



ESRF

Experiment title: X-ray diffraction study of a new polytype in the V-P-O system,  $\omega$ -VOPO<sub>4</sub>: a dynamic reversible amorphization process.

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CH105

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D1-SW/NOR

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Several biphasic VOPO<sub>4</sub>/(VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> redox partners seem to be active in the catalytic cycles involved in the mild oxidation of simple hydrocarbons to maleic anhydride. The V-P-O system is characterized by the easy formation and inter conversion of a lot of crystalline phases [1]. To date, five different polymorphs of the oxidized VOPO<sub>4</sub> derivative have been described in the literature. During the thermal decomposition of the oxidized hydrogen phosphates the crystal structure of the starting material seems to be the main factor determining the formation of one or another VOPO<sub>4</sub> intermediate polymorph. A X-ray time resolved thermal-diffractometric study revealed that in the case of the hydrogen phosphate hydrates VO(HPO<sub>4</sub>)<sub>n</sub>H<sub>2</sub>O (n= 2(α), 2(β)) [3] and β-NH<sub>4</sub>(VO<sub>2</sub>)(HPO<sub>4</sub>) [4] the decomposition pathway goes through the formation of a new anhydrous variety of the oxidized form which crystallizes after formation of an amorphous intermediate and evolutionates towards the αII-VOPO<sub>4</sub> phase and, finally, in the well known β-VOPO<sub>4</sub> [2].

Under the kinetic conditions of our experiments, this new phase,  $\omega$ -VOPO<sub>4</sub>, begins to grow from the amorphous solid at temperatures ranging from 440 to 480°C, depending on the precursor considered. Once this phase has been crystallized it is stable in the temperature range RT-490°C. Though an important peak broadening is observed when decreasing the temperature, the loss of crystallinity is not complete even at room temperature. This peculiar “amorphization” effect is completely reversible inside the mentioned stability temperature range and kinetically quite quick, but it is not possible to detect it by DSC measurements.

A previous structural study of the  $\omega$ -VOPO<sub>4</sub> was accomplished by means of laboratory X-ray powder diffraction techniques (425°C). The best fit and a good geometry for phosphate and vanadium polyhedra was obtained with a model where the oxygen atoms were disordered between two equivalent positions. To build the V-O-P network from this final model taking into account the alternate occupation of the split oxygen positions always an **impossible situation** was found (V=O-O=V bonds sequence) and the only way to get a realistic structural model was to consider a **cooperative twisting of all the phosphate groups coupled with the hopping of the vanadyl oxygen atoms** between their two split positions (from O=V...O to O...V=O). Hence, at high temperature the thermal vibration of the net would allow for this cooperative movement and when lowering the temperature the impossibility of this movement would give rise to the above mentioned "amorphization" of the compound. However, the poor resolution of our data did not allow us to get a sufficient number of independent reflections to satisfactorily refine this disordered model,

In order to unambiguously get a satisfactory description of this structure we planned to undertake a combined diffraction study using synchrotrons X-ray and neutron sources. The synthesis of the sample was going to be undertaken under the beam source from the decomposition of the precursor (NH<sub>4</sub>)(VO<sub>2</sub>)HPO<sub>4</sub>. However the different geometry of the sample holder in first place, and secondly, the heating method, gave rise to a change in the reaction pathway. During the experiences in our laboratory the  $\omega$ -VOPO<sub>4</sub> was registered as a pure phase. These experiments were undertaken in free air atmosphere (open flat sample holder), the sample was heated by direct heating of the platinum sample holder and the diffraction data was collected by reflection mode (Bragg-Brentano geometry). Being the station in a typical transmission mode arrangement we thought the differences in the sample holder geometry (closed capillary in this case) would affect only the possibility of scaping gases from the decomposition reaction and hence, the experiment was undertaken with a predecomposed precursor. However, the  $\omega$ -VOPO<sub>4</sub> solid was found to be only a secondary phase and another related phase, unknown until that moment, was found as a mayoritary phase. This fact prevented us from the collection of any useful diffraction data of the  $\omega$ -VOPO<sub>4</sub> phase though opened the possibility of getting new phases in this interesting V-O-P system.

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