J Incl Phenom Macrocycl Chem (2012) 73:33–53
DOI 10.1007/s10847-011-0097-1

REVIEW ARTICLE

Intercalation chemistry of layered vanadyl phosphate: a review

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Received: 20 September 2011 / Accepted: 7 December 2011 / Published online: 8 February 2012
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Abstract The intercalation chemistry of layered α_I modification of vanadyl phosphate and vanadyl phosphate dihydrate is reviewed. The focus is on neutral molecular guests and on metal cations used as guest species. The basic condition for the ability of the neutral molecules to be intercalated into vanadyl phosphate is a presence of an electron donor atom in them. The most commonly used guest compounds are those containing oxygen, nitrogen or sulfur as electron donor atoms. Regarding the molecules containing oxygen, various compounds were used as molecular guests starting from water to alcohols, ethers, aldehydes, ketones, carboxylic acids, lactones, and esters. An arrangement of the guest molecules in the interlayer space is discussed in connection with the data obtained by powder X-ray diffraction, thermogravimetry, IR and Raman spectroscopies, and solid-state NMR. In some cases, the local structure was suggested on the basis of quantum chemical calculations. Besides of those O-donor guests, also N-donor guests such as amines, nitriles and nitrogenous heterocycles and S-donor guests such as tetrathiafulvalene were intercalated into $VOPO_4$. Also intercalates of complexes like ferrocene were prepared. Intercalation of cations is accompanied by a reduction of vanadium(V) to vanadium(IV). In this kind of intercalation reactions, an iodide of the intercalated cation is often used as it serves both as a mild reduction agent and as a source of the intercalated species. Intercalates of alkali metals, hydronium and ammonium were prepared and characterized. In the case of lithium and sodium intercalates, a staging phenomenon was observed. These redox intercalated vanadyl phosphates undergo ion exchange reactions which are discussed from the point of the nature of cations involved in the exchange. Vanadyl phosphates in which a part of vanadium atom is replaced by other metals are also briefly reviewed.

Keywords Vanadyl phosphate · Intercalation · Layered phosphates · Review

Vanadyl phosphates

Vanadium phosphates represent a group of compounds having a very rich structural chemistry due to the possibility of vanadium to exist in three oxidation states and due to the variety of ways in which phosphate tetrahedra and vanadium polyhedra are linked together. Vanadium phosphates are extensively studied because of their prospective utilization as catalysts or precursors of catalysts for selective oxidations [1–3], in biodiesel production [4, 5], or Diels–Alder cycloadditions [6]. The catalytic properties of $VOPO_4$ supported on various oxides for the oxidative dehydrogenation of propane [7] and for the oxidative dehydrogenation of ethane to ethylene [8] has been studied. Besides $VOPO_4$, also niobyl phosphate has been tested as a starting materials from which a catalyst for the selective oxidation of ethane to ethylene was prepared by reduction in hydrogen [9].

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Another potential application of vanadium phosphates stems from their electrochemical properties. From this point of view, vanadyl phosphates are most interesting. The simplest vanadyl phosphate, $VOPO_4$, exists in several structural modifications: α_I-$VOPO_4$, α_{II}-$VOPO_4$, β-$VOPO_4$, γ- and δ-$VOPO_4$. Regarding the intercalation reactions the α_I form is the most interesting. The tetragonal layers of α_I ($a = 6.20$ Å, $c = 4.11$ Å) [10] and α_{II} ($a = 6.014$ Å, $c = 4.434$ Å) [11] are formed from vertex-sharing phosphate tetrahedra PO_4 linked to VO_5 square pyramids. These modifications differ by the position of the vanadium atoms within the octahedra. In the α_I-modification, the vanadium and phosphorus atoms are situated on the same side of the equatorial plane of the octahedron, whereas in α_{II}-$VOPO_4$ the vanadium and phosphorus atoms lie on alternate sides of that plane. In the α_I-modification, the coordination polyhedron of the vanadium atom is completed to an octahedron by the peak oxygen atom of the square pyramid from the adjacent layer (see Fig. 1). α_I-$VOPO_4$ can be prepared by thermal dehydration of layered $VOPO_4 \cdot 2H_2O$ near 400 °C at an oxygen pressure of 101.3 kPa [12] and α_{II}-$VOPO_4$ can be obtained by heating of a mixture of oxides [11]. In contrast to the α_I-modification, the α_{II}-modification does not undergo any intercalation reactions.

Three-dimensional structure of orthorhombic β-$VOPO_4$ ($a = 7.770$ Å, $b = 6.143$ Å, $c = 6.965$ Å) [13] is formed from a mixture of ammonium phosphate and ammonium metavanadate at 595 °C [14] or by the transformation of α_I-modification at 810 °C [10]. The modifications γ- and δ-$VOPO_4$ [15–17] with structures related to vanadyl pyrophosphate $(V^{IV}O)_2P_2O_7$, and ε-$VOPO_4$ [18] related to the β-modification are all from the view point of intercalation reactions uninteresting. Recently, the crystal structure of δ-VOPO4 was determined from powder X-ray diffraction data [19]. A ω-$VOPO_4$ modification can be prepared by calcination of $VOHPO_4 \cdot 0.5H_2O$ at 773 K in a N_2 stream for 3 h followed by calcination at 873 K in an O_2 stream for 14 h [20–22]. All these modifications were tested as cathodes for Li ion rechargeable batteries [20, 21, 23, 24].

The structure of α-$VOPO_4 \cdot 2H_2O$ was determined from the analogy with results of neutron diffraction of $VOPO_4 \cdot 2D_2O$ [25] and on the basis of X-ray diffraction [26]. The layers in $VOPO_4 \cdot 2H_2O$ have the same structure as the sheet of the anhydrous α_I-vanadyl phosphate. Coordination number six of the vanadium atom is reached by the coordination of the oxygen atom from the water molecule (Fig. 2). The structure consists of distorted vanadium(V)–oxygen octahedra which are condensed with four phosphate tetrahedra in their equatorial planes. One of the axial group in each octahedron is a short V=O bond, while the other is a replaceable water molecule. The space group *P4/nmm*, reported on the basis of X-ray diffraction, differs from *P4/n* found by neutron diffraction due to the limited ability of the X-ray diffraction method to find reliably the hydrogen positions. As follows from the neutron diffraction data, the first water molecule is coordinated to the vanadium atom with two possible orientations and the second one can occupy two possible positions, creating H-bridges either with the top or bottom phosphate oxygens.

Vanadyl phosphate dihydrate can be easily prepared by refluxing vanadium oxide suspended in concentrated trihydrogen phosphoric acid for several days [27]. Well crystallized vanadyl phosphate dihydrate can be obtained by the reaction of phosphoric acid with vanadium propoxide $VO(OR)_3$ (R = *n*-propyl, i-propyl) [28]. High energy density $VOPO_4 \cdot 2H_2O$ cathode material was prepared by ultrasonic irradiation of aqueous solution containing V_2O_5 and H_3PO_4 [29]. New method for the synthesis of $VOPO_4 \cdot 2H_2O$ has been proposed based on sonochemical treatment of he starting materials which allows to substantially decrease/shorten the reaction time from hours to 15 min [30].

The first review on intercalation reactions of vanadyl phosphate was published more than 10 years ago [31]. Since then, many new intercalates has been prepared and their structure or the arrangement of the guest molecules in the interlayer space has been proposed. This paper reviews the progress made in the last decade in this field.

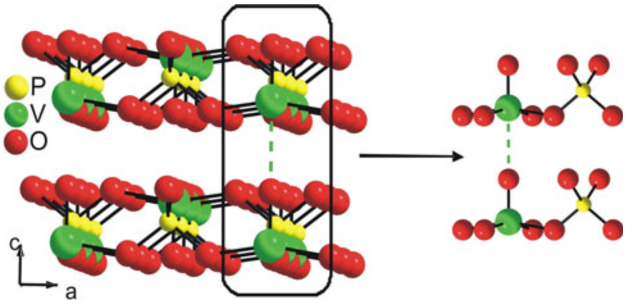

Fig. 1 Structure of the $VOPO_4$ layers viewed along the *a* axis. On the left, the coordination of the terminal oxygen to the vanadium atom of the neighboring layer is shown in detail (*dashed line*)

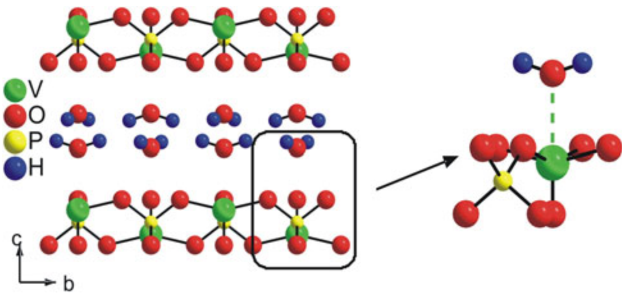

Fig. 2 Structure of the $VOPO_4 \cdot 2H_2O$ layers viewed along the *a* axis. On the left, the coordination of oxygen from the water molecule to the vanadium atom is shown in detail

Compounds derived from vanadyl phosphate dihydrate by replacement of a part of the vanadium atoms

Hydrated mixed vanadium–niobium phosphates occurs as a solid solution of vanadyl phosphate in niobyl phosphate with the formula $V_xNb_{(1-x)}OPO_4{\cdot}yH_2O$ ($x \leq 0.21$; $y = 2.6$–2.8). These compounds can be prepared by addition of H_3PO_4 into a solution of Nb_2O_5 and V_2O_5 in aqueous HF followed by heating until a crystalline solid precipitated [32, 33]. The products have a tetragonal structure derived from $NbOPO_4{\cdot}3H_2O$. The c parameter is twice as large as the basal spacing which indicates that the layers have a distribution sequence along the c-axis. These mixed phosphates can be intercalated with amines [34, 35] amides [36], and N-heterocycles [35]. Also redox intercalations of cations were described [33, 37].

Up to 7% of the vanadium atoms can be replaced with chromium(V) by mixing a $VOPO_4{\cdot}2H_2O$ xerogel with a CrO_3 solution [38]. The presence of Cr(V) was verified by EPR.

Layered crystalline solids with general formula $[M(H_2O)]_x(VO)_{1-x}PO_4{\cdot}2H_2O$ (M = Al, Cr, Fe, Ga, Mn; $x = 0.15$–0.20) have been prepared by a reaction of solid V_2O_5 with a boiling aqueous solution of phosphoric acid and a corresponding metal salt [39–42]. The structure of these compounds is derived from the structure of $VOPO_4{\cdot}2H_2O$ by substitution of $[M(H_2O)]^{3+}$ for a part of vanadyl groups $(VO)^{3+}$. The substituting groups are built in the layers randomly as it was observed from the magnetic susceptibility measurements of the paramagnetic ions. Manganese-modified vanadyl phosphate has been submitted to a reaction with selected liquid molecular guests and the intercalates prepared were compared with corresponding $VOPO_4$ intercalates [40]. Thermal and sorption behavior of these compounds was studied using powder X-ray diffraction, gas chromatography, XPS, TG/DTA and NH_3-TPD techniques [43–46]. M^{3+}-modified vanadyl phosphates were tested as precursors of catalysts for 1-butene isomerization [47], ammonia oxidation [48], ammoxidation of toluene [49], selective oxidation of 5-hydroxymethyl-2-furaldehyde to furan-2,5-dicarboxaldehyde [50], oxidative dehydrogenation of ethane [51], and transesterification of soybean oil [5].

Intercalation reaction of α_I-$VOPO_4$ and α-$VOPO_4{\cdot}2H_2O$

Intercalation reactions of α_I-$VOPO_4$ and α-$VOPO_4{\cdot}2H_2O$ can be divided into two groups.

(i) The first one includes reactions which proceed without redox changes and lead to the formation of layered complexes. If the guest molecules penetrate into the structure of anhydrous vanadyl phosphate, the $(VOPO_4)_\infty$ layers are drawn away from each other and the sixth coordination position of the vanadium atom is occupied by a donor atom of the guest molecule. Vanadyl phosphate dihydrate, which can be considered as an intercalate of water into $VOPO_4$, may serve as an example. Most intercalation reactions of vanadyl phosphate are in fact reintercalation reactions of vanadyl phosphate dihydrate. At that, water molecules in the interlayer space are replaced by other neutral molecules which can play similar roles in the structure of a new intercalation compound. No change in the uncharged nature of the layers is implied during this reaction. The reintercalation reaction of dihydrate occurs usually easier than the intercalation reaction of anhydrous vanadyl phosphate with the same molecular guest.

(ii) The second type of intercalation reactions is analogous to the reactions of reducible binary oxides and layered dichalcogenides. This type of the intercalation reactions involves a reduction of a fraction of the vanadium(V) atoms to vanadium(IV) with a concomitant intercalation of cations to counterbalance the induced negative layer charge. The structure of the host layers is preserved during the reaction, but the distance between the adjacent $(VOPO_4)_\infty$ layers decreases due to stronger interaction between positively charged guest species and negatively charged layers.

To the best of our knowledge, a total structure of a $VOPO_4$ intercalate containing molecular guests has not been determined yet. The main reason is that single crystals of sufficient size and quality for conventional single-crystal diffraction can not be prepared. Structure determination from powder diffraction data is complicated by a large overlap of reflections and, in addition, by the structural disorder and preferred orientation of crystallites. In such a case molecular mechanics simulations combined with powder X-ray diffraction and supported with vibrational spectroscopy can be used for suggesting the structure of the intercalate. Infrared and Raman spectroscopies can be used to distinguish various modes of the host-guest interaction.

In the case of intercalates of homologous series of guests, an angle α under which the aliphatic chains of the guest molecules are tilted to the plane of the host layer can be determined from the X-ray powder data. It is presumed that the straight chains of the guest have an *all-trans* configuration with all carbon atoms lying in the same plane [52]. The value of α is calculated from the increment of the basal spacing given by the prolongation of the guest chain by one carbon atom ($\Delta c/\Delta n$) according to the relationship

$$\alpha = \arcsin\left(\frac{1}{m} \cdot \frac{\Delta c/\Delta n}{\Delta h/\Delta n}\right)$$

where m is a number of the guest-molecule layers in the interlayer space of the intercalate and $(\Delta h/\Delta n) = 1.279$ Å is an increment of the chain length per one carbon atom presuming that the chains are perpendicular to the host layers.

Intercalation of molecular guests

Intercalation and deintercalation of water

The water content and consequently the basal spacing of vanadyl phosphate are influenced by relative humidity (RH) of the surrounding atmosphere [53]. Anhydrous vanadyl phosphate is stable if the RH is equal to zero, monohydrate has no distinct region of the occurrence, dihydrate exists in the region of RH between 15 and 50%, and the highly hydrated phase $VOPO_4 \cdot 5H_2O$ with the basal spacing of 10.5 Å has been observed at RH higher than 72%.

Thermal behavior of vanadyl phosphate dihydrate was studied using various experimental techniques. An anomalous decrease of the *c* parameter of the tetragonal lattice was observed in the temperature range 3–42 °C which is attributed to the hydrogen bonding changes with variation of temperature [54]. The course of the dehydration of $VOPO_4 \cdot 2H_2O$ leading to α_I-$VOPO_4$ has been studied by time-resolved X-ray diffraction, thermomechanical analysis, DTA, and thermoelectric power measurements [55]. The X-ray diffractograms indicate that the transformation of the dihydrate to monohydrate occurs mainly at about 43 °C and the practically pure monohydrate (the basal spacing of 6.3 Å) is present at 63 °C. The second dehydration step follows at about 80 °C, and the monohydrate is almost absent around 114 °C. The basal spacing of 4.18 Å for anhydrous vanadyl phosphate was found. Similar results were obtained by Casan et al. [56], but the values of dehydration temperature are strongly influenced by the experimental conditions (the method used, heating rate, amount of the sample). In accordance with the previous results reported for $VOPO_4 \cdot 2H_2O$ [12, 57], it can be assumed that the water evolved initially is that inserted into holes of the lattice, the remaining water being that directly coordinated to the vanadyl groups. The structure of vanadyl phosphate monohydrate (tetragonal cell, $a = 6.2203(2)$ Å, $c = 6.18867(7)$ Å) was determined from X-ray powder diffraction and the presence of stacking faults was confirmed using DFT-D calculations [58]. The thermomechanical measurements, TGA and thermoelectric power measurements confirmed two-step mechanism of dehydration. Kinetics of dehydration was studied using TGA, DTA and DSC methods and the activation energies, which are very similar for both steps of the dehydration, were calculated using the Kissinger's method [59].

Electrical transport properties of hydrated and anhydrous vanadyl phosphate were studied using ac/dc conductivity measurement, electromotoric force and thermoelectric power measurement [55, 60–62]. At room temperature, $VOPO_4 \cdot 2H_2O$ is a mixed protonic–electronic conductor with dominant protonic component. Proton conduction decreases with increasing temperature, due to the lower amount of the intercalated water, and vanishes at 70 °C concomitantly with the formation of $VOPO_4 \cdot H_2O$. The conductivity in anhydrous $VOPO_4$ is fully electronic as was demonstrated by means of the Seebeck effect measurement [55].

