Microstructural characterization of the standard VPO phases

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Vanadium phosphorus oxides, (VPO) are commercially used as catalysts for the synthesis of maleic anhydride, (MA) from 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. Among the main phase, $(VO)_2P_2O_7$, the catalyst contains pentavalent phases: α_{II}-$VOPO_4$, γ-$VOPO_4$ [1]. These phases are crucial for the conversion and selectivity rate of the final catalyst. It is belived 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 chracterization of the standard V^{5+} phases: α_I-$VOPO_4$, α_{II}-$VOPO_4$, β-$VOPO_4$ and γ-$VOPO_4$.

A combination of methods are applied: scanning electron microscopy (SEM) for the information of morphology, energy dispersive x-ray analysis (EDX) for qualitative and quantitative elemental analysis (both on a Hitachi S-4000 SEM); X-ray diffraction (XRD) for phase analysis (on a Stoe Powder Diffractometer with the position sensitive detector); TEM for microstructural analysis – operating in low magnification, high resolution images mode, diffraction patterns and EELS analysis – (on Philips CM 200 FEG electron microscope). Samples suitable for TEM investigations were prepared by dispersing the catalyst powder onto a carbon film supported copper mesh grid.

Scanning electron images, Fig. 1 clearly show that β-$VOPO_4$ is composed of a series of square- and rectangular-like particles with the size varying from 0.5μm to 2μm, while γ-$VOPO_4$ is made up of dense agglomerates of plate- and needle-like crystallites (where the size ranges from 0.2μm to 4μm). The surface morphology depends on the preparation route (e.g. calcination temperature) and is influenced by the starting material (dihydrate or hemihydrate). Typical EELS spectrum of two V^{5+}

phases (β-$VOPO_4$ and γ-$VOPO_4$) and the reference single crystal of VPO is shown in Fig. 2. The first peak can be assigned to vanadium-L_3 edge ($V2p_{3/2}$ – V3d transition); the second peak to V-L_2 ($V2p_{1/2}$ – V3d transition) and the last two peaks to O-K edge (1s – 2p transitions). Study of the spectrum in the energy loss range 500-570eV confirms that β-$VOPO_4$ and γ-$VOPO_4$ phases are in V^{5+} oxidation state - comparison with the reference spectrum of the single crystal of VPO which is in V^{4+} oxidation state. Characteristic energy loss values for V-L_3 edge are: 517.9eV for single crystal of VPO, 519.1eV for β-$VOPO_4$ and 519.2eV for γ-$VOPO_4$ compound. More detailed results from TEM, SEM and XRD will be presented.

Reference:

[1] F.J. Cabello Sanchez, J.A Lopez-Sanchez, R. Wells, C. Rhodes, A. Isfahani, G.J. Hutchings, Catalysis Letters, 2001, Vol. 77

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

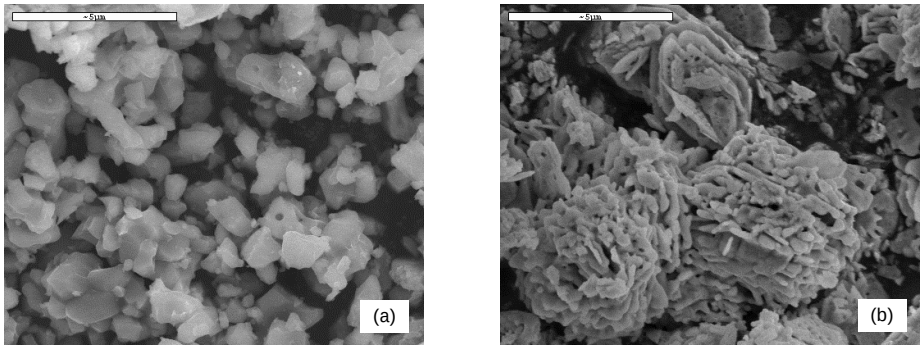

Fig. 1. SEM images, (a) β-$VOPO_4$, (b) γ- $VOPO_4$

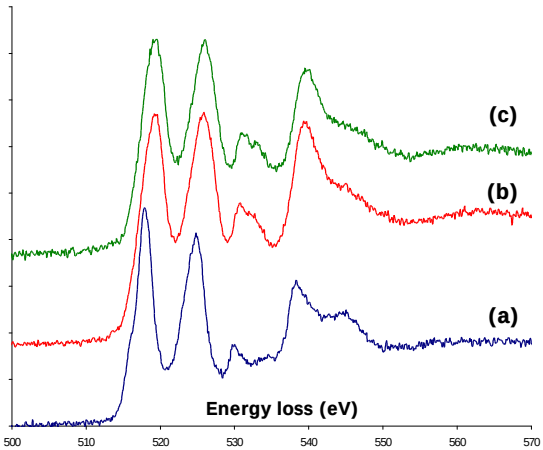

Fig. 2. EELS spectrum, (a) single crystal VPO, (b) β-$VOPO_4$, (c) γ- $VOPO_4$