VANADYL PHOSPHATE AND ITS INTERCALATION REACTIONS. A REVIEW

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The structure of the layered α_I-VOPO$_4$, VOPO$_4$·2 H$_2$O, and their intercalation reactions are discussed. These reactions are divided into two groups. The first includes intercalation reactions of molecular guests which proceed as acid-base processes between the host layered lattice (Lewis acid) and a donor atom of the guest (base). Interaction of water molecules, alcohols, amines, carboxylic acids and their derivatives, heterocyclic N- and S-donors, and complex compounds with vanadyl phosphates is discussed. Vanadyl phosphate, in particular vanadyl phosphate dihydrate can also undergo the second type of the reactions which involves the reduction of a fraction of vanadium(V) atoms to vanadium(IV) with concomitant intercalation of alkylammonium, hydronium or mono- and divalent metal cations to counterbalance the induced negative layer charge. A review with 76 references.
Key words: Intercalation; Layered compounds; Vanadyl phosphate.

1. VANADYL PHOSPHATES

Vanadium phosphates exhibit a wide range of structures due to different oxidation states of vanadium (V(V), V(VI) or V(III)) and variety of ways in which phosphate tetrahedra and vanadium octahedra can be interlinked. All vanadium phosphates including their hydrates have been studied because of their prospective utilization as catalysts or precursors of catalysts for selective oxidations[1,2] or Diels–Alder cycloadditions[3].

The simple vanadyl(V) phosphate, $VOPO_4$, exists in several structural modifications: The layered α_I- (ref.[4]) and the slightly different α_{II}- (ref.[5]) modifications seem to be predetermined for intercalation reactions and they will be discussed later. Three-dimensional structure of orthorhombic β-$VOPO_4$ (ref.[6]) is formed from a mixture of ammonium phosphate and ammonium metavanadate at 595 °C (ref.[7]) or by the transformation of α_I-modification at 810 °C before melting[4]. The modifications γ- and δ-$VOPO_4$ (refs[8,9]) with structures related to $(V^{IV}O)_2P_2O_7$ (refs[10,11]), and in the last year described ε-$VOPO_4$ (ref.[12]) related to β-modification are all from the view point of intercalation reactions uninteresting.

Thermal dehydration of layered $VOPO_4 \cdot 2\,H_2O$ near 400 °C at an oxygen pressure of 101.3 kPa (ref.[13]) leads to α_I-$VOPO_4$ ($a = b = 0.620$ nm, $c = 0.418$ nm), whose cell parameters are slightly different from those of the previously known as α-$VOPO_4$ obtained by heating of a mixture of oxides which is now called α_{II}-$VOPO_4$ ($a = b = 0.6014$ nm, $c = 0.4434$ nm)[5]. These compounds differ by the position of the vanadium atoms within the octahedra. It is shown in Fig. 1 that in 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. The layers of these both forms are uncharged but electrically conducting. The α_{II}-modification does not undergo any intercalation reactions.
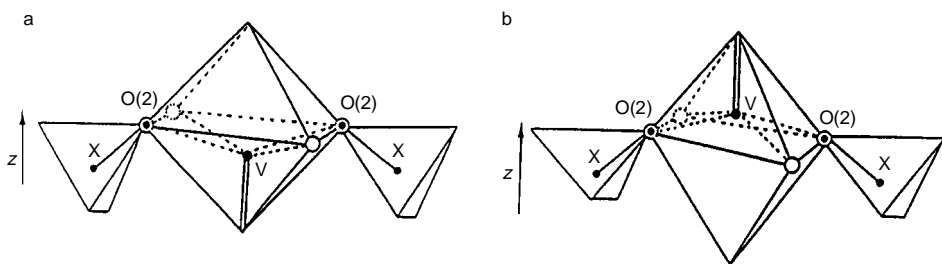
FIG. 1
Chain $–X–O(2)–V–O(2)–X–$, where X = P(V), Mo(V), Nb(V), Ta(V), S(VI): **a** for compounds of the α-$VOSO_4$ type: α_I-$VOPO_4$, $VOPO_4 \cdot 2\,D_2O$, $VOSO_4 \cdot 2\,H_2O$; **b** for compounds of the α_{II}-$VOPO_4$ type: $MoOPO_4$, $NbOPO_4$, $VOMoO_4$, $TaOPO_4$

An isolated corrugated sheet of layered α_I-VOPO$_4$, which is shown in Fig. 2 is formed from vertex-sharing phosphate tetrahedra PO$_4$ linked to VO$_5$ square pyramids. The mutual position of individual layers leads to two types of layered host lattices of VOPO$_4$ composition. The coordination polyhedron of the vanadium atom is in the α_I-modification completed to octahedron by the peak oxygen atom of the square pyramid from the adjacent layer. This arrangement corresponds to the α-VOSO$_4$ (ref.[14]).