The course of the intercalation of water into α_I-$VOPO_4$ at room temperature has been studied by powder X-ray diffraction, infrared and Raman spectroscopies and thermomechanical analysis [63, 64]. Neither formation of vanadyl phosphate monohydrate nor staging was observed during the intercalation. The broadening and the shift of the positions of the (00*l*) lines in the diffractograms have been explained by the random stacking of the intercalated and nonintercalated layers in the sample [63]. Variable temperature X-ray diffraction was used for the study of the intercalation of water into anhydrous vanadyl phosphate when the latter was cooled in air. A formation of a small amount of monohydrate was observed [56].

Intercalation of alcohols and diols

Intercalations of alcohols into $VOPO_4$ structure were described firstly by Ladwig [65]. Intercalates of the composition $VOPO_4 \cdot xC_nH_{2n+1}OH$ can be prepared either by the reaction of the anhydrous $VOPO_4$ with an excess of liquid alcohol (only for $n = 1$–4) [66] or by the reaction of finely ground solid $VOPO_4 \cdot 2H_2O$ with liquid (or melted solid) alcohol (for $n = 2$–18) in a microwave field [67]. The absorption of microwaves by the water molecules present in the structure of the dihydrate results in a rapid removal of these molecules from the space between the $(VOPO_4)_\infty$ layers to the surrounding dry guest and in an exfoliation of the host. After finishing the exposition and partial cooling of the reaction mixture, the $(VOPO_4)_\infty$ layers are reassociated taking the molecules of the new guest between them and a microcrystalline intercalate containing two alcohol molecules per formula unit is formed. The dependence of the basal spacing of the intercalates on the number of the carbon atoms in the guest chain is linear with a slope of 2.58 (Fig. 3). The molecules of alcohols are placed between the host layers in a bimolecular arrangement, being anchored to them by donor–acceptor bonds between the oxygen atom of the OH group and the vanadium atom as well as by hydrogen bonds. The aliphatic chains of the intercalated alcohol molecules possess an *all-trans* configuration and their axes are perpendicular to the host layers (Fig. 4). The intercalate with methanol shows lower content of alcohol ($x = 1.33$) and the basal spacing indicates a monolayer of the methanol molecules. Molecular mechanics simulations supported by powder X-ray diffraction have been used to

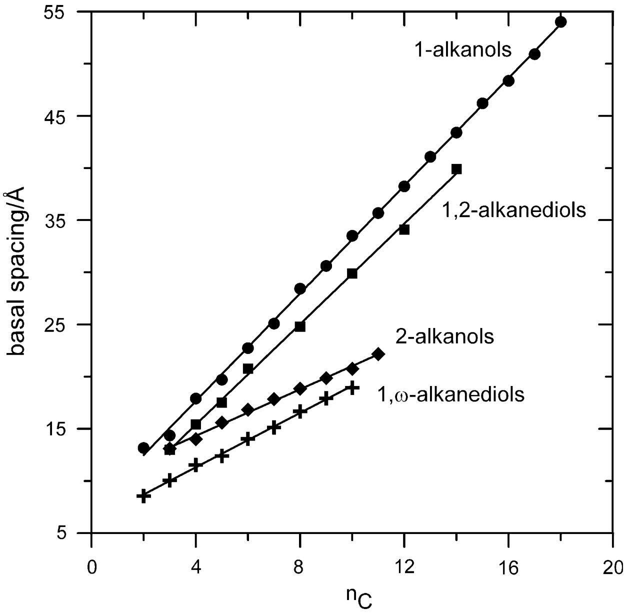

Fig. 3 Basal spacing *d* of the $VOPO_4$ intercalates with aliphatic alcohols as a function of the number of the carbon atoms in the chain of the guest molecules n_C

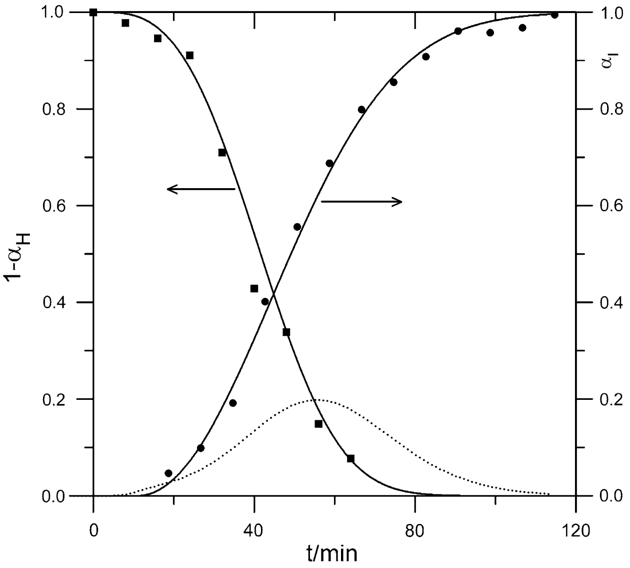

Fig. 5 Dependence of the extent of reaction of the parent host α_H and the product α_I on time *t* obtained by XRD during intercalation of ethanol into $VOPO_4$. The difference $\alpha_H - \alpha_I$ (*dotted line*) corresponds to the amount of the advancing phase boundary in the system. Reprinted with permission from Ref. [74]. Copyright 1996 Springer

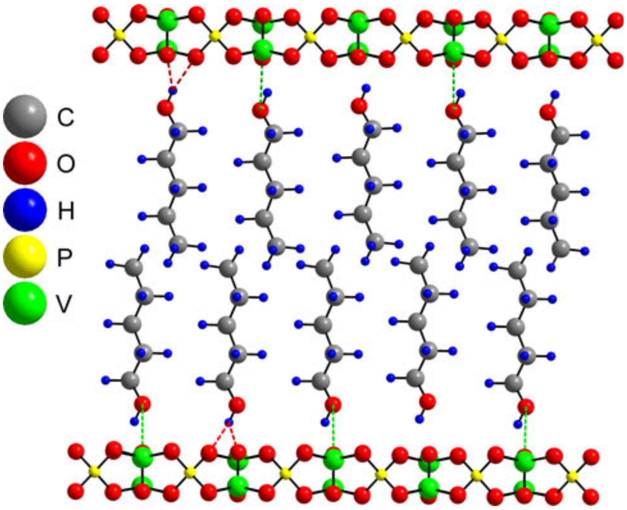

Fig. 4 Arrangement of the 1-pentanol molecules in the interlayer space of vanadyl phosphate viewed along the *ab* diagonal

investigate the structure of vanadyl phosphate intercalated with ethanol, 1-propanol, and 1-butanol [68, 69]. As follows from the calculations, the alcohol molecule coordinated to the vanadium atom is nearly perpendicular for all three guests. On the other hand, the tilting angle of the hydrogen bonded alcohol molecules increases with increasing molecule length.

Kinetics of the intercalation of ethanol into anhydrous vanadyl phosphate has been studied by time-resolved X-ray diffraction, thermomechanical analysis and a volumetric method [70, 71]. The kinetic curves were found to have a sigmoidal shape (Fig. 5). During this intercalation, only the fully intercalated phase is generated. A delay of formation of the intercalate in comparison with the decrease of starting host material is explained by the existence of an advancing phase boundary. The rate of the intercalation process could be influenced by the moisture in the liquid guest. The course of the replacement of ethanol by water molecules in the $VOPO_4 \cdot 2C_2H_5OH$ intercalate and of water by ethanol in $VOPO_4 \cdot 2H_2O$ has been studied by time-resolved X-ray diffraction, ATR FTIR and Raman spectroscopy [72]. Formation of a mixed intercalate $VOPO_4 \cdot C_2H_5OH \cdot H_2O$ was not observed. The kinetic curves of reintercalation of dihydrate do not have a sigmoidal shape. The shape of the kinetic curves indicates a transition of at least one reaction zone through the crystal.

The mixed intercalates of the type $VOPO_4 \cdot C_pH_{2p+1}OH \cdot C_qH_{2q+1}OH$ have been prepared by the reaction of either anhydrous $VOPO_4$ or $VOPO_4 \cdot 2H_2O$ with liquid binary mixtures of the 1-alkanols [73, 74]. The composition of these mixed intercalates is determined by the structure of the bilayer of alkanol molecules inserted between the host layers. This structure enables combination of the molecules of both alcohols in such a way that the bilayer thickness is determined by one short-chain molecule and one long-chain one (see Fig. 6). The same mixed-type complexes were also obtained as intermediary products of exchange reactions consisting in a replacement of one alkanol bound in the solid intercalate with another alkanol introduced in the form of vapor.

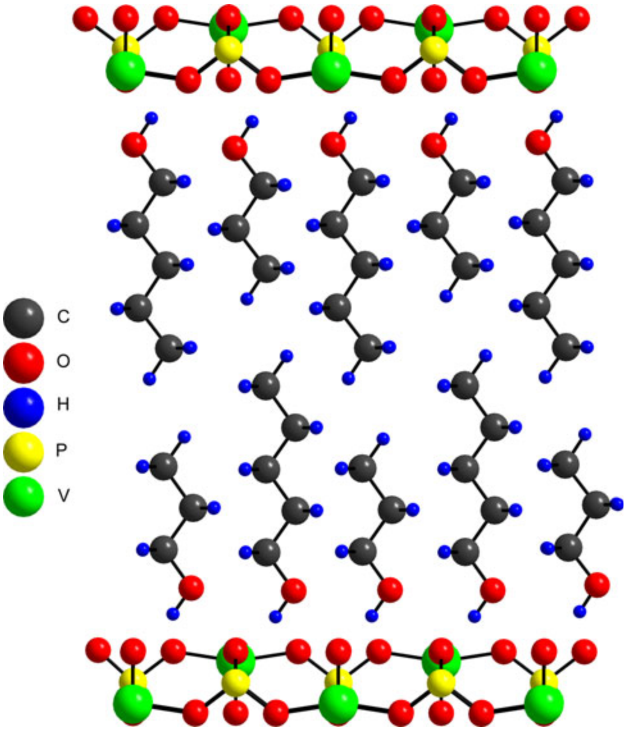

Fig. 6 Arrangement of 1-propanol and 1-pentanol molecules in the interlayer space of $VOPO_4$

Intercalates of vanadyl phosphate with 2-alkanols were prepared by a substitution of these 2-alkanols for 1-propanol in the $VOPO_4 \cdot 2C_3H_7OH$ [75]. Except 2-propanol and 2-butanol, these intercalates contain one 2-alkanol molecule per formula unit. The dependence of the basal spacing of the intercalates on the number of carbon atoms in the guest chain is linear with a slope of 1.107 (Fig. 3). Based on experimental values of basal spacing and stoichiometry, a bimolecular arrangement of the 2-alkanol molecules tilted to the host layers at an angle of 25.6° was proposed (Fig. 7). Besides the donor-acceptor bond of the alcohol oxygen to the vanadium, hydrogen bonds between hydroxy hydrogen of the alcohol and oxygen atoms of the layer are present. The large vanadium–oxygen distance obtained from the model explains the low thermal and humidity stabilities of the intercalates.

Intercalates of 12 alcohols with branched aliphatic chains were prepared and the influence of chain branching on the composition, basal spacing and stability of the intercalates was discussed [76]. The alcohol/host molar ratio decreases with increasing branching due to steric effects. Also unsaturated alcohols can be intercalated either by replacement of water in $VOPO_4 \cdot 2H_2O$ or 1-propanol in $VOPO_4 \cdot 2C_3H_7OH$ [77]. The intercalates of alcohols with terminal triple bonds are interesting due to their high stability at ambient conditions. On basis of IR and Raman spectra it is presumed that these alcohols are anchored to the host layers by donor–acceptor bonds between their oxygen atoms and the vanadium atom of the host and by H-bonding between the acetylenic hydrogen of the terminal carbon and the oxygen atoms of the host.

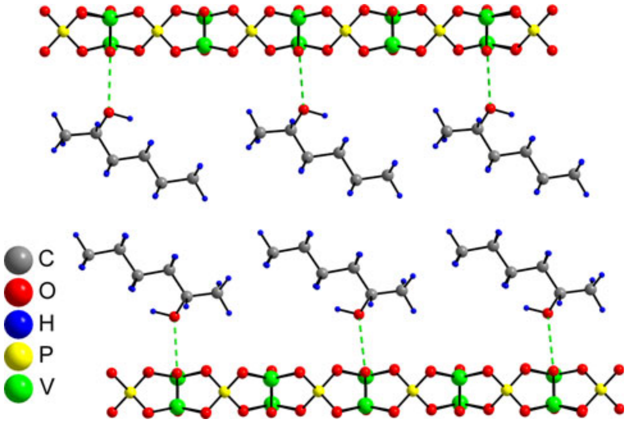

Fig. 7 Bimolecular arrangement of the 2-hexanol molecules in the interlayer space of vanadyl phosphate viewed along the *ab* diagonal

The composition and the morphology of vanadium phosphate catalyst precursors is shown to be controlled by the choice of the alcohol selected to carry out the dehydration and reduction of vanadyl phosphate dihydrate. Prolonged refluxing of $VOPO_4 \cdot 2H_2O$ with excess of C_2–C_8 alcohols gives $VOHPO_4 \cdot 0.5H_2O$ with different morphologies which is employed for the production of a widely used $(VO)_2P_2O_7$ catalyst [78–81]. It is assumed that the alcohols are incorporated in the structure of vanadyl phosphate at first so that a steric factor associated with the structure of the alcohol may play a role. Intercalations of alcohols into layers of vanadyl phosphate dihydrate, exfoliation using alcohol into delaminated sheets and subsequent reduction by reflux in alcohol into $VOHPO_4 \cdot 0.5H_2O$ were investigated [82, 83]. $VOPO_4 \cdot 2H_2O$ has been exfoliated in 2-propanol and the exfoliated solution dispersed on alumina to produce a novel catalyst for the selective oxidation of cyclohexane [84]. Exfoliation of $VOPO_4$ and of $VOHPO_4$ described by Beneš [67] and by Dasgupta [85], respectively, lead to precursors for the preparation of the vanadium-phosphorus based catalysts with a favorable texture. Mesostructured VPO phases have been synthesized from a solution of $VOPO_4 \cdot 2H_2O$ exfoliated in 2-propanol with CTAB as the structure directing agent [86].

Intercalation of 1,ω-alkanediols into $VOPO_4 \cdot 2H_2O$ leads to layered complexes of the composition $VOPO_4 \cdot C_nH_{2n}(OH)_2$ ($n = 2$–10) [67]. The molecules of diols form monomolecular bridges linking the adjacent layers of the host and their axes are perpendicular to the host layers (Figs. 3, 8). On the other hand, the intercalates of 1,2-alkanediols contains 1.5 guest molecule per formula unit [87]. The 1,2-alkanediol molecules are placed between the layers in a bimolecular way with their aliphatic chains tilted at an angle of 70° to the host layers (see Fig. 3). Three ways of bonding of diol molecules are proposed: coordination to the vanadium atom by first and second oxygen, respectively and by hydrogen bonds. The influence of various positions of OH groups in butanediols on the composition, basal spacing and stability of intercalates was studied [88]. Intercalation of glycerol into anhydrous vanadyl phosphate and vanadyl phosphate dihydrate was described [89–91].

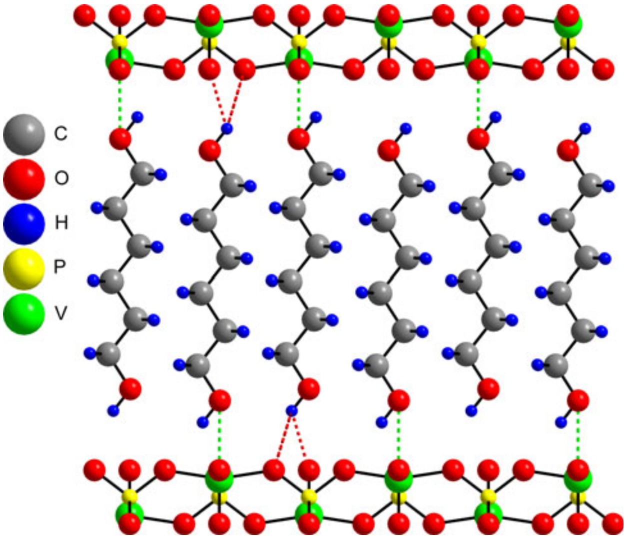

Fig. 8 The way how of the 1,ω-alkanediol molecules are anchored to the layers of the $VOPO_4$ host; the *dashed lines* show the coordination bonds between the oxygens atoms of the diol and the vanadium atoms of the host and the H bonds between the hydrogen atoms of the OH groups and the oxygen atoms of the phosphate tetrahedra

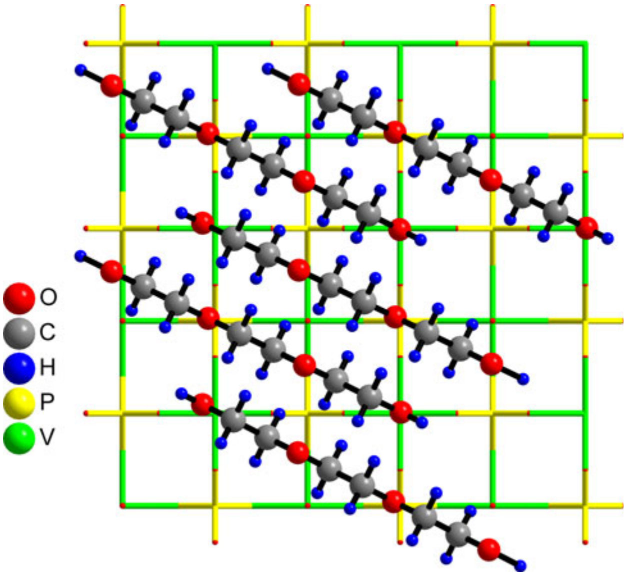

Fig. 9 Orientation of the polyethylene glycol molecules intercalated into $VOPO_4$. For clarity the $VOPO_4$ layer is drawn in *stick* representation

Intercalation of poly(ethylene glycol)s and ethers

Diethylene glycol, triethylene glycol and poly(ethylene glycol)s (PEG 200, PEG 400, and PEG 1000) form two types of intercalates depending on the reaction temperature: (i) phases with the basal spacing of about 12 Å containing two oxyethylene units per formula unit of the host were prepared at 40 °C and (ii) phases with the basal spacing of about 7.8 Å containing 1.1–1.2 oxyethylene units per formula unit of the host were prepared at 80 °C [92]. It is presumed that guest chains are deposited parallel to the host layer with every other oxygen atom coordinated to the vanadium atom (Fig. 9). The chains are arranged in a bimolecular (for the phase with the basal spacing of about 12 Å) or in a monomolecular way (for the phases with the lower basal spacings). The phase with the monomolecular arrangement has not been observed for the tripropylene glycol intercalate [92]. The structure of $VOPO_4 \cdot OH(CH_2)_2O(CH_2)_2OH$ intercalate ($P4/n$, $a = 6.223$ Å, $c = 11.417$ Å, $Z = 2$) have been determined using a combination of synchrotron powder diffraction and molecular mechanics simulation [93]. Figure 10 illustrates the anchoring of the diethylene glycol molecule to vanadium via its central oxygen. There are two possible orientations of diethylene glycol molecules.

