Microstructural differences between the catalyst and the standard V^{5+} phases of VPO

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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. 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 standard V^{5+} phases: α_I-$VOPO_4$, α_{II}-$VOPO_4$, β-$VOPO_4$ and γ-$VOPO_4$ and the real VPO catalyst.

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 clearly show that the morphology of the α_{II}-$VOPO_4$, (Fig. 1) is dominated by large (ca. 5-10μm) and flat plates with small particles on the surface, while the β-$VOPO_4$, (Fig. 2) is composed of a series of square- and rectangular-like particles with the size varying from 0.5μm to 2μm. γ-$VOPO_4$, (Fig. 3) is made up of dense agglomerates of plate- and needle-like crystallites (where the size ranges from 0.2μm to 4μm). 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).

Typical HR image from the catalyst is reproduced in Fig. 5. Sharp lattice fringes were obtained from [100] projection of vanadium pyrophosphate; the fringes resolved have a spacing of d=0.626 nm and the angle between them is 82°, therefore they correspond to (012) and (0-12) lattice planes of $(VO)_2P_2O_7$. The image in Fig. 6 was recorded from a very beam sensitive region of α_{II}-$VOPO_4$ sample. It shows an [001] projection in which the (110) and (1-10) lattice planes of α_{II}-phosphate phase are resolved. The measured fringes have a spacing of d=0.424 nm and the angle between them

is 90 degrees. More detailed results from TEM, SEM and XRD will be presented and microstructural differences between V^{5+} phosphates and the real catalyst will be compared.

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

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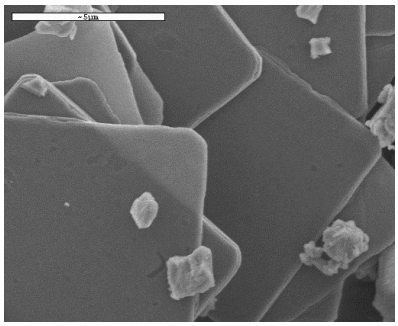

Fig. 1. SEM image of α_{II}-$VOPO_4$

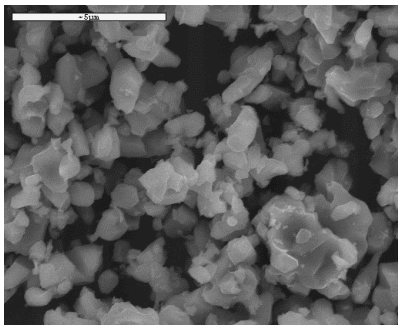

Fig. 2. SEM image of β-$VOPO_4$

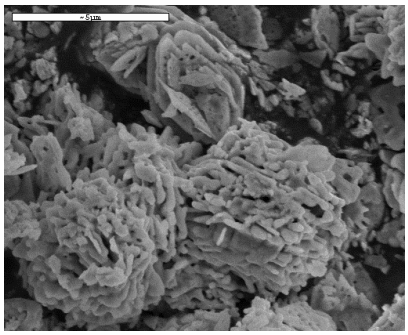

Fig. 3. SEM image of γ-$VOPO_4$

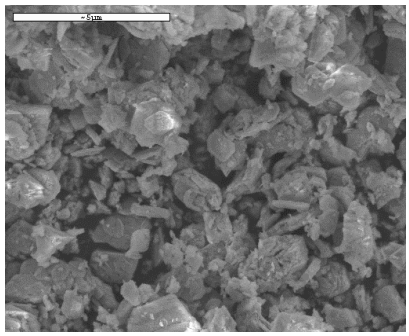

Fig. 4. SEM image of the catalyst

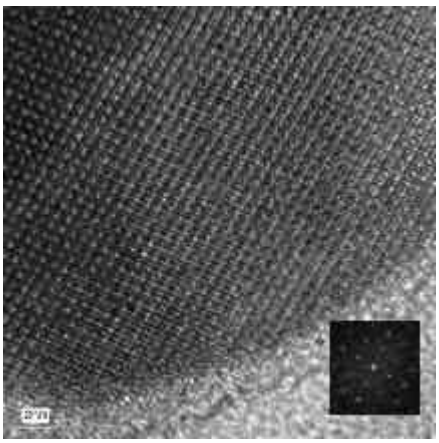

Fig. 5. HR image from [100] projection of $(VO)_2P_2O_7$

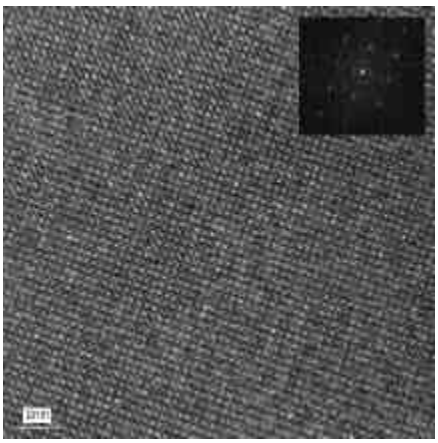

Fig. 6. HR image from [001] projection of α_{II}-$VOPO_4$