Vanadyl phosphate dihydrate α-VOPO$_4 \cdot 2\,H_2O$ (with the same structure of the layers as anhydrous α_I) can be easily prepared and crystallized when suspension of vanadium oxide in concentrated trihydrogen phosphoric acid is refluxed for several days[15]. Well crystallized vanadium phosphate dihydrate can be obtained by the reaction of phosphoric acid with vanadium propoxides VO(OPr^n)$_3$ and (or?) VO(OPr^i)$_3$ (ref.[16]). The preparation of vanadyl phosphate dihydrate from anhydrous vanadyl phosphate will be discussed later.

2. INTERCALATION REACTIONS OF α_I-VOPO$_4$ AND α-VOPO$_4 \cdot 2\,H_2O$

The following summary of the intercalation reactions cited here is in accord with many references but most intercalation reactions of vanadyl phosphate dihydrate are in fact reintercalation processes. At that, water molecules in the van der Waals band are replaced by other neutral molecules (stronger Lewis bases) 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 reintercalation. The reintercalation reactions of dihydrate occur very often easier than intercalation of anhydrous vanadyl phosphate with the same molecular guest.

Intercalation reactions of α_I-VOPO$_4$ and α-VOPO$_4 \cdot 2\,H_2O$ can be divided into two groups: (i) The first includes reactions which proceed without redox changes and lead to the formation of layered complexes. These coordination compounds prepared by the reactions of Lewis bases with anhydrous vanadyl phosphate or its dihydrate are characterized by covalent bonding of the ligand to vanadium atom in the host layer. The
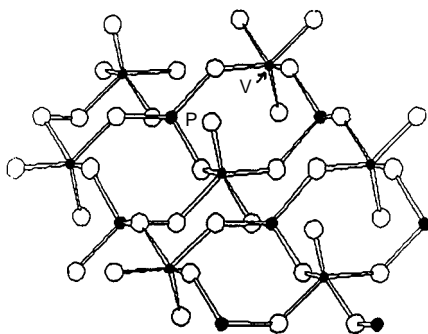

FIG. 2
An isolated corrugated sheet of α_I-VOPO$_4$

reactions of this type will be discussed in Chapter 3. (ii) Vanadium phosphate, in particular vanadium phosphate dihydrate can also undergo a second type of intercalation reactions analogous to reactions of reducible binary oxides and layered dichalcogenides. This type of intercalation reactions involves the reduction of a fraction of the vanadium(V) atoms to the vanadium(IV) with concomitant intercalation of cations to counterbalance the induced negative layer charge (Chapter 4). This redox intercalation process may conveniently be carried out using iodides. The redox process can also occur in a minor or higher degree by the interaction with a few Lewis bases which are intercalated at the first step into the interlayer space without redox changes (see Chapters 3.3. and 3.6.).