Cyclic ethers were intercalated by replacement 1-propanol in $VOPO_4 \cdot 2C_3H_7OH$. Tetrahydrofuran intercalate, $VOPO_4 \cdot C_4H_8O$, exhibit perfect ordering in layer stacking so that its structure ($P4/n$, $a = 6.208$ Å, $c = 8.930$ Å, $Z = 2$) could be determined using a combination of synchrotron powder diffraction and molecular mechanics simulation [93]. This structure is shown in Fig. 11. Surprisingly high thermal stability of this intercalate was found by variable temperature X-ray diffraction [94]. The

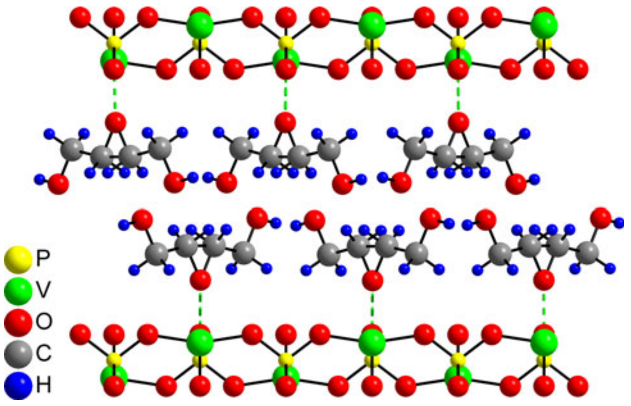

Fig. 10 The way how the diethylene glycol molecules are anchored in the interlayer space of $VOPO_4$. The coordination bond between the central oxygen atom of the guest and the vanadium atom of the host is shown as *dashed line*

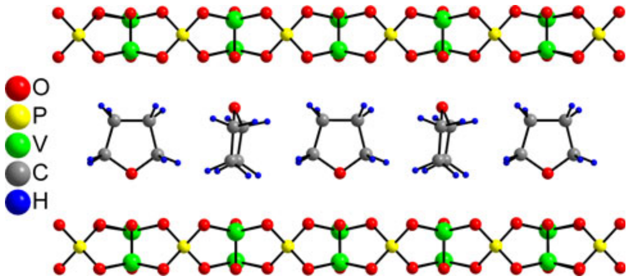

Fig. 11 The structure of tetrahydrofuran intercalate, $VOPO_4{\cdot}C_4H_8O$, viewed along the *ab* diagonal

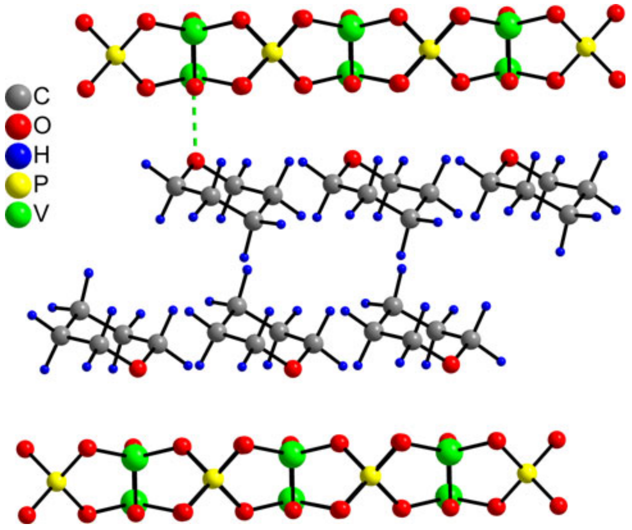

Fig. 12 Arrangement of the guest molecules in the interlayer space of tetrahydropyran intercalated vanadyl phosphate

position and intensity of its diffraction lines does not change up to 160 °C.

Interesting thermal behavior of the tetrahydropyran intercalate was observed using variable temperature X-ray diffraction [94]. Its basal spacing (12.2 Å at room temperature) slightly increases up to 85 °C. At this temperature, a new phase with the basal spacing of 12.8 Å appears. Another significant increase of the basal spacing (13.14 Å at 158 °C) is accompanied by broadening of (00*l*) diffraction lines. Both steps are reversible during cooling. The first reversible thermal transition was attributed to the boat/chair conformation changes of the tetrahydropyran molecules which were confirmed by variable-temperature ^{13}C CP/MAS NMR spectroscopy [95]. The second change is probably caused by weakening of the donor–acceptor bond between the oxygen of tetrahydropyran molecule and the vanadium atom of the host. The probable arrangement of the guest molecules in the chair conformation is shown in Fig. 12.

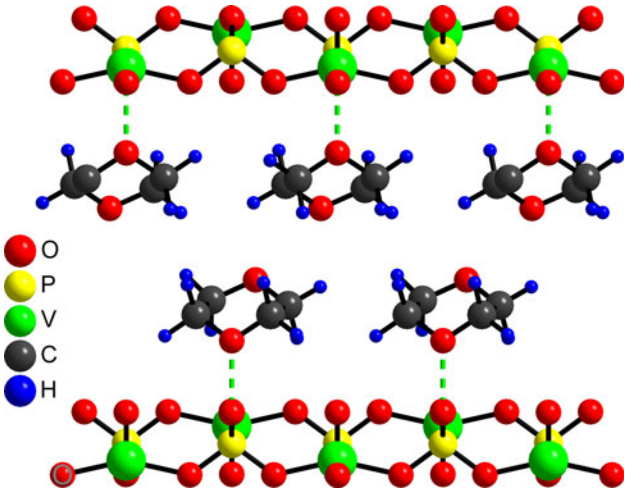

Fig. 13 Arrangement of the guest molecules in the interlayer space of the low-temperature phase of dioxane intercalated vanadyl phosphate. The structure is viewed along the *a* axis

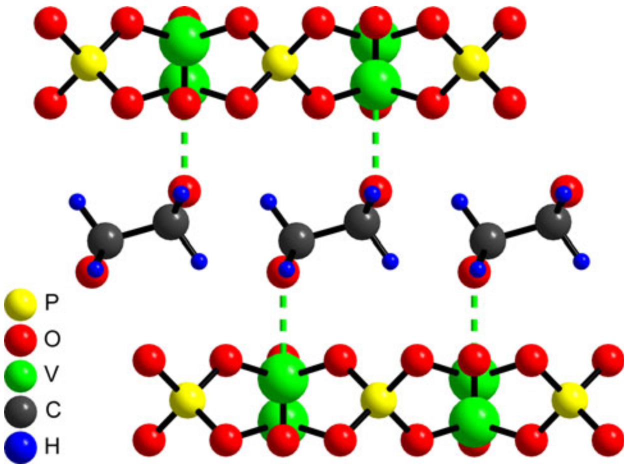

Fig. 14 High-temperature phase of dioxane intercalated vanadyl phosphate: orientation of the guest molecules viewed along the *ab* diagonal

Depending on the temperature of the preparation, the dioxane intercalated $VOPO_4$ forms two compounds with formulas $VOPO_4{\cdot}C_4H_8O_2$ (a low-temperature compound) and $VOPO_4{\cdot}0.5C_4H_8O_2$ (a high-temperature compound) [96]. The way of dioxane bonding to the host layers was studied by IR and Raman spectroscopies and the arrangement of dioxane molecules calculated by molecular modeling. In the low-temperature compound with the basal spacing of 11.56 Å, the dioxane molecules in a chair conformation are anchored to the host layers via one of their oxygen atoms coordinated to the vanadium atoms, forming a bilayer in the interlayer space (Fig. 13). In the high-temperature phase with the basal spacing of 7.89 Å, dioxane molecules are anchored to vanadium in lower and upper layers with both of its oxygen atoms (Fig. 14). Intercalates of trioxane ($VOPO_4{\cdot}0.5C_3H_6O_3$) and 18-crown-6 ($VOPO_4{\cdot}0.43C_{12}H_{24}O_6$) were also prepared and characterized [96]. Also these two guests are coordinated to vanadium via their oxygens as follows from IR and Raman spectra of the intercalates.

Similarly as the tetrahydrofuran intercalate, the diethyl ether intercalate $VOPO_4 \cdot (C_2H_5)_2O$ is thermally stable up to 100 °C as was observed by variable temperature X-ray diffraction [97]. The local structure and interactions in the intercalate have been suggested on the basis of quantum calculations. In contrast to the cyclic ethers intercalates, it is very moisture sensitive and the diethyl ether molecules are easily replaced by water molecules. The course of this reintercalation was studied using IR spectroscopy.

Intercalation of aldehydes and ketones

Intercalates of vanadyl phosphate with propionaldehyde, butyraldehyde, valeraldehyde, capronaldehyde, benzaldehyde and 4-methylbenzaldehyde were prepared by replacing 1-propanol or 2-propanol in corresponding $VOPO_4$ intercalates [98]. Aldehyde intercalation occurs without any appreciable reduction in the host lattice, but the aliphatic aldehyde intercalates are very unstable. They decompose during exposition to air and also when stored in an evacuated ampoule. Most probably the acidic character of the $VOPO_4$ layers causes partial aldolization of the intercalated aldehyde and subsequent condensation of aldol formed. In addition, aldehyde is oxidized to carboxylic acid by vanadium(V). In the case of propionaldehyde intercalate, the reduction of $VOPO_4$ was confirmed by changes in the UV–Vis spectra and the formation of aldol and propionic acid was proved by gas chromatography of the hydrolyzed sample. The aromatic aldehyde intercalates contain one aldehyde molecule per formula unit and are stable. The guest molecules are coordinated via their carbonyl oxygen to the vanadium atoms with their benzene rings perpendicular to the host layers as follows from comparison of basal spacings of benzaldehyde and 4-methylbenzaldehyde intercalates.

Intercalates of acetone and 2-butanone contain one ketone molecule per formula unit and their basal spacings are close to each other [99]. From that it can be inferred that their alkyl chains are probably parallel with the host layers. IR spectroscopy revealed the tautomerism in the interlayer space, i.e., a partial conversion of acetone to an enol form. The positions and orientations of acetone molecules and the mutual positions of two successive layers were determined using molecular mechanics simulations (see Fig. 15a, b) [100].

No formation of the enol forms was observed in the case of intercalation of cyclic ketones [101]. The cyclopentanone, cyclohexanone and 4-methylcyclohexanone intercalates contain one ketone molecule per formula unit. The local structure and interactions in the cyclopentanone intercalate was suggested on the basis of quantum chemical calculations. For the cyclohexanone and 4-methylcyclohexanone intercalates, an interdigitation of the guest rings is presumed. On the other hand, the 1,4-cyclohexanedione intercalate contains only a half of the guest molecule per formula unit and its basal spacing allows only monomolecular arrangement of the guest molecules, which—due to the presence of two ketonic oxygens—form pillars between the host layers.

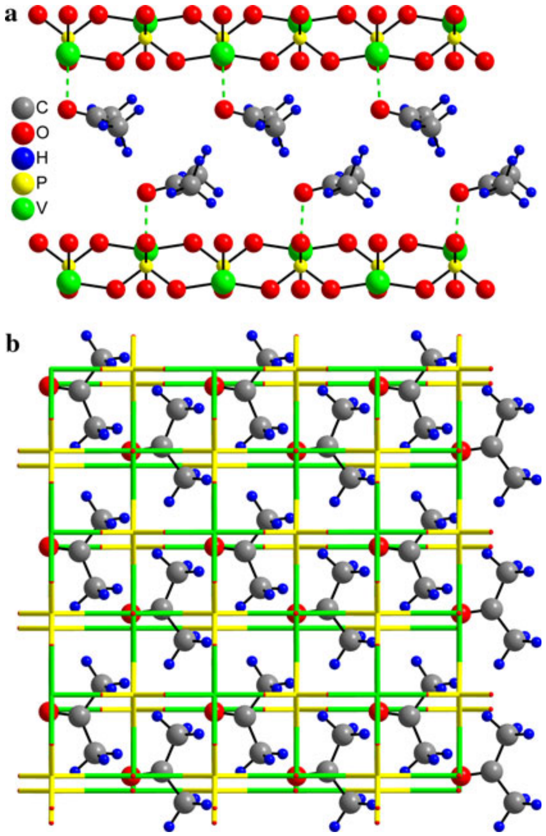

Fig. 15 Arrangement of acetone molecules intercalated between the layers of $VOPO_4$ viewed along the *a* axis (**a**) and along the *c* axis (**b**)—in this case, the $VOPO_4$ layer is drawn in *stick* representation for clarity

The structure of the *p*-benzoquinone intercalate, $VOPO_4 \cdot OC_6H_4O$, was determined using combination of powder X-ray diffraction and molecular simulations (see Fig. 16) [102]. In contrast to the 1,4-cyclohexanedione intercalate, only one oxygen of each *p*-benzoquinone molecule is coordinated to the vanadium atom.

The dimethylsulfoxide intercalate [103] can be compared with the acetone intercalate [100]. Both intercalates are similar in their guest content (one molecule per formula unit), tetragonal lattice parameters and molar volume of the guest molecules. The difference is in the guest molecule geometry: the acetone molecule has a planar skeleton whereas the dimethyl sulfoxide skeleton is bent and forms a flat trigonal pyramid. The proper arrangement of the bent dimethyl sulfoxide molecule is sterically more demanding

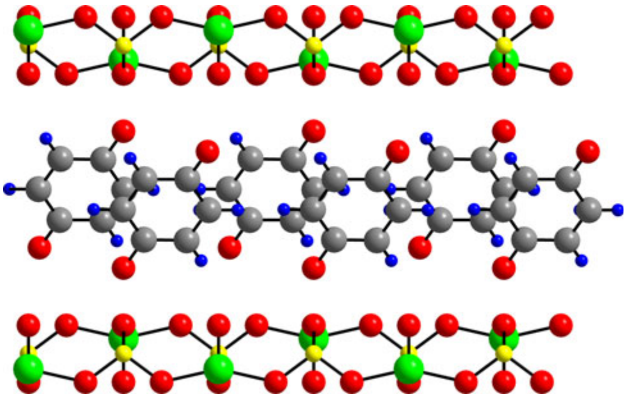

Fig. 16 Position and orientation of benzoquinone molecules intercalated into vanadyl phosphate

than in the case of acetone molecules and causes an increase of the O_{guest}–V_{host} distance as was estimated from molecular modeling for both intercalates.

Intercalation of carboxylic acids and their derivatives

Layered complexes with the general formula $VOPO_4 \cdot RCOOH$ (RCOOH is formic, acetic, propionic or butyric acid) were prepared [104]. The basal spacing increases by about 1.8 Å when going from the complexes with formic acid to those with acetic acid, and the change is the same (2 Å) when going from propionic to butyric acid. On the other hand, replacement of acetic acid with propionic acid leads to an increase of the basal spacing by only 0.4 Å. This phenomenon can be explained by an oblique arrangement of the chains. It follows from the IR spectra that the carboxylic acid molecules are anchored by their functional group and that obviously also a strong hydrogen bond is present. Any bands of the carboxylate ions are not present in these spectra, hence no proton transfer occurs from the carboxylic acids to the host lattice. On the basis of all these results, carboxylic acids are arranged in the interlayer space monomolecularly and are coordinated to the vanadium via their carbonyl oxygen.

