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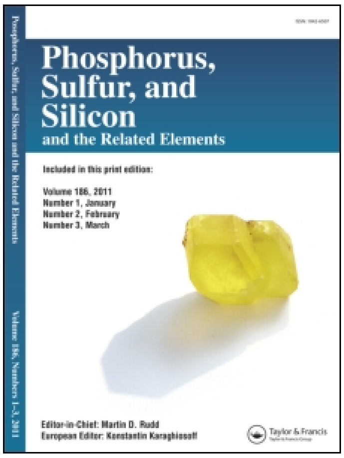

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NEW ASPECTS OF SOLID STATE TRANSFORMATION OF VANADIUM PHOSPHATES USED AS CATALYSTS FOR SELECTIVE OXIDATION OR AMMOXIDATION REACTIONS

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Abstract The influence of anion doping on the formation and properties of vanadyl pyrophosphates starting from $VOHPO_4 \cdot 0{,}5\ H_2O$ as well as the formation of ammonium containing vanadyl pyrophosphates from different vanadium monophosphates under the conditions of the ammoxidation process have been studied. Structural aspects of solid state transformations of these compounds and catalytical properties of various in this way obtained vanadium phosphates are discussed.

Vanadium phosphates of different structures are suitable precursors of very active and selective catalysts for the oxidation of C_4-hydrocarbons to maleic anhydride as well as for the ammoxidation of methylaromatics and methylheteroaromatics to the corresponding nitriles. Among the wide variety of vanadium containig phosphates the hemihydrate $VO(HPO_4) \cdot 0{,}5\ H_2O$ and the oxovanadium(IV) diphosphate, $(VO)_2P_2O_7$, play an outstanding role, especially for the selective oxidation of butane.

In earlier studies it was found that sulfuric acid has a directive influence to the formation of $VO(HPO_4) \cdot 0{,}5\ H_2O$ from aqueous solutions[1]. As we have found in further investigations, sulfate is incorporated statistically in the crystal lattice. On heating of this sulfate-doped precursors catalysts for the selective oxidation of butane are obtained which show increased catalytic performance compared to sulfate-free samples.

$$2\ VO(HPO_4) \cdot 0{,}5\ H_2O \xrightarrow{470°C} (VO)_2P_2O_7 + 2\ H_2O$$

The yield of $VO(HPO_4)\cdot 0,5\ H_2O$ and the content of incorporated sulfate depends to a high degree on the starting compound and on the amounts of sulfuric acid used[2]. Methane sulfonic and benzene sulfonic acid also act directive to the formation and crystallization of the hemihydrate. Whereas sulfate is incorporated into the hemihydrate lattice up to about 10% substitution of HPO_4^{2-} by SO_4^{2-} probably from steric reasons CH_3SO_3H will inserted only in small extent and $C_6H_5SO_3H$ not at all.

The differences concerning the behaviour of sulfate incorporation between different starting materials indicate that structural elements of the used vanadium phosphates are still present in the aqueous solutions influencing the doping process. Furthermore, sulfuric acid and the sulfonic acids, respectively, stimulate not only the nucleation of $VO(HPO_4)\cdot 0,5\ H_2O$ but also the cristal growth resulting in samples with low cristallinity.

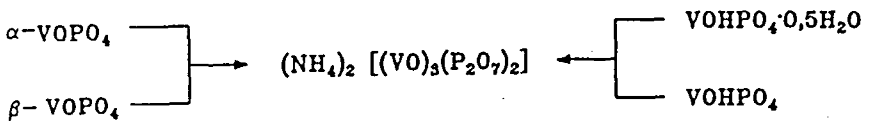
On heating of precursors obtained in this way samples of $(VO)_2P_2O_7$ are formed which show X-ray patterns with distinct broader reflections than it was found for undoped specimens (Table 1)

TABLE 1 Position and Full Width Half Maximum (FWHM) of the {020} and {204} X-ray reflections for $(VO)_2P_2O_7$ samples with varying doping agents

	{020}		{204}	
Doping agent	Position [2Θ]	FWHM [2Θ]	Position [2Θ]	FWHM [2Θ]
-	22.942(2)	0.280(5)	28.447(1)	0.206(3)
H_2SO_4	22.893(4)	0.498(12)	28.427(2)	0.298(5)
CH_3SO_3H	22.897(9)	0.940(33)	28.423(3)	0.354(8)
$C_6H_5SO_3H$	22.871(8)	1.082(33)	28.453(3)	0.415(8)

The influence of the degree of sulfate doping on the structure of the hemihydrate and the vandyl pyrophosphate was also studied by ESR spectroscopy. In the case of the hemihydrate the continuous change of line width and relative signal intensity in dependence of the sulfate content point to a statistical incorporation of the SO_4 tetrahedra. By studying the dehydration of different sulfate doped samples of the hemihydrate in a high-temperature resonator it was found that differently from the $VO(HPO_4)\cdot 0,5\ H_2O$ the arrangement of sulfate in the lattice of $(VO)_2P_2O_7$ does not occur in a statistical way but in form of local VO_6-SO_4 clusters.

