

PREPARATION AND THERMAL BEHAVIOUR OF OXOVANADIUM(IV) PHOSPHATES AND HYDROGENPHOSPHATES

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Dedicated to Professor Mihkel Veiderma on the occasion of his 70th birthday

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Abstract. The results of a systematic study on the conditions of the formation of different oxovanadium(IV) hydrogenphosphate and orthophosphate hydrates in dependence on the concentration, temperature, and pressure in the system $V_2O_5/H_3PO_4/(COOH)_2/H_2O$ are reported. Some structural data and the thermal dehydration of different oxovanadium(IV) orthophosphate hydrates are discussed.

Key words: oxovanadium(IV) hydrogenphosphate hydrates, oxovanadium(IV) orthophosphate hydrates, hydrothermal synthesis, X-ray powder diffraction, DTA.

INTRODUCTION

Vanadiumphosphates are well known to be active and selective catalysts for the oxidation of n-butane to maleic anhydride (see e.g. ref. [1] and references therein). Furthermore, these compounds have been used as catalysts for the ammoxidation of lower hydrocarbons [2–4] as well as methylaromatics and methylheteroaromatics [5, 6] to the corresponding imides and nitriles. From the large number of vanadiumphosphates, oxovanadium(IV) diphosphate $(VO)_2P_2O_7$

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plays an outstanding role. Numerous papers are concerned with the catalytic behaviour and characterization of $(VO)_2P_2O_7$ catalysts, which normally are prepared from oxovanadium(IV) hydrogenphosphates, especially from the hemihydrate $VOHPO_4 \cdot 0.5H_2O$.

Vanadyl hydrogenphosphate hydrates, $VOHPO_4 \cdot nH_2O$, show a great structural variety [7–12]. They can be classified into three structural types characterized by their main structural units: (i) edge-linked dimeric $[VO_6]$ octahedra* ($n = 0.5$), (ii) chains of corner-linked $[VO_6]$ octahedra ($n = 1, 2(\alpha), 3$), and (iii) isolated $[VO_6]$ octahedra ($n = 2(\beta), 4$). The up to now known and structurally characterized oxovanadium(IV) hydrogenphosphates and phosphates are summarized in Table 1.

Table 1. Known oxovanadium(IV) phosphates and hydrogenphosphates

Compound	Crystal system	Ref.
$VOHPO_4$	Orthorhombic	8
$VOHPO_4 \cdot 0.5H_2O$	Orthorhombic	9, 10
$VOHPO_4 \cdot H_2O$	Monoclinic	7
α - $VOHPO_4 \cdot 2H_2O$	Monoclinic	7
β - $VOHPO_4 \cdot 2H_2O$	Triclinic	7
$VOHPO_4 \cdot 3H_2O$	Monoclinic	7
$VOHPO_4 \cdot 4H_2O$	Triclinic	9
$(VO)_3(PO_4)_2 \cdot 9H_2O$	Monoclinic	11
$VO(H_2PO_4)_2$	Orthorhombic	12

Because of the enormous importance of the oxovanadium(IV) hydrogenphosphates, particularly of the hemihydrate, as precursors of vanadiumphosphate catalysts a multitude of papers in the patent literature are concerned with the preparation of this kind of compounds. Two different main synthetic routes have been reported [3]:

– Reduction of vanadium(V) compounds as e.g. V_2O_5 in an aqueous medium in the presence of phosphoric acid followed by evaporating to the dry state or crystallization from a concentrated solution.

– Reduction of vanadium(V) compounds in an organic medium mainly by alcohols such as isopropanol or benzyl alcohol, addition of phosphoric acid, and filtering off the formed solid reaction product afterwards.

The preparation of hemihydrate by reduction in an organic medium is the way used because the yields of the precursor are nearly quantitative. Its disadvantages lie in the costly and complicated transformation process into the active

* The coordination of vanadium in all oxovanadium compounds containing the $V^{IV}O^+$ group is not really octahedral, but consists of $[OVO_4]$ -pyramids, which are mostly connected via longer V–O bonds with neighbouring $[VO_x]$ polyhedra in the *trans* position to the vanadyl oxygen (V=O) forming the coordination $[VO_6]$ commonly described as octahedral.

pyrophosphate catalyst. Furthermore this precursor and the catalyst prepared from it are not well suited for basic studies on the mode of action of this catalytic active system because of organic inclusions. The disadvantages of the synthesis in an aqueous medium are the poor reproducibility and the lower efficiency of the catalysts prepared from these precursors.