Glycine-intercalated vanadyl phosphate ($VOPO_4 \cdot NH_2CH_2COOH$) retains the layered structure of parent phosphates with the basal spacing corresponding to a perpendicular arrangement of glycine chains in the interlayer space [105]. IR spectra confirm the presence of the glycine molecules in the intercalates as zwitterionic species. Similar to those observed for anhydrous $VOPO_4$ [61], impedance measurements of $VOPO_4 \cdot NH_2CH_2COOH$ support the idea that the conductivity in this intercalate is electronic and the glycine molecules in the interlayer space do not take part in the conductivity mechanism.

Intercalates of vanadyl phosphate with formates and acetates of C_1–C_8 alcohols and dimethylesters of C_2–C_6 dicarboxylic acids were prepared by replacing of 2-propanol in corresponding vanadyl phosphate intercalate [106]. The C=O stretching vibration in the IR spectra of the intercalates were shifted to the lower wavenumbers in comparison with the spectra of pure guests, indicating that all esters are anchored to the host layers by their carbonyl oxygen. The intercalates of formates and acetates contain about one ester molecule per formula unit. The guest molecules are arranged in a bimolecular way and tilted to the host layer at an angle of about 56°. In the case of dimethylesters, there are two types of the intercalates: the first one with the basal spacing of 12–12.5 Å and the second one with the basal spacing from 8.1 to 8.9 Å irrespective of the molecule size. The guest content decreases with the increasing guest size. It means that the guest molecules lie parallel to the host layer and are arranged either in a bimolecular or monomolecular way. Intercalates of vanadyl phosphate with γ-butyrolactone, α-methyl-γ-butyrolactone, γ-valerolactone, γ-caprolactone, δ-valerolactone, and ε-caprolactone also contain one guest molecule per formula unit and the guest molecule are anchored to the host layers by their carbonyl oxygen [107, 108]. The lactone molecules are arranged between the host layers in a bimolecular way and in the most cases are partially interdigitated. Similar arrangement of the guest molecules is supposed in the intercalates with dimethyl carbonate, diethyl carbonate and ethylene carbonate [109].

Vanadyl phosphate dihydrate interacts with primary and tertiary amides causing either dehydration or intercalation reactions, or sometimes both to form $VOPO_4 \cdot 1.6HCONH_2$, $VOPO_4 \cdot 0.1CH_3CONH_2 \cdot 1.8H_2O$, $VOPO_4 \cdot 0.82HCON(CH_3)_2$ and $VOPO_4 \cdot 0.34CH_3CON(CH_3)_2 \cdot 0.25H_2O$ [110]. Larger amides do not intercalate. If the obtained intercalates are hydrated, the primary amides also interact through the NH_2 groups to form hydrogen bridges. In the anhydrous compound resulting from the reaction of formamide, by refluxing with starting host material, the amide coordinates directly to the vanadium through the NH_2 group. The interaction between the tertiary amides and vanadyl phosphate dihydrate is through the C=O and V=O groups, either directly or indirectly through the coordinated water, as follows from the IR spectra. Prolonged heating of $VOPO_4 \cdot 2H_2O$ in dimethylformamide almost collapsed the layered structure [111]. Two types of acrylamide intercalates were prepared: $VOPO_4 \cdot 1.8(CH_2{=}CHCONH_2) \cdot nH_2O$ with a bilayer arrangement and $VOPO_4 \cdot 1.1(CH_2{=}CHCONH_2) \cdot nH_2O$ with a monolayer arrangement [111]. Both these intercalates were exfoliated in 1- or 2-butanol and layered materials reconstructed from the exfoliated $VOPO_4$ layers were characterized. In the intercalate of ethyleneurea, $VOPO_4 \cdot (C_3H_6N_2O) \cdot H_2O$, the ethyleneurea molecules are coordinated to the vanadium atoms of the layers by carbonyl oxygen

[112]. Various amides can be also intercalated into layered mixed niobyl–vanadyl phosphate [36].

The basal spacing of the intercalates of aliphatic nitriles $CH_3(CH_2)_nCN$ and dinitriles $CN(CH_2)_mCN$ ($n = 0$–5, $m = 1$–6) are practically identical [113, 114]. All these intercalates are moisture sensitive. The nitrile intercalates (except acetonitrile) contains one nitrile molecule per formula unit whereas the dinitrile content decreases with increasing chain length. The guest molecules are anchored to the layers by an N → V donor–acceptor bond and their aliphatic chains are parallel to the host layers. The intercalates of benzonitrile and tolunitrile contain one nitrile molecule per formula unit and are anchored to the layers by a $C{\equiv}N \rightarrow V$ bond [115]. In contrast to aliphatic nitriles, molecules of aromatic nitriles are oriented perpendicularly to the host layers. The guest molecules are interdigitated with the planes of aromatic rings being parallel as follows from quantum mechanical calculations and modeling.

Intercalation of amines

The yellow or yellow-green intercalates of the composition $VOPO_4{\cdot}xC_nH_{2n+1}NH_2$ ($n = 1$–10, $x = 1.68$–2.02) were obtained by the direct reaction of anhydrous vanadyl phosphate and aliphatic amines [116]. The basal spacing increases by about 1.4 Å by lengthening the chain from n(even) to $n + 1$, and by about 3.1 Å from n(odd) to $n + 1$. This type of dependence of the basal spacing on the number of carbon atom n in the amine chain indicates a bilayer arrangement of the molecules, which are inclined at the angle of 55° to the layer of the host. For the shortest chains this angle increases with increasing number of the carbon atoms in the chain. On the basis of IR spectra, a presence of two types of amine molecules, coordinated and hydrogen-bonded, is deduced.

For the intercalation of aliphatic amines into vanadyl phosphate dihydrate, the dependence of the basal spacing on n is linear in the range from butylamine to hexadecylamine ($n = 4$–16) and the amine chains are nearly perpendicular to the host layers [53]. The intercalation of alkylamines into $VOPO_4{\cdot}2H_2O$ was studied by combination of ^{51}V solid-state NMR with powder XRD. All amines form bimolecular layers. Whereas carbon chains of short amines are tilted to the host layers, carbon chains of longer amines (C_{12} and C_{16}) are perpendicular to the host layers. In the case of octylamine, the intercalation results in two coexisting phases with both chain orientations [117]. The n-butylamine intercalate with the basal spacing of 13.76 Å was characterized using magic-angle spinning NMR and EPR [6]. Dodecylamine intercalate $VOPO_4{\cdot}C_{12}H_{25}NH_2{\cdot}H_2O$ with the basal spacing of 28 Å was prepared by a solid state reaction [118]. The aliphatic amine molecules are oriented in a bilayer inside the host cavity tilted at an angle of 67° with respect to the inorganic lamella. A successive formation of two different compounds was observed during the interaction of $VOPO_4{\cdot}2H_2O$ with n-hexylamine [119]. On the basis of IR spectra the authors suggest that the $VOPO_4$ layers were destroyed and the connection manner of V–P–O unit was completely altered.

If layered vanadyl organophosphonates $VORPO_3$ (R = methyl, ethyl, phenyl) were brought into contact with primary alkylamines, hydrolysis of the phosphonate groups (by P–C bond cleavage) leading to hydrogen phosphonate group occurs, followed by oxidation of vanadium atoms (by dissolved oxygen) with subsequent formation of alkylamine intercalated compound of vanadyl phosphate dihydrate [120].

Three types of intercalation compounds were prepared by reaction of $VOPO_4{\cdot}2H_2O$ with aniline [121]. In aniline vapors, a dark green product containing a very small amount of protonated aniline and the basal spacing of 6.3–7.0 Å was formed. The intercalate prepared from neat aniline had the basal spacing of 14.8 Å, did not hold any water and contained about two molecules of aniline per vanadium atom which were included mainly as aniline molecules. Small amounts of protonated aniline and polyaniline was also present. The large amount of polyaniline was found in an intercalate prepared from aniline solutions either in tetrahydrofuran or acetonitrile. Similarly, powdered $VOPO_4{\cdot}2H_2O$ suspended in excess of neat aniline gives intercalation compounds $VOPO_4{\cdot}xH_2O{\cdot}yC_6H_5NH_3H^+$ ($0.6 < x < 1.1$; $0.5 < y < 1.0$) with the vanadium atom reduced [122]. Anilinium cations in the compounds with $y > 0.7$ can be polymerized by the addition of a Cu^{2+} ion to afford polyaniline. Compounds intercalated with both anilinium cation and polyaniline can be prepared by contacting $VOPO_4{\cdot}2H_2O$ with a solution of $C_6H_5NH_3{}^+Cl^-$ in ethanol. The vanadium(V) atoms of the $VOPO_4$ layer are expected to cause an oxidative polymerization of a $PhNH_3{}^+$ ion forming polyaniline in the interlayer space. A wide range of the stoichiometries and interlayer distances were found for composites formed by the interaction of $VOPO_4{\cdot}2H_2O$ and an aniline solution in anhydrous or 95% ethanol [123]. The compound $VOPO_4{\cdot}C_6H_4N$ with the basal spacing of 16 Å was prepared by reaction of $VOPO_4{\cdot}2H_2O$ with aqueous aniline [124]. An increase of the conductivity and decrease of the optical band gap of vanadyl phosphate due to the insertion of polyaniline was observed [125].

The reaction of $VOPO_4{\cdot}2H_2O$ with 4-butylaniline yielded intercalation compounds with formula $VOPO_4{\cdot}nH_2O{\cdot}xC_4H_9C_6H_4NH_2$ ($x = 1.2$–2.3, depending on the reaction time) which can be exfoliated in tetrahydrofuran [116, 126]. Intercalation compounds of N-methylaniline, 2-ethylaniline and 2-propylaniline containing both monomer and polymer species were prepared [127]. An influence of synthesis condition on intercalation of o-methoxyaniline and *o*-methylaniline was observed [128]. The FTIR, UV–Vis and EPR spectra confirm the generation of organic polymers in the interlayer space and reduction of vanadium(V) to vanadium(IV) induced by monomers. Vanadyl phosphate dihydrate/polyaniline derivatives hybrid films synthesized via the exfoliation and reconstruction approach were tested as cathode in lithium batteries [129]. 4-Anilinoaniline and 4-anilinoanilinium iodide can be intercalated as anilinoanilinium cations into the $VOPO_4$ interlayer space, where no further reaction, such as protonation of the imino groups and/or oxidative polymerization, occur [119, 130].

Benzidine gives two benzidinium (Bz^+) charge transfer complexes: $VOPO_4{\cdot}(Bz)_{0.5}{\cdot}2H_2O$ and $VOPO_4{\cdot}(Bz)_{0.7}{\cdot}3.5H_2O$, with interlayer distance of 7.05 and 6.65 Å, respectively—lower than that in α-$VOPO_4{\cdot}2H_2O$ alone [123]. The interlayer "pocket" orientation with layer shifting and turbostraticity to accommodate Bz^+ cations is suggested.

Intercalation of heterocyclic N- and S-donors

Vanadyl phosphate or vanadyl phosphate dihydrate react with pyridine, 4-phenylpyridine and 4,4′-bipyridine to give $VOPO_4$·(pyridine), $VOPO_4$·(4-phenylpyridine), and $VOPO_4{\cdot}(4,4'\text{-bipyridine})_{0.5}$ intercalates [131]. Anhydrous host reacts very slowly. In the intercalates, the pyridine molecules are coordinated to the vanadium atom as follows from IR spectra and are perpendicular to the layers. Little or no reduction of the V(V) centers occurs. The reactions with 4-substituted pyridines are much slower than that with pyridine itself. Intercalation compounds of $VOPO_4{\cdot}2H_2O$ with pyridine, 4-methylpyridine, and 4-phenylpyridine were synthesized by two orders of magnitude more quickly using microwave dielectric loss heating effects than with conventional thermal methods [132]. Another type of bipyridine intercalates, $VOPO_4{\cdot}0.33H_2O{\cdot}0.31C_2H_5OH{\cdot}0.46$(4,4′-bipyridine) and $VOPO_4{\cdot}0.1H_2O{\cdot}0.57C_2H_5OH{\cdot}0.4$(2,2′-bipyridine) containing cointercalated molecules of water and ethanol in the interlayer space, were prepared from ethanolic solutions [133]. The interlayer distance of 13.3 Å found for the $VOPO_4{\cdot}0.55$(2,2′-bipyridine)·$1.57H_2O$ intercalate suggests a vertical orientation of the bipyridine molecules within the layers via an NH···O=V interaction and without pocket lodgment [123].

The intercalation compounds obtained by the reaction of $VOPO_4{\cdot}2H_2O$ with 2,2′-dithiodipyridine, 1,2-bis(2-pyridyl)ethene, and 1,2-bis(4-pyridyl)ethene in ethanol contain heterocyclic moieties together with the ethanol and water molecules in the interlayer space [133, 134]. The interlayer distances depend on the size of the guest arranged approximately perpendicular to the host layers. An intercalation of 4,4′-dithiodipyridine was not successful [134].

Vanadyl phosphate dihydrate reacts with an imidazole solution in ethanol to give two layered compounds with the general formula $VOPO_4{\cdot}(\text{imidazole})_{1.0}{\cdot}nH_2O$ ($n = 0.2$, a 8.8-Å phase; $n = 0.6$, a 10.3-Å phase) depending on content of water in ethanol [135]. Imidazole is coordinated to the vanadium atom and is either oriented vertically to the planes in the 10.3 Å phase or lies almost flat between the layers in the 8.8 Å phase.

Pyrazole, pyrazine and phenazine intercalate into α-$VOPO_4{\cdot}2H_2O$ as protonated, non-coordinated species under mild conditions [123]. Three phases are formed consecutively during the intercalation of pyrazine. The larger interlayer distance of 13.26 Å for the metastable phase suggests that a bilayer is formed first, followed by a "nestled" structure with basal spacing of 7.2 Å in which the pyrazine molecules lies horizontally in the pockets generated by corner-attached $VOPO_4$ units. In the final $VOPO_4{\cdot}0.46$(pyrazine)·$0.78H_2O$ intercalate with basal spacing 8.65 Å, the pyrazine molecules adopt a more vertical orientation. Pyrazole in $VOPO_4{\cdot}0.28$(pyrazole)·$1.44H_2O$ appears to adopt a similar orientation. The low interlayer distance (7.63 Å) in the $VOPO_4{\cdot}0.07$(phenazine)·$1.75H_2O$ intercalate was explained by assuming that the phenazine molecules lie deep in the channels and that the layers slide with respect to one another to form such channels.

Pyrrole almost completely polymerizes on direct intercalation into $VOPO_4{\cdot}2H_2O$, giving "nestled" polymer composites with several stoichiometries and different polypyrrole oxidation levels [123]. A set of $VOPO_4{\cdot}x(\text{polypyrrole}){\cdot}nH_2O$ ($x = 0.41$–0.97; $n = 1.89$–1.18) intercalates was prepared [136]. The room temperature conductivity of the nanocomposites is about 1,000 times superior to the host vanadyl phosphate. Small polaron tunneling is observed for smaller content of polypyrrole. Electrical dc conductivity at low temperature is dominated by Mott's one-dimensional variable range hopping for the higher concentration of polypyrrole. Finely powdered $VOPO_4{\cdot}2H_2O$ suspended in an ethanol solution containing 3-methyl or 3,4-dimethylpyrrole leads to an intercalative polymerization of these pyrrole derivatives through the 2, 5-coupling to yield $VOPO_4{\cdot}1.4H_2O{\cdot}0.2C_2H_5OH{\cdot}0.65$(meth ylpyrrole) and $VOPO_4{\cdot}1.8H_2O{\cdot}0.2C_2H_5OH{\cdot}0.6$(dimethylpyrrole) [137, 138].

A compound with formula $VOPO_4{\cdot}0.25$(tetrathiafulvalene)·H_2O was prepared by a 15-day's reaction of an acetone solution of tetrathiafulvalene with vanadyl phosphate dihydrate at room temperature [139]. The supposed layered structure has not been confirmed by XRD. The system is probably more complex than a simple intercalate. Infrared spectrum indicated the presence of the TTF^+ cation in this material. Electrical properties of the product were studied.

Intercalation of complex compounds

Intercalation of ferrocene from acetone medium into $VOPO_4{\cdot}2H_2O$ undergoes as a redox topotactic reaction between ferrocene and the vanadium(V) atom [140]. The content of ferricinium (Fc^+) is relatively low (0.11–0.12 per formula unit) and the water content decreases with the contact time. An increase of the basal spacing indicates that the ferricinium cations are arranged in monolayers with their fivefold symmetry axis parallel to the host layers. The bulky dimethylaminomethylferrocene was not intercalated into vanadyl phosphate dihydrate.