3. INTERCALATION OF LEWIS BASES

3.1. Intercalation of Water Molecules into Anhydrous α_I-VOPO$_4$

The course of intercalation of water into α_I-VOPO$_4$ has been studied by the thermomechanical and X-ray diffraction analysis[17]. The changes of the lattice during intercalation of water into the interlayer band manifested in the diffractogram are shown in Fig. 3. The original α_I-VOPO$_4$ lattice (the lines denoted by index A) is changed to VOPO$_4$·2 H$_2$O (the lines denoted by H). The lines of vanadyl phosphate monohydrate were not observed during hydration but the broadening and the shift of the (001) lines was observed. These phenomena can be explained by the random stacking of the intercalated and nonintercalated layers in the sample. A one-step hydration process of anhydrous VOPO$_4$ leading to dihydrate was confirmed by the thermomechanical analysis. The curve showing the dependence of the crystal thickness on time during hydration had an exponential shape. No significant dwell corresponding to a monohydrate formation or staging was observed.
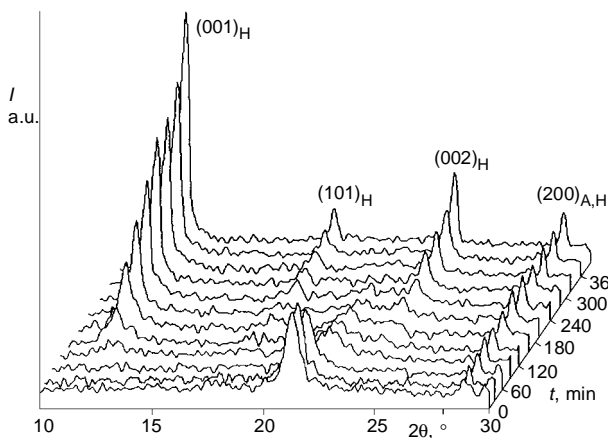

Fig. 3

The changes in the diffractograms during intercalation of water into α_I-VOPO$_4$ (subscript A stands for anhydrous vanadyl phosphate, subscript H for VOPO$_4$·2 H$_2$O)

The isolated sheet of V–O–P in $VOPO_4 \cdot 2 H_2O$ is the same as the sheet of the anhydrous α_I-vanadyl phosphate. Coordination number six of the vanadium atom is reached by the coordination of oxygen atom from the water molecule. 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 structure of $VOPO_4 \cdot 2 H_2O$ was determined from the analogy with results of neutron diffraction of $VOPO_4 \cdot 2 D_2O$ (ref.[18]) and on the basis of X-ray diffraction[19]. 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 the H-bridges either with the top or bottom phosphate oxygens. The decrease of *c*-parameter with increasing temperature in the temperature range of 3–42 °C supports the great role of the interlayer hydrogen bonds[20]. The EPR spectrum of vanadyl phosphate dihydrate confirmed the concentration of vanadium(IV) present in this layered host in an amount *ca* 1–2% of the total vanadium content[3].

Formation of vanadyl phosphate dihydrate can serve as a model of penetration of foreign molecules into the structure of anhydrous vanadyl phosphate: the $(VOPO_4)_\infty$ layers stand apart and the six coordination positions of the vanadium atom are occupied by a donor atom of the guest molecule.

The course of dehydration of $VOPO_4 \cdot 2 H_2O$ leading to α_I-$VOPO_4$ has been studied by X-ray diffraction, thermomechanical analysis, DTA, and thermoelectric power measurements[21]. The thermomechanical measurements show two sharply different steps of dehydration. Maximum changes in the thickness of the crystal during dehydration occurs at 44 and 79 °C. The X-ray diffractograms indicate that the transformation of the dihydrate (basal spacing 0.74 nm) to monohydrate occurs mainly at about 43 °C and the practically pure monohydrate (0.63 nm) is present at 63 °C. In accordance with previous results reported for $VOPO_4 \cdot 2 H_2O$ (refs[22,23]), 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 vanadyl groups. The second dehydration step follows at about 80 °C, and the monohydrate is almost absent around 114 °C. Thermoelectric power measurements also confirm the two-step mechanism of dehydration. The negative sign of the Seebeck coefficient at higher temperatures defines electrons as the predominant charge carriers in anhydrous $VOPO_4$, whereas protons created by dissociation of water in the van der Waals band function as charge carriers in the temperature regions of the monohydrate and dihydrate existence.

The dependence of the water content and the basal spacing on relative humidity at 25 °C for $VOPO_4$ has been determined[23]. Anhydrous vanadyl phosphate is stable if the relative humidity is equal to zero, monohydrate has no distinct region of the occur-

rence, dihydrate exists in the region of relative humidity between 15 to 50%, and the highly hydrated phase denoted as $VOPO_4 \cdot 5\,H_2O$ (1.05 nm) has been observed at relative humidity higher than 72%.