Recently, it was found that the interaction of various vanadium monophosphates with the ammoxidation feed leads to structural transformations of the precursor, generating new phases, e.g. NH_4^+-containing vanadium diphosphates[3].



Now, the structural transformation of vanadium phosphate hemihydrate, $VO(HPO_4) \cdot 0{,}5\ H_2O$ *into ammonium vanadyl pyrophosphate* $(NH_4)_2[(VO)_3(P_2O_7)_2]$ *during* the ammoxidation of substituted methylaromatics was studied in detail by FTIR, XRD, and Raman spectroscopy. This solid state transformation can take place in an NH_3/O_2 environment without participation of aromatics. It probably proceeds via an intermediate phase which has a lamellar structure. The transformation is finished within 10 hours under the reaction conditions. Treatment only with NH_3 leads to destruction of the structure of the hemihydrate. The first step seems to be the formation of an intercalation compound which will be then transformed into the layer-like β-$(NH_4)_2[(VO)_3(P_2O_7)_2]$. This compound is not stable under the conditions of ammoxidation and invert to the α-modification:

$$VO(HPO_4) \cdot 0{,}5\ H_2O \Rightarrow \underset{\text{compound}}{\text{intercalation}} \Rightarrow \beta\text{-}(NH_4)_2[(VO)_3(P_2O_7)_2] \Rightarrow \alpha\text{-}(NH_4)_2[(VO)_3(P_2O_7)_2]$$

From stoichiometrical reasons one or more vanadium-rich compounds should be formed during the transformation. The investigation by FTIR and Raman spectroscopy suggests the formation of vanadate-like compounds but other vanadium compounds as the oxides V_2O_4 or V_4O_9 may also be formed:

$$8\ VO(HPO_4) \cdot 0{,}5\ H_2O + 10\ NH_3 + 0{,}5\ O_2 \rightarrow 2\ (NH_4)_2[(VO)_3(P_2O_7)_2] + 2\ \text{'}(NH_4)_3VO_4\text{'} + 3\ H_2O$$

$$10\ VO(HPO_4) \cdot 0{,}5\ H_2O + 8\ NH_3 + 0{,}5\ O_2 \rightarrow 2\ (NH_4)_2[(VO)_3(P_2O_7)_2] + V_4O_9 + 12\ H_2O$$

However, V_2O_4 is infrared and Raman inactive. To clear up the kind of vanadium-rich compound further investigations are in progress. From the catalytic tests it is evident that this up to now unknown vanadium compound plays an important role for the catalytic performance of the catalyst system. This was shown by comparison of the catalytic activity and selectivity of the catalyst, obtained from the hemihydrate during the ammoxidation and a pure α-$(NH_4)_2[(VO)_3(P_2O_7)_2]$, prepared from ammonium hydrogenphosphate and vanadium pentoxide under special conditions. This different behaviour of the two catalysts can be explained by a cooperative mechanism involving the known crystalline α-$(NH_4)_2[(VO)_3(P_2O_7)_2]$ phase and the up to now unknown non-crystalline vanadium-rich phase (Remote Control Mechanism).

Furthermore, the thermal behaviour of the ammonium vanadyl diphosphate phase has been studied by using temperature programmed methods in combination with a quadrupol mass spectrometer. In the following scheme the results are summarized:

$$\begin{array}{lcl}
\alpha\text{-}(NH_4)_2[(VO)_3(P_2O_7)_2] & \longrightarrow & \underset{\textbf{(A)}}{[(VO)_3(P_2O_6NH_2)_2]} + 2\,H_2O \\
2\,\alpha\text{-}(NH_4)_2[(VO)_3(P_2O_7)_2] & \longrightarrow & 2\,\underset{\textbf{(B)}}{[(VO)_3(P_2O_6OH)_2]} + 4\,NH_3 \\
A + 2\,B & \longrightarrow & 2\,(VO)_3[P_3O_9N] + 3\,VO(PO_3)_2 + 4\,H_2O \\
\hline
\end{array}$$

$$3\,\alpha\text{-}(NH_4)_2[(VO)_3(P_2O_7)_2] \rightarrow 2\,(VO)_3[P_3O_9N] + 3\,VO(PO_3)_2 + 6\,H_2O + 4\,NH_3$$

$$2\,(VO)_3[P_3O_9N] \longrightarrow V_4[P_2O_7]_3 + N_2 + V_2O_3$$

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