The intercalates $VOPO_4{\cdot}H_2O{\cdot}0.21(Fc^+)$ and $VOPO_4{\cdot}H_2O{\cdot}0.35(Fc^+)$ were prepared by stirring a $VOPO_4{\cdot}H_2O{\cdot}C_2H_5OH$ intercalate in an ethanolic solution of ferrocene [141]. An increase of the basal spacing corresponds to an arrangement in which cyclopentadienyl rings are parallel to the sheets of the host. The basal spacings of the $VOPO_4{\cdot}H_2O{\cdot}0.21(Fc^+)$ intercalate and the similar intercalate with 1,1′-dimethylferrocene $VOPO_4{\cdot}H_2O{\cdot}0.21(Me_2Fc^+)$ change after 30 days at room temperature, so that the arrangement of the guest molecules corresponds to the form with the cyclopentadienyl rings perpendicular to the layers. However, $VOPO_4{\cdot}H_2O{\cdot}0.35(Fc^+)$ does not change the primary interlayer spacing to form an arrangement with cyclopentadienyl planes perpendicular to the layers. In the case of ethyl- and *n*-butylferricinum intercalates, metallocenium cations are oriented with their cyclopentadienyl rings perpendicular to the host layers.

The alkyl-bridged biferrocene compounds can be also intercalated into the interlayer space of the layered $VOPO_4$ through the redox reaction [142]. The long-axis direction of these guest molecules is arranged approximately parallel to the sheet of the host lattice. Both Fe^{2+} atoms are oxidized to form the Fe^{3+} in $VOPO_4{\cdot}H_2O{\cdot}0.15(Fc^+CH_2CH_2Fc^+)$. On the other hand, in the $VOPO_4{\cdot}H_2O{\cdot}0.12(Fc^+CH_2Fc)$ intercalate, one of the Fe^{2+} centers of diferrocenylmethane is not oxidized because only one center can access to the vanadium site. Ferrocene and some its derivatives were also intercalated into mixed vanadium-niobium phosphates [143].

Vanadyl phosphate dihydrate reacts with a $Rh_2(CO)_4Cl_2$ solution in tetrahydrofuran to form a layered dark green solid with the interlayer distance of 9.2 Å [144]. The FTIR spectrum shows a broad band with distinct components centered at 2,098 and 2,107 cm^{-1} which is indicative of Rh(I) rather than Rh(III) carbonyl species in the intercalated compound. This compound exhibits catalytic activity and shape selectivity in the hydrogenation of olefinic substrates.

Redox intercalations

Redox intercalation of inorganic cations

Redox intercalation reactions of $VOPO_4{\cdot}2H_2O$ were first described by Johnson and Jacobson [145]. It was found that $VOPO_4{\cdot}2H_2O$ readily undergoes redox intercalation reaction with alkali-, alkaline-earth-, transition metal cations, hydronium cation, NH_4^+ and organic ammonium cations in the presence of a reducing agent. Metal iodides were found to be the most suitable reducing agents, as they are, in the same time, also a source of the desired intercalated cation. A general method for the preparation of cation intercalated vanadyl phosphate was suggested based on the reaction of metal or organic ammonium iodides according to the equation

$$\begin{aligned} &VOPO_4 \cdot 2H_2O + x/nM^{n+}I_n^{\,-} + yH_2O \\ &\quad \rightarrow M_{x/n}VOPO_4 \cdot (2+y)H_2O + x/2I_2. \end{aligned} \tag{1}$$

It is worth noting that the amount of the intercalated cation, *x*, depends on the reaction conditions, mostly on the reaction time or the iodide/host molar ratio. The interlayer distance generally decreases upon redox intercalation of metal cations, a phenomenon which is quite opposite to that observed for molecular intercalates. This decrease is also influenced by the amount of the intercalated cation, as proved for cesium, hydronium [146] and sodium intercalates [147]. On intercalation, V(V) is reduced to V(IV) and the layers become negatively charged. These layers are then brought closer together by electrostatic interaction with the intercalated cation causing the decrease of the interlayer distance. Also the amount of water of hydration is influenced by the nature and the amount of the intercalated cation.

The redox intercalates of $VOPO_4{\cdot}2H_2O$ became a subject of interest for their applications as materials for batteries and catalysts. Alkali metal intercalates were therefore studied more in detail from the point of their structure and morphology [148] and the local environment of the vanadium atom [149, 150]. The conductivity of $VOPO_4{\cdot}2H_2O$, $K_{0.11}VOPO_4{\cdot}2H_2O$ and $H_{0.11}VOPO_4{\cdot}nH_2O$ was studied and it was stated that the major contribution of the conductivity comes from proton mobility along the layer surface given by the presence of water molecules in the interlayer space [151].

In the reaction of $VOPO_4{\cdot}2H_2O$ with an excess of NaI, the content of sodium in the intercalate formed, $Na_xVOPO_4{\cdot}yH_2O$, increases with reaction time [152, 153]. The content of water y remains the same ($y = 2$) up to $x = 0.5$, then decreases linearly with x to $y = 1$. It was found that during the intercalation of the sodium cation into

$VOPO_4 \cdot 2H_2O$ three phases are gradually created with the compositions $Na_{0.3}V_{0.3}^{IV}V_{0.7}^{V}OPO_4 \cdot 2H_2O$, $Na_{0.5}V_{0.5}^{IV}V_{0.5}\text{-}^{V}OPO_4 \cdot 2H_2O$ and $NaV^{IV}OPO_4 \cdot H_2O$. From the basal spacing of these phases it was deduced that they corresponded to stages 3, 2 and 1 (Fig. 17) as defined for instance by Hibma [154]. Staging means a situation in layer compounds in which certain interlayer spaces (called galleries) are filled, whereas others are empty. The intercalate thus forms sequences in which empty galleries vary with a full gallery. The stages are numbered according to number of galleries in one sequence (empty ones plus full one). Two empty galleries and a full one ($x = 0.33$) exist in stage 3, in stage 2 one empty gallery varies with one full gallery ($x = 0.5$). Stage 1 consists only of full galleries ($x = 1.0$). The calculated lattice constants are in agreement with the concept of staging as discussed in detail in the paper [152].

The conductivity of these intercalates decreases with increasing x. Seebeck effect measurements indicated that the charge carriers in the intercalate have a positive charge. The sodium cations do not influence the conductivity in this case, as they are anchored to the negatively charged vanadyl phosphate layers. Thus the conductivity is given predominantly by the movement of protons formed by dissociation of water. Reduction of vanadium causes an increase of basicity of water molecules. The penetration of the sodium cations diminishes the proton mobility in the water layer. Also the elimination of water at higher degrees of intercalation must have a similar effect. All these phenomena contribute to the decrease of conductivity with the increased amount of the intercalated cation.

A similar study was carried out for the intercalation of lithium cations using LiI [155]. A decrease of conductivity with increasing amount of intercalated lithium was also observed. As in the case of sodium, the intercalation of lithium causes a formation of several phases. These phases are formed consecutively, with maximum relative ratio at lithium content in the samples with $x = 0.33$, 0.5, 0.66 and 1.0. The phases with $x = 0.33$, 0.5 and 1.0 correspond to stages 3, 2 and 1, respectively. Out of the definition of staging is the phase with $x = 0.66$. The most plausible structure for this stage is a sequence consisting of two full galleries and one empty gallery (see Fig. 17, part denoted 3/2). The stage numbering was therefore newly defined as a ratio of number of all galleries (empty and full ones) to a number of full galleries in one sequence. The phase with $x = 0.66$ can be then denoted as stage 3/2. The values of the lattice parameters for this phase are consistent with these considerations [155].

In contrast to the lithium or sodium intercalates, no staging was observed during the formation of potassium intercalates [156]. The basal spacing and the content of water decrease with the amount of the intercalated potassium x. Also the conductivity decreases up to $x = 0.5$ and then remains almost constant.

Two phases with interlayer distance of 7.03 and 6.44 Å are formed during the intercalation of rubidium cations into vanadyl phosphate [157]. The character of conductivity was determined in dependence on RH. It was found that the conductivity changes from fully electronic at RH < 30% to a mixed ionic–electronic one at higher humidities. Electromotive force measurements showed that the diffusion of the Rb^+ ions contributed significantly to the ionic part of conductivity.

Redox intercalation of NH_4^+ into $VOPO_4 \cdot 2H_2O$ also leads to a two-phase $(NH_4)_xVOPO_4 \cdot H_2O$ ($x = 0.2$–0.9) compound with interlayer distances of 6.7 and 6.4 Å [158].

Hydrogen is intercalated into vanadyl phosphate by the reaction of $VOPO_4 \cdot 2H_2O$ with HI [156]. The content of water increases with the degree of intercalation thus it can be deduced that protons enter the interlayer space in the form of hydronium ions. As in the previous cases, the intercalation causes a decrease of conductivity of the intercalate.

Alkali-metal and hydronium redox intercalated vanadyl phosphate behaves as an ion exchanger [159]. An ion exchange of the $HVOPO_4 \cdot 3.6H_2O + K^+$ system was studied more in detail. The potassium ions are fully exchanged for H^+ up to $x = 0.4$, then the further exchange becomes difficult. The basal spacing d decreases nonlinearly with the amount of exchanged potassium. This nonlinear dependence can be explained by using a finite layer rigidity model [160]. From this model, a parameter of the rigidity of the host layer p was calculated to be 2.0. This

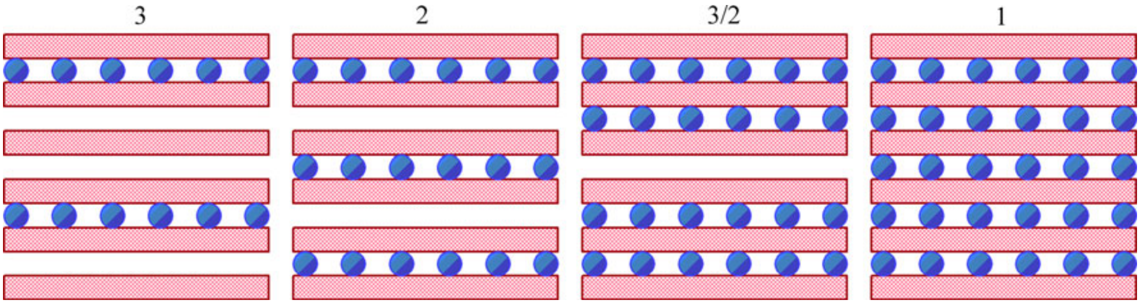

Fig. 17 Schematic representation of staging

parameter p determines an area which is influenced by the intercalation of ion A in a gallery which is otherwise filled with ions B. The higher the parameter p, the more rigid is the host layer. The value $p = 2.0$ indicates that vanadyl phosphate belongs to the most flexible host layers used in intercalation chemistry, which is in agreement with the conclusions made previously [161].

Also other systems, namely $NaVOPO_4 \cdot H_2O + K^+$, $KVOPO_4 \cdot H_2O + Na^+$, $HVOPO_4 \cdot 3.6H_2O + Na^+$, $MVOPO_4 \cdot H_2O$ (M = H, Na, K) + Rb^+ or Cs^+, were studied [159]. The ability of a cation A to exchange another cation M in the interlayer space of the host, according to the equation

$$M_{x/z}VOPO_4 \cdot yH_2O + x/nA^{n+} + mH_2O \rightarrow A_{x/n}VOPO_4 \cdot (m+y)H_2O + x/zM^{z+} \quad (2)$$

is influenced by three phenomena: (i) the electrostatic interaction between negatively charged host layer and the exchanging cations, (ii) the free energy involved in the changes in hydration of M and A during the exchange process (let us suppose that there is no hydration change on the host layers), and (iii) the energy needed for the change in an interlayer geometry, i.e., the change of the basal spacing of the intercalate. The electrostatic energy given by the interaction between the host layer and the counterion decreases with the radius of this counterion. This energy arising from the interaction of the host and exchanging cation A is compensated by the energy necessary for the release of an exchanged cation M. The free energy of hydration is connected with the standard free energy of hydration of the corresponding ion. For alkali metal ions, the hydration energy decreases in the sequence Na > K > Rb > Cs. As regards the electrostatic and hydration energies, it follows from our observation that the hydration energy governs the exchange processes for smaller cations. The exchanging ability of larger cations (Rb and Cs) is influenced by the energy necessary for the change of the basal spacing. Therefore, sodium cannot replace cesium anchored to $VOPO_4$ as hydration energy of Na^+ is too high compared with that of Cs^+. On the other hand, Cs^+ ion is too large to be able to enter the interlayer space of $NaVOPO_4$.

The ion exchange properties were employed in the preparation of ammonium intercalated vanadyl phosphate as NH_4^+ can be substituted for an alkali metal in $M_xVOPO_4 \cdot yH_2O$ (M = Li, Na, K, Rb). An opposite ion exchange of M^+ for NH_4^+ in $(NH_4)_xVOPO_4 \cdot H_2O$ does not proceed [158].

Due to the potential applications of vanadyl phosphate as an electrode material, electrochemical lithium insertion in the α-form of $VOPO_4$ was studied together with electrochemical behavior of α-$VOPO_4 \cdot 2H_2O$, α-Na_xVOPO_4, α-K_xVOPO4, and α-Mg_xVOPO_4 [162]. It was found that an intercalation of lithium into α_I-$VOPO_4$ and α_{II}-$VOPO_4$ leads to the same compound: α_I-$LiVOPO_4$ [163]. To facilitate the intercalation of lithium, vanadyl phosphate preintercalated with neutral molecules (H_2O, HCOOH, and CH_3COOH) was used as the host material [164]. The interest in lithium containing vanadyl phosphates as materials for energy storage still persists as documented by recent publications on this topic, even the structure of the studied compounds differs from that of α-$VOPO_4$ [165–167].

Magnetic properties of the redox intercalated vanadyl phosphates, $M_{0.5}VOPO_4 \cdot yH_2O$ (M = Na, K, Rb, Sr), were also investigated [168].

It is worth noting that many compounds with formula $M_xVOPO_4 \cdot yH_2O$, which are structurally related to $VOPO_4 \cdot 2H_2O$, can be prepared by hydrothermal synthesis as for instance those with M = Ag, Cu, Zn [169], Na and K [170, 171], Mg and Zn [172] and Ba [173]. Vanadyl phosphates containing divalent metals with general formula $M(VOPO_4)_2 \cdot 4H_2O$ (M = Cd and $Mg_{1-x}Zn_x$ [174], Ca, Ba and Cd [175], Co and Ni [176]) were also studied from the point of their magnetic properties. All these vanadyl phosphates containing mono- and divalent metals were reviewed and their main structure features were summarized [177].

Redox intercalation of organic ammonium ions

Due to the possibility of reducing vanadium atom, the intercalates of alkylammonium ions into $VOPO_4 \cdot 2H_2O$ were prepared by the reaction of alkylammonium iodides in acetone solution [178]. The course of this reaction can be represented by the following equation

$$VOPO_4 \cdot 2H_2O + xRNH_3I \rightarrow (RNH_3)_xV_x{}^{IV}V_{1-x}{}^{V}OPO_4 \cdot yH_2O + (x/2)I_2 + (2-y)H_2O, \quad (3)$$

where R = $PhCH_2$, or C_nH_{2n+1} (n = 3–8), and x = 0.4–0.6. As in the intercalations of inorganic cations, a part of V(V) is reduced by the iodide to V(IV) which produces a charge deficiency in the host lattice subsequently compensated by the organic cations. The starting material retains its layered arrangement but with distorted PO_4 tetrahedra due to V(V) → V(IV) transformations, and with an increase in the basal spacing. Alkylammonium ions are oriented perpendicularly to the host layers. Reaction of $VOPO_4$ with benzyldimethyl- and benzyltrimethylammonium iodide is described [179].

The mechanism of redox intercalation reactions between alkylammonium iodides and $VOPO_4 \cdot 2H_2O$ has been investigated by synthesis of mixed- and single-ion intercalates, by ion exchange experiments, and by EPR study of in situ reactions [180]. The intercalation was found to occur first at the edge of crystallites. With alkyl chains of butyl and longer, the intercalation of ions was seen to proceed throughout the interlayer galleries, resulting in a bilayer arrangement, with the chains tilted at an average angle of 39° to the host layers. Smaller ions were not intercalated to any great degree, with the reaction occurring only on crystal edges and faces. Intercalation of these smaller ions at crystal edges in mixed intercalation reactions prevented larger, co-present octylammonium ions to enter into the host interlayer space, indicating that they were a barrier to free interlayer diffusion of further reactant. This barrier is suggested as being the result of smaller ions intercalating parallel to the host layers at crystallite edges.

Five different stilbazolium chromophores were inserted into the interlamellar space of $VOPO_4$ [181]. Unfortunately, these intercalates exhibit no second-order nonlinear optical activity.

Some ferrocenylalkylammonium iodides and also ferrocenylalkylammonium chlorides react with $VOPO_4{\cdot}H_2O{\cdot}EtOH$ suspended in ethanol to afford intercalation compounds [179]. The composition and basal spacing of the intercalates prepared are given in Table 1. The ferrocenylalkylammonium iodides reduce the vanadium(V) in the $VOPO_4$ sheet by the iodide ion and ferrocenylalkylammonium cation is intercalated to give charge compensation, the ferrocenyl center remains non-oxidized (except for (2-ferrocenylethyl)trimethylammonium) because it is well separated from vanadium(V) site. In contrast, ferrocenyl compounds with alkylammonium chloride moieties are intercalated into the $VOPO_4$ interlayer through oxidation of the ferrocenyl centers.

