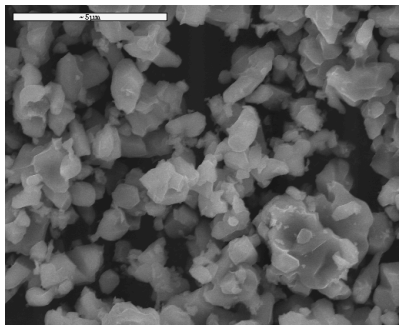

Fig. 2. SEM image of β-$VOPO_4$

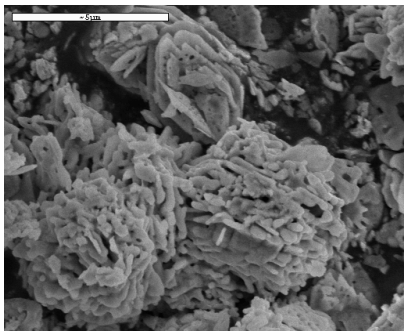

Fig. 3. SEM image of γ-$VOPO_4$

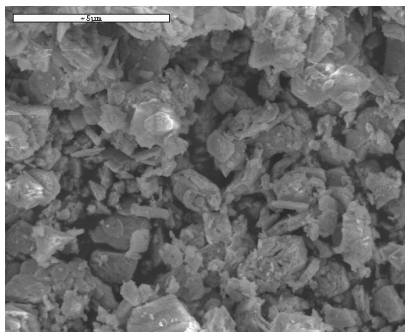

Fig. 4. SEM image of the catalyst

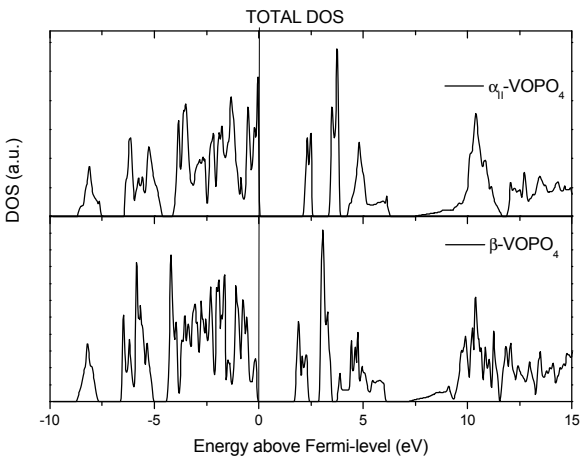

Fig. 5. Total density of states (DOS) of α_{II}-$VOPO_4$ and β-$VOPO_4$

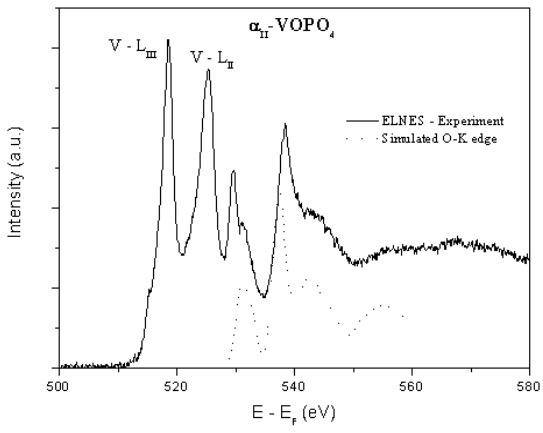

Fig. 6. EELS spectrum recorded form α_{II}-$VOPO_4$.