In connection with our studies on the reaction mechanism of the selective oxidation of n-butane to maleic anhydride on $(VO)_2P_2O_7$ catalysts it was necessary to start from reproducible, well defined hemihydrate precursors. Therefore we have investigated in detail the reduction of vanadium(V) oxide with oxalic acid in the presence of phosphoric acid in an aqueous solution to find out the exact conditions of the formation of various vanadium(IV) hydrogenphosphates and phosphates, depending on different reaction conditions, such as concentration, temperature, and pressure [13]. The main purpose of these studies was to develop a new synthetic variant that allows preparation of well characterized hemihydrate in a reproducible way in high yields. The results of this part of the study have already been published elsewhere [14].

Here some new results concerning the crystallization behaviour of oxovanadium(IV) hydrogenphosphate hydrates and phosphate hydrates under hydrothermal conditions and the thermal dehydration of some of these compounds will be reported.

EXPERIMENTAL

Oxovanadium(IV) phosphates were obtained from a standard solution, prepared by slowly adding 43.5 g V_2O_5 to a solution from 48 mL 85% H_3PO_4 , 45.3 g oxalic acid dihydrate, and 150 mL water at $70^\circ C$ [15]. The solution was heated for 10 h and then concentrated to a concentration of about 3 mol V/L. This parent solution was taken for the preparation of the different oxovanadium(IV) phosphates, mainly under hydrothermal conditions.

Oxovanadium(IV) hydrogenphosphate hydrates

Single crystals of $VOHPO_4 \cdot 0.5H_2O$ were obtained from the parent solution, which was heated to $100^\circ C$ in a closed round bottom flask and kept at this temperature for 3 days, and after that held at $90^\circ C$ for 2 weeks.

Single crystals of $\mathbf{A}\text{-}VOHPO_4 \cdot 2H_2O$ were obtained from a diluted parent solution (about 1.6 mol V/L) after heating at $90^\circ C$ in an autoclave for 10 days. The product was suspended in water, filtered off, washed with water, and dried at $50^\circ C$.

Only a few single crystals of the new dihydrate $\mathbf{G}\text{-}VOHPO_4 \cdot 2H_2O$ could be obtained from a concentrated parent solution (about 4.2 mol V/L) after heating at $100^\circ C$ in an autoclave for 2 weeks. The solid crystallization product was mostly accompanied by $\mathbf{A}\text{-}VOHPO_4 \cdot 2H_2O$ and the hemihydrate.

$\text{VOHPO}_4 \cdot 4\text{H}_2\text{O}$ was obtained in needle-shaped crystals from the parent solution, which was warmed at 70°C in a closed round bottom flask for 2 weeks.

The elemental analyses (vanadium and phosphorus) of all oxovanadium(IV) hydrogenphosphate hydrates were in good accordance with the calculated values.

Oxovanadium(IV) orthophosphate hydrates

Oxovanadium(IV) orthophosphates are obtained under the same conditions as described above from diluted solutions, i.e. with decreasing the concentration of protons.

$\alpha\text{-(VO)}_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ crystallizes from a parent solution, diluted in a ratio 1:16 with water, which was held at 140°C in an autoclave for 2 days. The light green polycrystalline material was filtered off, washed with water, and dried at 70°C for 24 h (elemental analysis: V 30.6%, P 12.4%; calc.: V 30.63%, P 12.41%).

$\alpha\text{-(VO)}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$ was obtained from a diluted standard solution (1:32) after heating at 110°C in an autoclave for 2 days. The formed light green crystals were separated by filtering, washed with water, and air dried at 25°C (elemental analysis: V 29.5%, P 12.3%; calc.: V 29.57%, P 11.98%).

$(\text{VO})_3(\text{PO}_4)_2 \cdot 9\text{H}_2\text{O}$ was obtained from a 1:4 diluted parent solution, which was maintained for one week at 90°C in an autoclave. The coarse-crystalline bright deep blue platelets were filtered, washed with water, and air dried at 50°C (elemental analysis: V 27.2%, P 11.3%; calc.: V 27.64%, P 11.20%).

Crystallization experiments were also carried out under an increased nitrogen pressure at 100 bar. Under these conditions new modifications of orthophosphate six- and seven-hydrate were formed besides the known phases of oxovanadium(IV) hydrogenphosphates.

$\beta\text{-(VO)}_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ was obtained from a diluted parent solution (1:8) under 100 bar at 115°C in the form of light green microcrystalline powder, which was filtered and dried at 50°C (elemental analysis: V 31.5%, P 12.5%; calc.: V 30.63%, P 12.41%).

$\beta\text{-(VO)}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$ was formed under the same conditions as β -six-hydrate but at 90°C (elemental analysis: V 29.2%, P 12.0%; calc.: V 29.57%, P 11.98%).