A layered compound of the composition $VOPO_4{\cdot}H_2O{\cdot}0.52[Co(C_5H_5)_2{}^+]$ was obtained by stirring a suspension of $VOPO_4{\cdot}H_2O{\cdot}C_2H_5OH$ in ethanol/acetonitrile solution containing an excess of an equimolar mixture of $[Co(C_5H_5)_2][PF_6]$ and $N(n\text{-}C_4H_9)_4I$. In this reaction the $VOPO_4$ moieties were reduced by the iodide ion to include the $[Co(C_5H_5)_2]^+$ cation [141].

Table 1 The composition and basal spacing of ferrocenylalkylammonium intercalates [179]

Intercalate	Basal spacing (Å)
$VOPO_4{\cdot}0.45[Fe^{II}(C_5H_5)(C_5H_4CH_2NHMe_2)]$	17.1
$VOPO_4{\cdot}0.20[Fe^{II}(C_5H_5)(C_5H_4CH_2NMe_3)]$	9.8
$VOPO_4{\cdot}0.43[Fe^{II}(C_5H_5)(C_5H_4CH_2CH_2NH_3)]$	21.0
$VOPO_4{\cdot}0.17[Fe^{III}(C_5H_5)(C_5H_4CH_2CH_2NMe_3)]$	10.3
$VOPO_4{\cdot}0.29[Fe^{III}(C_5H_5)(C_5H_4CH_2NHMe_2{}^+Cl^-)]$	9.9
$VOPO_4{\cdot}0.18[Fe^{III}(C_5H_5)(C_5H_4CH_2CH_2NH_3{}^+Cl^-)]$	10.3

Conclusion

The α_I modification of vanadyl phosphate belongs to the most flexible host structures used in intercalation chemistry. This is given by its possibility to undergo two types of intercalation reaction: (i) intercalation of molecular (neutral) guests and (ii) redox intercalation of cationic guests.

The essential condition for the intercalation of neutral molecular guests is a presence of a free electron pair on a donor atom of the guest. As a donor atom, oxygen or nitrogen usually serves. On intercalation of neutral molecules, the interlayer distance, and consequently the basal spacing observed by powder XRD, usually increases. Most of molecular guests cannot be intercalated directly into anhydrous vanadyl phosphate but their intercalates can be prepared by replacing either water molecules in $VOPO_4{\cdot}2H_2O$ or short alkanols in a corresponding intercalate.

For the redox intercalation of cations, reduction of V(V) to V(IV) is condition to create a negative charge on the host layer. The driving force for the intercalation is then an electrostatic interaction between the negatively charged host layer and positively charged guest cation. Iodides are the most suitable reduction agent as it can in the same time reduce vanadium (which is accompanied by oxidation of iodide to iodine) and to provide a cation to be intercalated. In contrast to the intercalation of the molecules, the interlayer distance usually decreases during redox intercalation due to the electrostatic interactions.

Three possible mechanisms can be used to describe the course of intercalation of vanadyl phosphate (see Fig. 18) [182]:

- Intercalation proceeds via exfoliation of host layers in an excess of a guest. The host layers are then reassociated, taking the guest molecules between them and forming an intercalate. This phenomenon is rare and has been observed during reintercalation of water molecules in $VOPO_4{\cdot}2H_2O$ with alcohols and diols [67].
- Particles of the guest start intercalation by nucleation of the first subsurface van der Waals zone. Growth of the intercalate in this layer causes nucleation of the adjacent van der Waals zone. This process continues, further causing intercalation in the whole crystal. This process is manifested by a coexistence of the original host and the intercalate in one crystal. Both phases are separated by an advancing phase boundary. This mechanism was observed during an intercalation of short 1-alkanols into anhydrous vanadyl phosphate [70, 71].
- Particles of the guest start intercalation along the whole side of the host crystal. Stages, superlattices or randomly stacked intercalated and unintercalated layers are formed during intercalation. Stages were observed

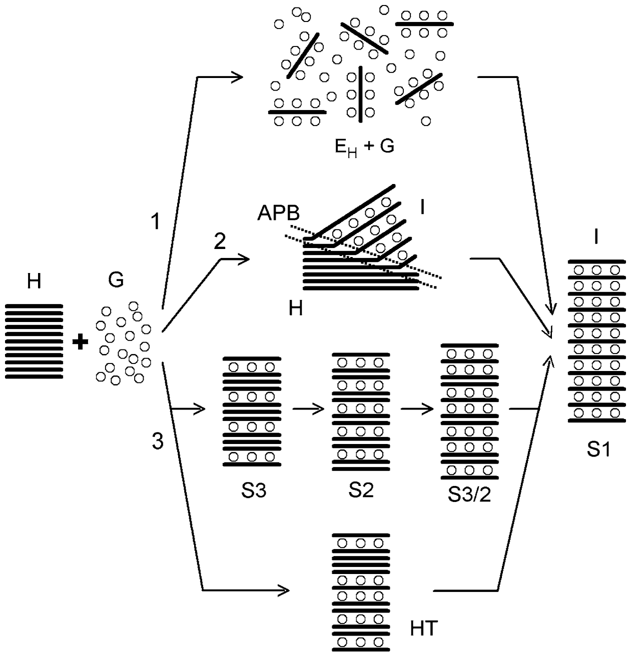

Fig. 18 Schematic representation of the intercalation mechanisms. *H* host, *G* guest, *I* intercalate, E_H exfoliated host layers, *APB* advancing phase boundary, *S3, S2, S3/2 and S1* stages, *HT* Hendricks-Teller disordered layer structure. Reprinted with permission from Ref. [182]. Copyright 1998 Springer

during intercalation of alkali metal cations [152, 155]. Random stacking of intercalated and nonintercalated layers was observed during intercalation of water into anhydrous vanadyl phosphate [63].

Acknowledgment This work was supported by the Academy of Sciences of the Czech Republic (AV0Z40500505) and the Ministry of Education, Youth and Sports of the Czech Republic (MSM 0021627501).

References

1. Centi, G., Trifirò, F., Ebner, J.R., Franchetti, V.M.: Mechanistic aspects of maleic-anhydride synthesis from C_4-hydrocarbons over phosphorus vanadium-oxide. Chem. Rev. **88**, 55–80 (1988)
2. Centi, G., Cavani, F., Trifirò, F.: Maleic anhydride from *n*-butane on vanadium/phosphorus oxides. In: Ruiz, P., Delmon, B. (eds.) Selective Oxidation by Heterogeneous Catalysis, p. 143, Kluwer Academic, New York (2001)
3. Hutchings, G.J.: Vanadium phosphate: a new look at the active components of catalysts for the oxidation of butane to maleic anhydride. J. Mater. Chem. **14**, 3385–3395 (2004)
4. Di Serio, M., Cozzolino, M., Tesser, R., Patrono, P., Pinzari, F., Bonelli, B., Santacesaria, E.: Vanadyl phosphate catalysts in biodiesel production. Appl. Catal. A **320**, 1–7 (2007)
5. Li, H., Xie, W.: Fatty acid methyl ester synthesis over Fe^{3+}-vanadyl phosphate catalysts. J. Am. Oil Chem. Soc. **85**, 655–662 (2008)
6. Morris, M., Dyer, A., McCabe, R.W.: MAS NMR-study of the layered host α-vanadyl phosphate dihydrate–potential as a shape selective catalyst. J. Mater. Chem. **5**, 1427–1431 (1995)
7. Casaletto, M.P., Landi, G., Lisi, L., Patrono, P., Pinzari, F.: Effect of the support on the catalytic properties of vanadyl phosphate in the oxidative dehydrogenation of propane. J. Mol. Catal. A **329**, 50–56 (2010)
8. Lisi, L., Patrono, P., Ruoppolo, G.: Vanadyl phosphate dihydrate supported on oxides for the catalytic conversion of ethane to ethylene. J. Mol. Catal. A **204**, 609–616 (2003)
9. Weng, W.H., Davies, M., Whiting, G., Solsona, B., Kiely, C.J., Carley, A.F., Taylor, S.H.: Controlling vanadium phosphate catalyst precursor morphology by adding alkane solvents in the reduction step of $VOPO_4{\cdot}2H_2O$ to $VOHPO_4{\cdot}0.5H_2O$. Phys. Chem. Chem. Phys. **13**, 17395–17404 (2011)
10. Tachez, M., Theobald, F., Bordes, E.: A structural explanation for the polymorphism of the α form of anhydrous vanadyl phosphate. J. Solid State Chem. **40**, 280–283 (1981)
11. Jordan, B., Calvo, C.: Crystal structure of α-$VOPO_4$. Can. J. Chem. **51**, 2621–2625 (1973)
12. Bordes, E., Courtine, P., Pannetier, G.: Crystallochemical properties of vanadyl phosphate. Analysis of structural factors having an effect on the formation of vanadyl phosphate. Ann. Chim. (Paris) **8**, 105–113 (1973)
13. Gopal, R., Calvo, C.: Crystal structure of *β*-$VOPO_4$. J. Solid State Chem. **5**, 432–435 (1972)
14. Bordes, E., Courtine, P.: Preparation and structural properties of oxovanadium phosphate $VOPO_4$. C. R. Acad. Sci. Paris **274**, 1375–1378 (1972)
15. Bordes, E., Courtine, P.: New phases in V-P-O catalysts and their role in oxidation of butane to maleic anhydride. J. Chem. Soc. Chem. Commun. 294–296 (1985)
16. Li, Z.G., Harlow, R.L., Heron, N., Horowitz, H.S., McCarron, E.M.: Unit cell information for *δ*- and *γ*-$VOPO_4$. J. Catal. **171**, 506–508 (1997)
17. Bordes, E., Johnson, J.W., Raminosona, A., Courtine, P.: Topotactic reactions yielding new phases in vanadium-phosphorus-oxygen system. Mater. Sci. Monogr. **28B**, 887–892 (1985)
18. Lim, S.C., Vaughey, J.T., Harrison, W.T.A., Dussack, L.L., Jacobson, A.J., Johnson, J.W.: Redox transformations of simple vanadium phosphates: the synthesis of ε-$VOPO_4$. Solid State Ionics **84**, 219–226 (1996)
19. Girgsdies, F., Schneider, M., Brueckner, A., Ressler, T., Schlogl, R.: The crystal structure of *δ*-$VOPO_4$ and its relationship to *ω*-$VOPO_4$. Solid State Sci. **11**, 1258–1264 (2009)
20. Azmi, B.M., Ishihara, T., Nishiguchi, H., Takita, Y.: Cathodic performance of $VOPO_4$ with various crystal phases for Li ion rechargeable battery. Electrochim. Acta **48**, 165–170 (2002)
21. Azmi, B.M., Ishihara, T., Nishiguchi, H., Takita, Y.: Vanadyl phosphates: of $VOPO_4$ as a cathode of Li-ion rechargeable batteries. J. Power Sources **119**, 273–277 (2003)
22. Joint Committee on Powder Diffraction Standards, International Centre of Diffraction Data, Swarthmore, PA (JCPDS 37-809)
23. Dupre, N., Gaubicher, J., Angenault, J., Wallez, G., Quarton, M.: Positive electrode materials for lithium batteries based on $VOPO_4$. J. Power Sources **97–98**, 532–534 (2001)
24. Sun, Y.F., Wu, C.Z., Xie, Y.: Sonochemical synthesis of nanostructured $VOPO_4{\cdot}2H_2O$/carbon nanotube composites with improved lithium ion battery performance. J. Nanopart. Res. **12**, 417–427 (2010)
25. Tachez, V., Theobald, F., Bernard, V., Hewat, A.W.: Intercalation of water molecules in a layer structure $VOPO_4$. Crystal structure of $VOPO_4{\cdot}2D_2O$. Rev. Chim. Miner. **19**, 291–300 (1982)
26. Tietze, H.R.: The crystal and molecular structure of oxovanadium(V) orthophosphate dihydrate, $VOPO_4{\cdot}2H_2O$. Aust. J. Chem. **34**, 2035–2038 (1981)
27. Ladwig, G.: Über die Konstitution des $VPO_5{\cdot}nH_2O$. Z. Anorg. Allg. Chem. **338**, 266–278 (1965)

28. Ennaciri, S.A., Rkha, C., Bardoux, P., Livage, J.: Synthesis of vanadium phosphates from molecular precursors. Eur. J. Solid State Inorg. Chem. **30**, 227–236 (1993)
29. Park, N.G., Kim, K.M., Chang, S.H.: Sonochemical synthesis of the high energy density cathode material $VOPO_4 \cdot 2H_2O$. Electrochem. Commun. **3**, 553–556 (2001)
30. Wong, Y.C., Taufiq-Yap, Y.H.: $VOPO_4 \cdot 2H_2O$ and the vanadium phosphate catalyst produced by sonochemical synthesis. Asian J. Chem. **23**, 3853–3858 (2011)
31. Kalousová, J., Votinský, J., Beneš, L., Melánová, K., Zima, V.: Vanadyl phosphate and its intercalation reactions. A review. Collect. Czech. Chem. Commun. **63**, 1–19 (1998)
32. Garcia-Ponce, A.L., Moreno-Real, L., Jimenez-Lopez, A.: Synthesis and characterization of mixed niobium-vanadium phosphates. Inorg. Chem. **27**, 3372–3376 (1988)
33. Jimenez-Lopez, A., Garcia-Ponce, A.L.: Synthesis and reactivity of mixed niobium-vanadium phosphates. J. Chim. Phys. **88**, 1957–1962 (1991)
34. Garcia-Ponce, A.L., Moreno-Real, L., Jimenez-Lopez, A.: Intercalation of N-alkylamines into mixed niobyl-vanadyl phosphates. J. Solid State Chem. **87**, 20–28 (1990)
35. Garcia-Ponce, A.L., Moreno-Real, L., Jimenez-Lopez, A.: Intercalation of basic molecules into niobyl-vanadyl phosphate. Can. J. Chem. **68**, 592–596 (1990)
36. Garcia-Ponce, A.L., Moreno-Real, L., Jimenez-Lopez, A.: Sorption of amides by mixed niobyl-vanadyl phosphate. J. Incl. Phenom. Mol. Recognit. Chem. **9**, 355–366 (1990)
37. Jimenez-Lopez, A., Garcia-Ponce, A.L., Moreno-Real, L.: Intercalation of cations into niobyl-vanadyl phosphate by redox reactions. Can. J. Chem. **68**, 1616–1620 (1990)
38. Yakovleva, T.N., Vykhodtseva, K.I., Tarasova, D.V., Soderzhinova, M.M.: Interaction of vanadium(V) phosphate dihydrate with chromium(VI) Oxide. Zh. Neorg. Khim. **39**, 1948–1950 (1994)
39. Beneš, L., Richtrová, K., Votinský, J., Kalousová, J., Zima, V.: Synthesis and powder data for $[Mn(H_2O)_{0.25}(VO)_{0.75}PO_4] \cdot 2H_2O$. Powder Diffr **8**, 130–131 (1993)
40. Richtrová, K., Votinský, J., Kalousová, J., Beneš, L., Zima, V.: Synthesis, characterization, and intercalation of vanadyl phosphate modified with manganese. J. Solid State Chem. **116**, 400–405 (1995)
41. Melánová, K., Votinský, J., Beneš, L., Zima, V.: Layered compounds derived from vanadyl phosphate dihydrate. Mater. Res. Bull. **30**, 1115–1120 (1995)
42. Melánová, K., Beneš, L., Vlček, M., Patrono, P., Massucci, M.A., Galli, P.: Preparation and characterization of vanadyl phosphates modified with two trivalent metal cations. Mater. Res. Bull. **34**, 895–903 (1999)
43. Bagnasco, G., Beneš, L., Galli, P., Massucci, M.A., Patrono, P., Turco, M., Zima, V.: TG/DTA, XRD and NH_3-TPD characterization of layered $VOPO_4 \cdot 2H_2O$ and its Fe^{3+}-substituted compound. J. Therm. Anal. Calorim **52**, 615–630 (1998)
44. Bagnasco, G., Busca, G., Galli, P., Larubbia, M.A., Massucci, M.A., Beneš, L., Ramis, R., Turco, M.: Selective reduction of NO with NH_3 on a new iron-vanadyl phosphate catalyst. J. Therm. Anal. Calorim **61**, 625–836 (2000)
45. Hradil, P., Votinský, J., Komárek, K., Zima, V., Kalousová, J., Melánová, K., Beneš, L.: Adsorption of vapours of some organic compounds on surface of iron-substituted layered vanadyl phosphate. Collect. Czech. Chem. Commun. **65**, 47–57 (2000)
46. Casaletto, M.P., Kaciulis, S., Lisi, L., Mattogno, G., Mezzi, A., Patrono, P., Ruoppolo, G.: XPS characterisation of iron-modified vanadyl phosphate catalysts. Appl. Catal. A **218**, 129–137 (2001)
47. Beneš, L., Galli, P., Massucci, M.A., Melánová, K., Patrono, P., Zima, V.: Thermal, structural and acidic characterization of some vanadyl phosphate materials modified with trivalent metal cations. J. Therm. Anal. Calorim. **50**, 355–364 (1997)
48. Bagnasco, G., Beneš, L., Galli, P., Massucci, M.A., Patrono, P., Russo, G., Turco, M.: Iron modified vanadyl phosphate as oxidation catalyst. Stud. Surf. Sci. Catal. **119**, 653–657 (1998)
49. Martin, A., Steinike, U., Melánová, K., Zima, V.: Solid-state reactions of vanadium(V) phosphates in the presence of ammonia. J. Mater. Chem. **9**, 2523–2527 (1999)
50. Carlini, C., Patrono, P., Galletti, A.M.R., Sbrana, G., Zima, V.: Selective oxidation of 5-hydroxymethyl-2-furaldehyde to furan-2,5-dicarboxaldehyde by catalytic systems based on vanadyl phosphate. Appl. Catal. A **289**, 197–204 (2005)
51. Ciambelli, P., Lisi, L., Patrono, P., Ruoppolo, G., Russo, G.: $VOPO_4 \cdot 2H_2O$ and $Fe(H_2O)_x(VO)_{1\text{-}x}PO_4 \cdot 2H_2O$ supported on TiO_2 as catalysts for oxidative dehydrogenation of ethane. Catal. Lett. **82**, 243–247 (2002)
52. Lagaly, G.: Kink-block and gauche-block structures of bimolecular films. Angew. Chem. Int. Ed. Engl. **15**, 575–586 (1976)
53. Beneke, K., Lagaly, G.: Intercalation into $NbOPO_4 \cdot 3H_2O$ and comparison with $VOPO_4 \cdot 2H_2O$. Inorg. Chem. **22**, 1503–1507 (1983)
54. Čapková, P., Vácha, J., Votinský, J.: Anomalous thermal-behavior and hydrogen-bond in $VOPO_4 \cdot 2H_2O$. J. Phys. Chem. Solids **53**, 215–218 (1992)
55. Zima, V., Beneš, L., Málek, J., Vlček, M.: Thermomechanical and thermoelectrical properties of vanadyl phosphate dihydrate. Mater. Res. Bull. **29**, 687–692 (1994)
56. Casan, N., Amoros, P., Ibanez, R., Martinez-Tamayo, E., Beltran-Porter, A., Beltran-Porter, D.: Vanadyl phosphate dihydrate, a solid acid: the role of water in $VOPO_4 \cdot 2H_2O$ and its sodium derivatives $Na_x(V_x{}^{IV}V_{1-x}{}^{V}O)PO_4 \cdot (2-x)H_2O$. J. Incl. Phenom. **6**, 193–211 (1988)
57. R'Kha, C., Vandenborre, M.T., Livage, J., Prost, R., Huard, E.: Spectroscopic study of colloidal $VOPO_4 \cdot 2H_2O$. J. Solid State Chem. **63**, 202–215 (1986)
58. Gautier, R., Audebrand, N., Furet, E., Le Fur, E.: $VOPO_4 \cdot 2H_2O$: a stacking faults structure studied by X-ray powder diffraction and DFT-D calculations. Inorg. Chem. **50**, 4379–4383 (2011)
59. Beneš, L., Černošková, E., Málek, J., Melánová, K., Patrono, P., Zima, V.: A kinetic study of the dehydration of $VOPO_4 \cdot 2H_2O$ by thermal methods. J. Incl. Phenom. Mol. Recognit. Chem. **36**, 163–178 (2000)
60. Lomax, J.F., Fontanella, J.J., Wintersgill, M.C., Kotarski, A.: Dielectric loss in vanadyl pnictates. Mat. Res. Soc. Symp. Proc. **210**, 681–686 (1991)
61. Zima, V., Vlček, M., Beneš, L., Casciola, M., Massinelli, L., Palombari, R.: Electrical-transport properties of hydrated and anhydrous vanadyl phosphate in the temperature range 20–200°C. Chem. Mater. **8**, 2505–2509 (1996)
62. Zima, V., Beneš, L., Melánová, K., Casciola, M., Cruccolini, A.: Electrical conductivity of $MOXO_4$ ($M = V$, Nb; $X = P$, As) compounds intercalated with H_2O and H_3XO_4. J. Solid State Chem. **178**, 1778–1785 (2005)
63. Beneš, L., Zima, V.: Formation of a disordered layer lattice during the intercalation of water into anhydrous vanadyl phosphate. J. Incl. Phenom. Mol. Recognit. Chem. **20**, 381–391 (1995)
64. Trchová, M., Čapková, P., Matějka, P., Melánová, K., Beneš, L., Uhlířová, E.: Intercalation of water into anhydrous vanadyl phosphate studied by the infrared and Raman spectroscopies. J. Solid State Chem. **148**, 197–204 (1999)
65. Ladwig, G.: Intercalation of bimolecular normal-alkanol films in a layer sulfate—α-$VOSO_4 \cdot 2ROH$. Z. Chem. **20**, 70–71 (1980)
66. Beneš, L., Votinský, J., Kalousová, J., Klikorka, J.: Layer-type complexes consisting of $VOSO_4$ or $VOPO_4$ and aliphatic-alcohols. Inorg. Chim. Acta **114**, 47–50 (1986)

