XXXIX. Jahrestreffen Deutscher Katalytiker
Weimar, 15. - 17. März 2006

New Contributions to the Structural Chemistry of Vanadyl Orthophosphate $VOPO_4$

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Introduction

Vanadyl orthophosphate $VOPO_4$ exists as a large number of polymorphs: α_I, α_{II}, β, γ, δ, ε and ω. This group of compounds is especially interesting for electrochemists and catalysis researchers. Particularly ε-$VOPO_4$, which is capable of reversible lithium intercalation, exhibits promising properties with respect to potential applications as an electrode material [1]. In catalysis research, the polymorphs α_{II}-, γ-, and δ-$VOPO_4$ have been observed as phases formed *in situ* in activated $(VO)_2P_2O_7$ catalysts [2], which are employed industrially for the partial oxidation of *n*-butane to maleic anhydride. However, a consensus concerning the relevance of these minority phases in the active catalyst has not yet been reached.

The phases γ- and δ-$VOPO_4$, which have been known for 20 years [2], have so far resisted any detailed structural characterization. Two different hypothetical structure models have been proposed in the literature for each of these phases [2, 3], although, the respective models have never been checked experimentally.

Recently, we have successfully determined the crystal structures of ε- and δ-$VOPO_4$. Thus, the structures of all known polymorphs, with the exception of γ-$VOPO_4$, are now characterized in sufficient detail to discuss the general trends in the structural chemistry of vanadyl phosphates in a systematic way.

Results

The determined crystal structure of ε-$VOPO_4$ confirms the features predicted in the literature [4]. This phase follows the same structural building principles as the β form, while exhibiting a different connectivity of the building blocks and topotactic relationship to monoclinic $VPO_4 \cdot H_2O$. In comparison to a recently published, very similar structure model [1], our structure solution yields a better agreement with the experimental data.

The structure determination of δ-$VOPO_4$ disproves both the hypothetical structure models found commonly in the literature. Instead, a close structural relationship to the ω polymorph [5] is found. In contrast to ω-$VOPO_4$, however, the crystal structure of the δ form is ordered.

All polymorphs of $VOPO_4$ that have had their structures solved exhibit the following common characteristics: each distorted VO_6 octahedron features one short (V=O), four medium (V-O) and one long (V···O) vanadium oxygen bond. Each octahedron shares a corner with four different PO_4 tetrahedra, as well as with two more *trans*-positioned octahedra. Thus, the octahedra form infinite chains, the backbone of which can be described as $[V{=}O{\cdots}V{=}O{\cdots}]_n$. Because of the pronounced asymmetry in the bonding situation, these chains have a direction in addition to their general orientation. The various polymorphs may now be grouped according to the following attributes: (i) arrangement of the chains of octahedra; (ii) number of chains linked by a single phosphate tetrahedron; (iii) dimensionality of the structure when neglecting V···O as a bond. The application of these criteria to the $VOPO_4$ polymorphs results in their subdivision into three structural families, with two members in each group.

Literature

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