$\text{H}_2[(\text{VO})_2(\text{PO}_4)_2(\text{COO})_2] \cdot 6\text{H}_2\text{O}$ was prepared in the following way: the parent solution was slowly thickened in a drying oven at 130°C , then suspended with water and filtered from the solid. The filtrate was evaporated in the drying oven to a viscous consistence. After storage at room temperature in the air for several months the light green oxalatophosphate crystallized spontaneously. The product was washed with a small amount of water and dried at 50°C (elemental analysis: V 17.2%, P 12.1%, C 4.6%; calc.: V 19.44%, P 11.8%, C 4.3%).

Analytical techniques: Vanadium and its oxidation state were determined volumetrically [16], and the phosphate content was determined gravimetrically as quinoline molybdophosphate [17].

RESULTS AND DISCUSSION

Systematic investigation of the crystallization behaviour of oxovanadium(IV) phosphates in the system V_2O_5 , phosphoric acid, and an excess oxalic acid as a reducing agent in dependence on concentration, temperature, and pressure under hydrothermal conditions yielded, as a main result, a possibility to determine the optimum ranges of crystallization for the different hydrogenphosphate and orthophosphate phases [15]. From most of these compounds single crystals could be obtained and so it was possible to improve data on the structure reported in the literature (see Table 1) by X-ray crystal-structure analysis for α - $VOHPO_4 \cdot 2H_2O$ [18] and $VOHPO_4 \cdot 4H_2O$ [19].

In addition to the already known phases three new compounds could be isolated: γ - $VOHPO_4 \cdot 2H_2O$ and β - $(VO)_3(PO_4)_2 \cdot nH_2O$ ($n = 6$ or 7), the last two at increased pressure instead of the corresponding α -phases obtained under "normal" hydrothermal conditions.

Further it was found that upon pressure increase to 100 bar the regions of phase limit for the different oxovanadium(IV) hydrogenphosphates are shifting by about $30^\circ C$ to higher temperatures. Thus, α - $VOHPO_4 \cdot 2H_2O$ crystallizes under these conditions only in the small range between 125 and $135^\circ C$ from relatively concentrated solutions (2.6 – 4.2 mol V/L) whereas the range of formation under "normal" hydrothermal conditions lies between 85 and $105^\circ C$ and the concentrations are from about 0.6 to 4.2 mol V/L. The crystallization behaviour of the other phases is very similar: at 100 bar the formation of $VOHPO_4 \cdot 4H_2O$ is observed up to $115^\circ C$ while under intrinsic pressure it was found only up to $85^\circ C$. The temperature range for the formation of the hemihydrate $VOHPO_4 \cdot 0.5H_2O$ was found at 100 bar between 135 and $180^\circ C$ and under intrinsic pressure between 105 and $180^\circ C$. Under increased pressure crystallization occurred generally more slowly and mostly large crystals were obtained.

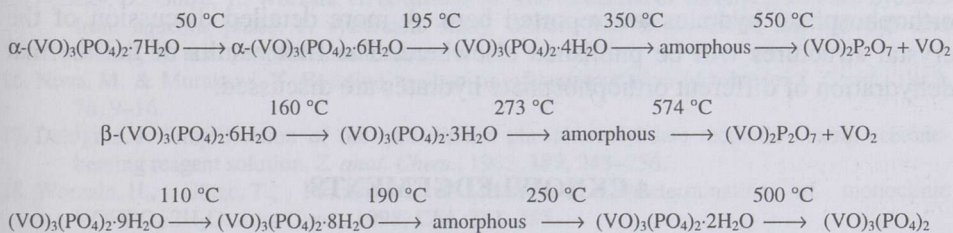
As described above, the oxovanadium(IV) orthophosphate hydrates were obtained as polycrystalline powders (or in the case of the nonahydrate also as single crystals) by hydrothermal synthesis. The unit cell data of these compounds (with the exception of the nonahydrate) were determined by X-ray powder diffraction analysis and are summarized in Table 2.

Comparison of the data on the structure of the hydrates indicates that there are extensive similarities between the respective α - or β -forms of the hexa- and heptahydrates. Thus, both α -forms crystallize in the triclinic system in the space group P-1, and both β -forms are monoclinic with the space group Cc (hexahydrate) and P-1 (heptahydrate). Also the cell parameters such as the lattice constants a , b , and c as well as angles are very similar for the α - and β -forms. Only the lattice constant a of the β -hexahydrate is about twice as big as that of the β -heptahydrate resulting in four formula units per unit cell compared with two formula units as was found in the case of the β -heptahydrate.