67. Beneš, L., Melánová, K., Zima, V., Kalousová, J., Votinský, J.: Preparation and probable structure of layered complexes of vanadyl phosphate with 1-alkanols and 1, ω-alkanediols. Inorg. Chem. **36**, 2850–2854 (1997)
68. Čapková, P., Janeba, D., Beneš, L., Melánová, K., Schenk, H.: Molecular mechanics simulations in structure analysis of intercalate $VOPO_4.2CH_3CH_2OH$. J. Mol. Model. **4**, 150–157 (1998)
69. Čapková, P., Melánová, K., Beneš, L., Schenk, H.: Modeling in structure analysis of vanadyl phosphate intercalated with 1-alkanols. J. Mol. Model. **6**, 9–15 (2000)
70. Votinský, J., Kalousová, J., Beneš, L., Baudyšová, I., Zima, V.: Volumetric method for the following rate of intercalation of liquid molecular guests into layered hosts. J. Incl. Phenom. Mol. Recognit. Chem. **15**, 71–78 (1993)
71. Beneš, L., Zima, V., Baudyšová, I., Votinský, J.: A kinetic study of the intercalation of ethanol into vanadyl phosphate. J. Incl. Phenom. Mol. Recognit. Chem. **26**, 311–319 (1996)
72. Beneš, L., Melánová, K., Trchová, M., Čapková, P., Matějka, P.: Water/ethanol displacement reactions in vanadyl phosphate. Eur. J. Inorg. Chem. 2289–2294 (1999)
73. Beneš, L., Zima, V., Kalousová, J., Votinský, J.: Intercalation of anhydrous vanadyl phosphate with aliphatic alcohol mixtures. Collect. Czech. Chem. Commun. **59**, 1616–1619 (1994)
74. Melánová, K., Beneš, L., Zima, V., Kalousová, J., Votinský, J.: Intercalation of 1-alkanol binary mixtures into the layered structure of vanadyl phosphate. J. Incl. Phenom. Mol. Recognit. Chem. **33**, 391–402 (1999)
75. Beneš, L., Zima, V., Melánová, K.: 2-Alkanol intercalated $VOPO_4$ and $NbOPO_4$: structure modeling of intercalate layers. J. Incl. Phenom. Mol. Recognit. Chem. **40**, 131–138 (2001)
76. Beneš, L., Zima, V., Melánová, K.: Intercalates of vanadyl phosphate with branched alcohols. Eur. J. Inorg. Chem. 1883–1887 (2001)
77. Beneš, L., Melánová, K., Zima, V., Trchová, M., Uhlířová, E., Matějka, P.: Intercalates of vanadyl phosphate with unsaturated alcohols. Eur. J. Inorg. Chem. 713–719 (2001)
78. Johnson, J.W., Johnston, D.C., Jacobson, A.J., Brody, J.F.: Preparation and characterization of $VO(HPO_4)\cdot 0.5H_2O$ and its topotactic transformation to $(VO)_2P_2O_7$. J. Am. Chem. Soc. **106**, 8123–8128 (1984)
79. Horowitz, H.S., Blackstone, C.M., Sleight, A.W., Truffer, G.: V-P-O catalysts for oxidation of butane to maleic-anhydride—influence of $(VO)_2H_4P_2O_9$ precursor morphology on catalytic properties. Appl. Catal. **38**, 193–210 (1988)
80. Ellison, I.J., Hutchings, G.J., Sananes, M.T., Volta, J.C.: Control of the composition and morphology of vanadium phosphate catalyst precursors from alcohol treatment of $VOPO_4\cdot 2H_2O$. J. Chem. Soc. Chem. Commun. 1093–1094 (1994)
81. Weng, W.H., Al Otaibi, R., Alhumaimess, M., Conte, M., Bartley, J.K., Dummer, N.F., Hutchings, G.J., Kiely, C.J.: Controlling vanadium phosphate catalyst precursor morphology by adding alkane solvents in the reduction step of $VOPO_4\cdot 2H_2O$ to $VOHPO_4\cdot 0.5H_2O$. J. Mater. Chem. **21**, 16136–16146 (2011)
82. Yamamoto, N., Hiyoshi, N., Okuhara, T.: Thin-layered sheets of $VOHPO_4\cdot 0.5H_2O$ prepared from $VOPO_4\cdot 2H_2O$ by intercalation-exfoliation-reduction in alcohol. Chem. Mater. **14**, 3882–3888 (2002)
83. Kamiya, Y., Ueki, S., Hiyoshi, N., Yamamoto, N., Okuhara, T.: Preparation and characterization of lamellar vanadyl alkylphosphates. Catal. Today **78**, 281–290 (2003)
84. Borah, P., Datta, A.: Exfoliated $VOPO_4\cdot 2H_2O$ dispersed on alumina as a novel catalyst for the selective oxidation of cyclohexane. Appl. Catal. A **376**, 19–24 (2010)
85. Dasgupta, S., Agarwal, M., Datta, A.: Surfactant assisted organization of an exfoliated vanadyl orthophosphate to a mesostructured lamellar vanadium phosphate phase. Microporous Mesoporous Mater **67**, 229–234 (2004)
86. Datta, A., Sakthivel, S., Kaur, M., Venezia, A.M., Pantaleo, G., Longo, A.: Novel transformations amongst mesostructured VPO phases synthesized through surfactant assisted organization from an exfoliated solution of $VOPO_4\cdot 2H_2O$. Microporous Mesoporous Mater. **128**, 213–222 (2010)
87. Melánová, K., Beneš, L., Zima, V.: Intercalation of 1,2-alkanediols into vanadyl and niobyl phosphate. J. Incl. Phenom. Mol. Recognit. Chem. **36**, 301–309 (2000)
88. Beneš, L., Melánová, K., Zima, V.: Intercalates of vanadyl and niobyl phosphates with C_4 diols. J. Solid State Chem. **151**, 225–230 (2000)
89. Yakovleva, T.N., Vykhodtseva, K.I., Tarasova, D.V., Soderzhinova, M.M.: Intercalation compounds of vanadium(V) phosphates with glycerol. Zh. Neorg. Khim. **42**, 700–704 (1997)
90. Tarasova, D.V., Kozlova, G.A., Yakovleva, T.N., Vykhodseva, K.I., Avetisov, A.K.: Preparation of oxide vanadium-phosphorus catalyst using intercalated compounds. Kinet. Catal. **40**, 275–281 (1999)
91. Tarasova, D.V., Vykhodtseva, K.I., Bovina, E.A., Soderzhinova, M.M., Chernysheva, T.N.: Thermolysis of vanadium(V) phosphate dihydrate intercalation compounds with glycerol. Russ. J. Inorg. Chem. **46**, 1031–1036 (2001)
92. Melánová, K., Beneš, L., Zima, V., Vahalová, R., Kilián, M.: Intercalation of poly(oxyethylene) compounds into the $MOXO_4$ ($M = V$, Nb; $X = P$, As) host lattice. Chem. Mater. **11**, 2173–2178 (1999)
93. Goubitz, K., Čapková, P., Melánová, K., Molleman, W., Schenk, H.: Structure determination of two intercalated compounds $VOPO_4\cdot(CH_2)_4O$ and $VOPO_4\cdot OH–(CH_2)_2–O–(CH_2)_2–OH$; synchrotron powder diffraction and molecular modelling. Acta Crystallogr. B **57**, 178–183 (2001)
94. Zima, V., Melánová, K., Beneš, L., Čapková, P., Trchová, M., Matějka, P.: Intercalation of cyclic ethers into vanadyl phosphate. Chem. Eur. J. **8**, 1703–1709 (2002)
95. Melánová, K., Beneš, L., Zima, V., Černošková, E., Brus, J., Urbanová, M., Trchová, M., Dybal, J.: Thermal behavior of tetrahydropyran-intercalated $VOPO_4$: structural and dynamics study. Eur. J. Inorg. Chem. 444–451 (2007)
96. Beneš, L., Zima, V., Melánová, K., Trchová, M., Čapková, P., Koudelka, B., Matějka, P.: Synthesis and characterization of vanadyl phosphate intercalated with dioxane, trioxane, and 18-crown-6. Chem. Mater. **14**, 2788–2795 (2002)
97. Melánová, K., Beneš, L., Zima, V., Trchová, M., Dybal, J.: Vanadyl phosphate intercalated with diethyl ether. Eur. J. Inorg. Chem. 2493–2497 (2004)
98. Melánová, K., Beneš, L., Zima, V., Votinský, J.: Intercalation of aldehydes into vanadyl phosphate. J. Solid State Chem. **157**, 50–55 (2001)
99. Melánová, K., Beneš, L., Zima, V., Čapková, P., Trchová, M.: Intercalation of ketones in vanadyl phosphate and isostructural hosts. Collect. Czech. Chem. Commun. **64**, 1975–1979 (1999)
100. Čapková, P., Trchová, M., Zima, V., Schenk, H.: Structure analysis of vanadyl phosphate intercalated with acetone. J. Solid State Chem. **150**, 356–362 (2000)
101. Zima, V., Melánová, K., Beneš, L., Trchová, M., Dybal, J.: Intercalation of cyclic ketones into vanadyl phosphate. J. Solid State Chem. **178**, 314–320 (2005)
102. Koudelka, B., Čapková, P.: Supramol—a program for structure analysis of intercalates using molecular simulations: the structure of $VOPO_4\cdot C_6H_4O_2$. J. Mol. Model. **8**, 184–190 (2002)
103. Beneš, L., Melánová, K., Zima, V., Trchová, M., Čapková, P., Koudelka, B.: Vanadyl phosphate intercalated with dimethyl sulfoxide. J. Phys. Chem. Solids **67**, 956–960 (2006)
104. Beneš, L., Votinský, J., Kalousová, J., Handlíř, K.: Intercalation of aliphatic carboxylic acids into layered of vanadyl sulphate, phosphate and arsenate. Inorg. Chim. Acta **176**, 255–259 (1990)