Table 2. Unit cell data of oxovanadium(IV) orthophosphate hydrates

Cell parameters	Compounds and crystal system				
	α -(VO) ₃ (PO ₄) ₂ ·6H ₂ O, triclinic	β -(VO) ₃ (PO ₄) ₂ ·6H ₂ O, monoclinic	α -(VO) ₃ (PO ₄) ₂ ·7H ₂ O, triclinic	β -(VO) ₃ (PO ₄) ₂ ·7H ₂ O, monoclinic	(VO) ₃ (PO ₄) ₂ ·9H ₂ O, monoclinic
a, Å	7.052	19.767	7.146	9.755	6.294
b, Å	9.909	7.290	10.043	7.421	16.62
c, Å	5.001	9.204	5.107	9.601	7.420
α , °	102.51	90	103.57	90	90
β , °	109.25	100.8	103.94	104.04	92.33
γ , °	83.17	90	84.28	90	90
Z	1	4	1	2	2
V, Å ³	321.7	1304.55	345.4	674.2	775.5

It also seemed to be of interest to study the thermal behaviour of the oxovanadium(IV) orthophosphate hydrates because of their potential suitability as precursors for vanadiumphosphate catalysts. For that dehydration was investigated with the help of a Guinier heating camera and differential thermogravimetry. On the basis of the obtained thermoanalytical and X-ray data the following scheme of dehydration was determined:



Scheme 1. Thermal behaviour of oxovanadium(IV) orthophosphate hydrates.

As can be seen the dehydration of α -(VO)₃(PO₄)₂·7H₂O begins at about 50 °C and leads to α -(VO)₃(PO₄)₂·6H₂O, which is stable up to about 200 °C. On further heating a second molecule of water is lost under the formation of a crystalline tetrahydrate and after increasing the temperature above 350 °C an amorphous phase is formed. Above 550 °C crystalline vanadyl pyrophosphate was detected. Because of stoichiometry it is assumed that amorphous vanadium dioxide is formed as a second reaction product.

The transition of α -(VO)₃(PO₄)₂·7H₂O into hexahydrate is reversible. Thus, after storing α -(VO)₃(PO₄)₂·6H₂O in air at room temperature for several days it will be rehydrated to heptahydrate as can be shown by X-ray powder diffraction.

The dehydration of β -(VO)₃(PO₄)₂·6H₂O proceeds distinctly differently from that of α -hexahydrate. In the DTA diagram two sharp endothermic peaks at 160

and 273°C can be observed, both corresponding to a loss 3 moles of crystal water. An exothermal peak at 574°C indicates the formation of crystalline pyrophosphate.

In the case of the nonahydrate $(VO)_3(PO_4)_2 \cdot 9H_2O$ in a first step up to 110°C one mole of water is liberated under the formation of a crystalline octahydrate. At about 190°C it is transformed with the loss of 5 moles of water into an amorphous phase. At around 250°C further dehydration leads to a crystalline phase of the composition $(VO)_3(PO_4)_2 \cdot 2H_2O$, from which a new crystalline phase, probably a water-free orthophosphate, is formed between 400 and 550°C. A detailed characterization of these two crystalline phases is not yet possible. Further studies are in progress.

SUMMARY

Our systematic investigation of the oxovanadium(IV) phosphate system has shown that depending on the concentration (which was varied by dilution of a starting solution with a distinct V/P ratio), temperature, and pressure limited ranges of formation exist for different oxovanadium(IV) hydrogenphosphate and orthophosphate hydrate phases. This has made possible a selective synthesis of distinct phases. Also preparation of some new hydrogenphosphate and phosphate phases has become possible. Some crystallographic data on the oxovanadium(IV) orthophosphate hydrates are reported here. A more detailed discussion of the crystal structures will be published elsewhere. The first results of the thermal dehydration of different orthophosphate hydrates are discussed.

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VANAADIUM(IV)OKSIIDFOSFAATIDE JA -VESINIKFOSFAATIDE SAAMINE JA NENDE TERMIISED OMADUSED

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On määratud vanaadium(IV)oksiidfosfaatide ja -vesinikfosfaatide hüdraatide saamise tingimused süsteemis $\text{V}_2\text{O}_5/\text{H}_3\text{PO}_4/(\text{COOH})_2/\text{H}_2\text{O}$ sõltuvalt lähtelahuse kontsentratsioonist, termotöötamise temperatuurist ja rõhust. On esitatud andmed saadud vanaadium(IV)oksiidfosfaatide hüdraatide struktuuri ja termilise dehüdratsiooni käigu kohta.