105. Zima, V., Beneš, L., Melánová, K.: Glycine intercalated vanadyl and niobyl phosphates. Solid State Ionics **106**, 285–290 (1998)
106. Melánová, K., Beneš, L., Svoboda, J., Zima, V.: Intercalation of esters into vanadyl phosphate. J. Phys. Chem. Solids **68**, 765–769 (2007)
107. Zima, V., Melánová, K., Beneš, L., Trchová, M., Dybal, J.: Intercalation of gamma-butyrolactone into vanadyl phosphate and niobyl arsenate. Eur. J. Inorg. Chem. 570–574 (2004)
108. Melánová, K., Beneš, L., Svoboda, J., Zima, V.: Intercalation of lactones into vanadyl phosphate. J. Phys. Chem. Solids **67**, 961–964 (2006)
109. Beneš, L., Melánová, K., Zima, V., Svoboda, J., Kincl, M.: Intercalation of dimethyl carbonate, diethyl carbonate and ethylene carbonate into vanadyl phosphate. J. Incl. Phenom. Macrocycl. Chem. **54**, 271–274 (2006)
110. Martinez-Lara, M., Moreno-Real, L., Jimenez-Lopez, A., Bruque-Gamez, S., Rodriguez-Garcia, A.: Interaction of Amides with $VOAO_4 \cdot nH_2O$ (A = P, As). Mater. Res. Bull. **21**, 13–22 (1986)
111. Yamamoto, N., Okuhara, T., Nakato, T.: Intercalation compound of $VOPO_4 \cdot 2H_2O$ with acrylamide: preparation and exfoliation. J. Mater. Chem. **11**, 1858–1863 (2001)
112. DeFarias, R.F., Airoldi, C.: The first $VOPO_4 \cdot 2H_2O$ intercalation compound synthesized through a solid-state reaction at room temperature. J. Solid State Chem. **166**, 277–278 (2002)
113. Beneš, L., Zima, V., Melánová, K., Trchová, M., Matějka, P.: Intercalates of vanadyl phosphate with aliphatic nitriles. J. Incl. Phenom. Macrocycl. Chem. **43**, 95–99 (2002)
114. Beneš, L., Zima, V., Melánová, K., Trchová, M., Matějka, P.: Intercalates of vanadyl phosphate with dinitriles. J. Incl. Phenom. Macrocycl. Chem. **45**, 235–239 (2003)
115. Beneš, L., Zima, V., Melánová, K., Dybal, J., Trchová, M., Matějka, P.: Intercalates of vanadyl phosphate with benzonitrile and tolunitrile. Eur. J. Inorg. Chem. 3662–3667 (2003)
116. Beneš, L., Kalousová, J., Votinský, J., Hyklová, R.: Intercalation of aliphatic amines into layered structure of vanadyl phosphate. Inorg. Chim. Acta **177**, 71–74 (1990)
117. Zhu, J., Huang, Y.: Solid-state (51)V NMR investigation of the intercalation of alkylamines into layered α-vanadyl phosphate. Langmuir **26**, 10115–10121 (2010)
118. Machado, M.O., de Farias, R.F., Airoldi, C.: Two different synthetic routes involving the reaction of dodecylamine or nicotinamide with crystalline lamellar vanadyl phosphate. J. Phys. Chem. Solids **65**, 1697–1703 (2004)
119. Nakato, T., Furumi, Y., Terao, N., Okuhara, T.: Reaction of layered vanadium phosphorus oxides, $VOPO_4 \cdot 2H_2O$ and $VOHPO_4 \cdot 0.5H_2O$, with amines and formation of exfoliative intercalation compounds. J. Mater. Chem. **10**, 737–743 (2000)
120. Gendraud, P., Deroy, M.E., Besse, J.P.: Intercalation reactions of layered vanadyl organophosphonates with alkylamines. Inorg. Chem. **351**, 6108–6112 (1996)
121. Kinomura, N., Toyama, T., Kumada, N.: Intercalative polymerization of aniline in $VOPO_4 \cdot 2H_2O$. Solid State Ionics **78**, 281–286 (1995)
122. Nakajima, H., Matsubayashi, G.E.: Intercalation polymerization of the anilinium cation in the $VOPO_4$ interlayer space. Chem. Lett. **22**, 423–426 (1993)
123. DeStefanis, A., Foglia, S., Tomlinson, A.A.G.: Assembly and polymerisation of some aromatic amines in α-$VOPO_4 \cdot 2H_2O$. J. Mater. Chem. **5**, 475–483 (1995)
124. de Farias, R.F., Airoldi, C.: Synthesis and characterization of an $VOPO_4$-polyaniline lamellar hybrid compound. Solid State Sci. **5**, 611–613 (2003)
125. De, S., Dey, A., De, S.K.: Electrical transport and optical properties of vanadyl phosphate-polyaniline nanocomposites. J. Phys. Chem. Solids **68**, 66–72 (2007)
126. Nakato, T., Furumi, Y., Okuhara, T.: Exfoliation of layered oxovanadium phosphate $VOPO_4 \cdot 2H_2O$ in tetrahydrofuran through intercalation of 4-butylaniline. Chem. Lett. 611–612 (1998)
127. Bissessur, R., MacDonald, J.: Novel alkyl substituted polyanilines/$VOPO_4$ nanocomposites. Solid State Sci. **8**, 531–536 (2006)
128. Zampronio, E.C., Oliveira, H.P.: Synthesis, spectroscopic and structural characterization of poly-*o*-methoxyaniline and poly-*o*-methylaniline intercalated into layered vanadyl phosphate. Mater. Res. Bull. **39**, 1525–1538 (2004)
129. Zampronio, E.C., Ferreira, J.P.L., Oliveira, H.P.: Synthesis and electrochemical properties of vanadyl phosphate dihydrate/polyaniline derivatives hybrid films. J. Non-Cryst. Solids **355**, 2355–2360 (2009)
130. Nakajima, H., Matsubayashi, G.E.: Intercalation and polymerization of 4-anilinoaniline and 4-anilinoanilinium iodide in the $VOPO_4$ and V_2O_5 interlayer spaces. J. Mater. Chem. **5**, 105–108 (1995)
131. Johnson, J.W., Jacobson, A.J., Brody, J.F., Rich, S.M.: Coordination intercalation reaction of the layered compounds $VOPO_4$ and $VOAsO_4$ with pyridine. Inorg. Chem. **21**, 3820–3825 (1982)
132. Chatakondu, K., Green, M.L.H., Mingos, D.P.M., Reynholds, S.M.: Application of microwave dielectric loss heating effects for the rapid and convenient synthesis of intercalation compounds. J. Chem. Soc. Chem. Commun. 1515–1517 (1989)
133. Yatabe, T., Nakano, M., Matsubayashi, G.E.: Intercalation of substituted pyridine derivatives and bipyridine compounds into gel-V_2O_5 and $VOPO_4$ interlayer spaces and protonation of the guest molecules. J. Mater. Chem. **8**, 699–703 (1998)
134. Yatabe, T., Matsubayashi, G.E.: Intercalation of 2-, 4-sulfanylpyridine, 2,2'- and 4,4'-dithiobispyridine into $VOPO_4$, and gel-V_2O_5 interlayer spaces. J. Mater. Chem. **61**, 1849–1852 (1996)
135. DeStefanis, A., Tomlinson, A.A.G.: Variable assembly of imidazole into α-$VOPO_4 \cdot 2H_2O$. J. Mater. Chem. **5**, 319–322 (1994)
136. De, S., Arup, D., De, S.K.: Characterization and electrical properties of vanadyl phosphate-polypyrrole nanocomposites. J. Phys. D **39**, 500–505 (2006)
137. Matsubayashi, G.E., Nakajima, H.: Intercalative polymerization of 3-methylpyrrole and 3,4-dimethylpyrrole in the $VOPO_4$ interlayer space. Chem. Lett. **1**, 31–34 (1993)
138. Nakajima, H., Matsubayashi, G.E.: Intercalation of polymerized 3-methyl-pyrrole and 3,4-dimethyl-pyrrole in the $VOPO_4$ interlayer space. J. Mater. Chem. **4**, 1325–1329 (1994)
139. Pozas-Tormo, R., Moreno-Real, L., Bruque, S., Martinez-Lara, M., Ramos-Barado, J.: Modification of electrical response after intercalation of TTF in vanadyl and uranyl phosphates. Mater. Sci. Forum **91–93**, 511–516 (1992)
140. Rodriguez-Castellon, E., Jimenez-Lopez, A., Martinez-Lara, M., Moreno-Real, L.: Intercalation of ferrocene and dimethylaminoferrocene into α-$Sn(HPO_4)2 \cdot H_2O$ and α-$VOPO_4 \cdot 2H_2O$. J. Incl. Phenom. Mol. Recognit. Chem. **5**, 335–342 (1987)
141. Matsubayashi, G.E., Ohta, S.: Intercalation of ferrocene and related compounds into interlayer space of vanadyl phosphate. Chem. Lett. **19**, 787–790 (1990)
142. Okuno, S., Matsubayashi, G.E.: Intercalation of alkyl-bridged biferrocene compounds into $VOPO_4$ and gel-V_2O_5 interlayer spaces. Chem. Lett. **22**, 799–802 (1993)
143. Okuno, S., Matsubayashi, G.E.: Intercalation of ferrocene and its derivatives into $V_xNb_{1-x}OPO4$ (x = 0, 0.06, 0.11, and 0.21) interlayer spaces. Bull. Chem. Soc. Jpn. **67**, 398–404 (1994)
144. Datta, A., Bhaduri, S., Kelkar, R.Y., Khwaja, H.I.: Intercalation of a rhodium carbonyl into the layered vanadyl phosphate $VOPO_4 \cdot 2H_2O$ and its catalytic activity. J. Phys. Chem. **98**, 11811–11813 (1994)

145. Johnson, J.W., Jacobson, A.J.: Redox intercalation reactions of $VOPO_4 \cdot 2H_2O$. Angew. Chem. Int. Ed. Engl. **22**, 412–413 (1983)

146. Jacobson, A.J., Johnson, J.W.: Chemical modification of vanadium phosphates. Mater. Sci. Monogr. **28A**, 469–472 (1985)

147. Jacobson, A.J., Johnson, J.W., Brody, J.F., Scanlon, J.C., Lewandowski, J.T.: Redox intercalation reactions of $VOPO_4 \cdot 2H_2O$ with mono- and divalent cations. Inorg. Chem. **24**, 1782–1787 (1985)

148. Chauvel, A., DeRoy, M.E., Besse, J.P., Benarbia, A., Legrouri, A., Barroug, A.: Redox intercalation of alkali metals into vanadyl phosphate dihydrate. Mater. Chem. Phys. **40**, 207–211 (1995)

149. Chauvel, B., Bondot, P., DeRoy, M., Besse, J.P.: Spectroscopic study of $VOPO_4 \cdot 2H_2O$ intercalation compounds. Mat. Sci. Forum **91–93**, 351–356 (1992)

150. Chauvel, B., Bondot, P., DeRoy, M., Besse, J.P.: Local environment in mixed valence $VOPO_4 \cdot 2H_2O$ intercalated compounds. Solid State Ionics **63–65**, 494–500 (1993)

151. Ramos-Barrado, J.R., Criado, C., Rodriguez-Castellon, E., Olivera-Pastor, P., Jimenez-Lopez, A.: Impedance spectroscopy analysis of some vanadyl phosphate intercalation compounds. Solid State Ionics **97**, 213–216 (1997)

152. Šišková, R., Beneš, L., Zima, V., Vlček, M., Votinský, J., Kalousová, J.: Redox intercalation reaction of crystalline $VOPO_4 \cdot 2H_2O$ with NaI solution in acetone. Polyhedron **12**, 181–185 (1993)

153. Zima, V., Beneš, L., Votinský, J., Kalousová, J.: Intercalation of alkali-metal ions into layered $VOPO_4 \cdot 2H_2O$. Mol. Cryst. Liq. Cryst. Sci. Technol. A **244**, 121–126 (1994)

154. Hibma, T.: Structural aspects of monovalent cation intercalates of layered dichalcogenides. In: Whittingham, M.S., Jacobson, A.J. (eds.) Intercalation Chemistry, Chap. 9, pp. 304–305. Academic Press, New York (1982)

155. Zima, V., Beneš, L., Šišková, R., Fatěna, P., Votinský, J.: Intercalation of $VOPO_4 \cdot 2H_2O$ with lithium ions. Solid State Ionics **67**, 277–280 (1994)

156. Zima, V., Beneš, L., Votinský, J., Kalousová, J.: Intercalation of $VOPO_4 \cdot 2H_2O$ with hydronium and potassium ions. Solid State Ionics **82**, 33–38 (1995)

157. Zima, V., Kilián, M., Casciola, M., Massinelli, L.: Intercalation compounds of vanadyl phosphate dihydrate with rubidium ion and their electrical properties. Chem. Mater. **11**, 3258–3262 (1999)

158. Zima, V., Beneš, L., Melánová, K., Svoboda, J.: Preparation of ammonium intercalated vanadyl phosphate by redox intercalation and ion exchange. J. Solid State Chem. **117**, 1173–1178 (2004)

159. Zima, V., Beneš, L., Melánová, K., Vlček, M.: Ion-exchange properties of alkali-metal redox-intercalated vanadyl phosphate. J. Solid State Chem. **163**, 281–285 (2002)

160. Thorpe, M.F.: Layer rigidity and spacing in intercalation compounds. Phys. Rev. B **39**, 10370–10372 (1989)

161. Votinský, J., Beneš, L.: Dependence between calculated flexibility of lamellas of layered materials and their ability to undergo intercalation reactions. Collect. Czech. Chem. Commun. **56**, 2859–2868 (1991)

162. Dupré, N., Gaubicher, J., Le Mercier, T., Wallez, G., Angenault, J., Quarton, M.: Positive electrode materials for lithium batteries based on $VOPO_4$. Solid State Ionics **140**, 209–221 (2001)

163. Dupré, N., Wallez, G., Gaubicher, J., Quarton, M.: Phase transition induced by lithium insertion in α_I- and α_{II}-$VOPO_4$. J. Solid State Chem. **177**, 2896–2902 (2004)

164. Dupré, N., Gaubicher, J., Angenault, J., Quarton, M.: Electrochemical study of intercalated vanadyl phosphate. J. Solid State Electrochem. **8**, 322–329 (2004)

165. Caignaert, V., Satya Kishore, M., Pralong, V., Raveau, B., Creon, N., Fjellvag, H.: From a 3D protonic conductor $VO(H_2PO_4)_2$ to a 2D cationic conductor $Li_4VO(PO_4)_2$ through lithium exchange. J. Solid State Chem. **180**, 2437–2442 (2007)

166. Satya Kishore, M., Pralong, V., Caignaert, V., Malo, S., Hebert, S., Varadaraju, U.V., Raveau, B.: Topotactic insertion of lithium in the layered structure $Li_4VO(PO_4)_2$: the tunnel structure $Li_5VO(PO_4)_2$. J. Solid State Chem. **181**, 976–982 (2008)

167. Dubarry, M., Gaubicher, J., Guyomard, D., Wallez, G., Quarton, M., Baehtz, C.: Uncommon potential hysteresis in the $Li/Li_{2x}VO(H_{2-x}PO4)_2$ ($0 \leq x \leq 2$) system. Electrochim. Acta **53**, 4564–4572 (2008)

168. Papoutsakis, D., Jackson, J.E., Nocera, D.G.: Magnetic properties of metal-intercalated layered vanadyl phosphates. Inorg. Chem. **35**, 800–801 (1996)

169. Ayyappan, P., Ramanan, A., Torardi, C.C.: New metal-intercalated layered vanadyl phosphates, $M_xVOPO_4 \cdot yH_2O$ (M = Ag, Cu, Zn). Inorg. Chem. **37**, 3628–3634 (1998)

170. Wang, S.L., Kang, H.Y., Cheng, C.Y., Lii, K.H.: Hydrothermal synthesis and structural characterization of two layered mixed-valence vanadyl phosphate hydrates $Na_{0.5}VOPO_4 \cdot 2H_2O$ and $K_{0.5}VOPO_4 \cdot 1.5H_2O$. Inorg. Chem. **30**, 3496–3499 (1991)

171. Ayyappan, P., Ramanan, A., Joy, P.A., Pring, A.: A convenient hydrothermal route for the synthesis of $M_xVOPO_4 \cdot yH_2O$ (M = Na and K). Solid State Ionics **107**, 53–57 (1998)

172. Le Fur, E., Pivan, J.Y.: Synthesis and crystal structure of the new zinc-magnesium vanadium(IV) phosphate hydrate $Mg_{(1-x)}Zn_x(VOPO_4)_2 \cdot 4H_2O$ (x similar to 0.28). Mater. Res. Bull. **34**, 1117–1127 (1999)

173. Roca, M., Marcos, M.D., Amoros, P., Alamo, J., Beltran-Porter, A., Beltran-Porter, D.: Synthesis and crystal structure of a novel lamellar barium derivative: $Ba(VOPO_4)_2 \cdot 4H_2O$. Synthetic pathways for layered oxovanadium phosphate hydrates $M(VOPO_4)_2 \cdot nH_2O$. Inorg. Chem. **366**, 3414–3421 (1997)

174. Le Fur, E., Pena, O., Pivan, J.Y.: Low dimensional magnetism of $M(VOPO_4)_2 \cdot 4H_2O$ layered compounds: the 2D ferromagnet $Cd(VOPO_4)_2 \cdot 4H_2O$ and the 2D antiferromagnet $Mg_{1-x}Zn_x(VOPO_4)_2 \cdot 4H_2O$ with x = 0.28. J. Mater. Chem. **9**, 1029–1032 (1999)

175. Le Fur, E., Pena, O., Pivan, J.Y.: Magnetic and thermal properties of vanadium phosphates hydrates $M^{II}(VOPO_4)_2 \cdot 4H_2O$ ($M^{II} = Ca^{2+}$, Ba^{2+} and Cd^{2+}). J. Alloys Compd. **285**, 89–97 (1999)

176. Zheng, L.M., Lii, K.H.: Magnetic properties of $M(VOPO_4)_2 \cdot 4H_2O$ (M = Co(II), Ni(II)), layered compounds containing distinct magnetic linear trimers. J. Solid State Chem. **137**, 77–81 (1998)

177. Boudin, S., Guesdon, A., Leclaire, A., Borel, M.-M.: Review on vanadium phosphates with mono and divalent metallic cations: syntheses, structural; relationships and classification, properties. Int. J. Inorg. Mater. **2**, 561–579 (2000)

178. Martinez-Lara, M., Jimenez-Lopez, A., Moreno-Real, L., Bruque, S., Casal, B., Ruiz-Hitzky, E.: Redox intercalation of alkylammonium ions into $VOAO_4 \cdot nH_2O$ (A = P, As). Mater. Res. Bull. **20**, 549–555 (1985)

179. Okuno, S., Matsubayashi, G.E.: Intercalation of ferrocenylalkylammonium cations into the layered lattice of $VOPO_4$. J. Chem. Soc. Dalton Trans. 2441–2444 (1992)

180. Morris, M., Adams, J.M., Dyer, A.: Mechanism of n-alkylammonium ion intercalation into the layered host α-$VOPO_4 \cdot 2H_2O$. J. Mater. Chem. **1**, 43–49 (1991)

181. Yang, C., Zhou, H., Chen, X., Liu, Y., Qin, J.: Synthesis and characterization of intercalation compounds of stilbazolium chromophores into layered vanadyl phosphate. J. Mater. Chem. **15**, 1637–1639 (2005)

182. Beneš, L., Melánová, K., Zima, V., Kalousová, J., Votinský, J.: Possible mechanisms of intercalation. J. Incl. Phenom. Mol. Recognit. Chem. **31**, 275–286 (1998)