3.2. Intercalation of Alcohols

Interactions of alcohols with the $VOPO_4$ structure have been studied by Ladwig[24,25], recently, these systems have been studied more in detail[26]. Corresponding intercalates of the composition $VOPO_4 \cdot x\,C_nH_{2n+1}OH$ have been prepared by the reaction of the anhydrous host with an excess of liquid alcohol. The value of x being 2 for $n = 2–4$. Bilayer chain aggregation of the guest molecules in the van der Waals gap is suggested. No alcohols longer than butanols could be intercalated by this method. When alcohols with a branched chain are intercalated, the alcohol/host molar ratio is reduced ($x = 1.75$). This is obviously caused by sterical reasons. The intercalate with methanol shows the lowest content of alcohol ($x = 1.33$) and the basal spacing indicates a monolayer of methanol molecules.

A study of rate of the intercalation of alcohols into anhydrous vanadyl phosphate has been carried out by a volumetric method[27]. The rate of the intercalation process could be influenced by the moisture in the liquid guest. The very distinct effect of this kind was found in the system $VOPO_4$ and moist ethanol, in which a strong acceleration of the reaction was observed.

Kinetics of the intercalation of ethanol into vanadyl phosphate has been studied by X-ray diffraction, thermomechanical analysis and a volumetric method and the kinetic curves were found to have a sigmoidal shape. During this intercalation only the fully intercalated phase is generated in contrast to the intercalation of water, where the distorted layered lattice composed of intercalated and nonintercalated layers is formed[28].

The mixed intercalates of the type $VOPO_4 \cdot (2 - x)\,C_pH_{2p+1}OH \cdot x\,C_qH_{2q+1}OH$ have been prepared by the reaction of anhydrous $VOPO_4$ with liquid binary mixtures of the alcohols (C2 to C4) with nonbranched chain[29]. The relations between the basal spacings of the intercalates formed, their composition and the composition of the liquid alcohols mixtures were studied. Different compositions of the products in the systems of $VOPO_4$ with a mixture of methanol and a longer alcohol were observed. The intercalation of the EtOH–n-BuOH mixture into $VOPO_4$ has practically the same course as the intercalation of this mixture into $VOSO_4$ (ref.[30]). Basal spacing of the product obtained by the intercalation of the starting mixture of these alcohols with a content of n-BuOH less than 60 wt.% corresponds to basal spacing of $VOPO_4 \cdot 2\,EtOH$. If the content of n-BuOH in the starting mixture lies between 70 and 95%, the intercalate of the composition $VOPO_4 \cdot n\text{-BuOH} \cdot EtOH$ is formed. The pure $VOPO_4 \cdot n\text{-BuOH}$ is formed when the content of n-BuOH in the mixture is near 100%. The intercalate $VOPO_4 \cdot 1.33\,CH_3OH$ was formed even at high content of the longer alcohol (30% for ethanol, 70% for n-propanol, and 91% for n-butanol)

in the reaction mixture. At a higher content of the longer alcohol in the mixture, the intercalates with the composition expected for the mixed intercalates were formed.

The direct reaction of solid finely ground $VOPO_4 \cdot 2\,H_2O$ with liquid (or melted solid) alkan-1-ols or alkane-1,ω-diols in a microwave field leads to layered complexes of the composition $VOPO_4 \cdot 2\,C_nH_{2n+1}OH$ (n = 1 to 18) or $VOPO_4 \cdot C_nH_{2n}(OH)_2$ (n = 2 to 10)[31]. The structure of all these polycrystalline layered complexes retains the original layers of $(VOPO_4)_\infty$. The absorption of microwaves by the water molecules present in the structure of the dihydrate results in rapid removal of these molecules from the space between the $(VOPO_4)_\infty$ to the surrounding dry quest and in exfoliation of host. After finishing the exposition and partial cooling of the reaction mixture, the $(VOPO_4)_\infty$ layers are reassociated taking the molecules of new guest between them and a micro-crystalline intercalate without water is formed. The molecules of alcohols are placed between the host layers in bimolecular arrangement, being anchored to them by donor–acceptor bonds between oxygen atom of OH group and vanadium atom as well as by hydrogen bonds. The molecules of diols, on the other hand, using similar bonds, form in monomolecular arrangement bridges linking the adjacent layers of the host. The aliphatic chains of both intercalated alcohol and diol molecules possess *all-trans* configuration and their axes are perpendicular to the host layers.

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[32]. $VOPO_4 \cdot 2\,H_2O$ refluxed for 20 h with a 50 molar excess of predried C_4–C_8 alkan-1- or -2-ols gives $VOHPO_4 \cdot 0.5\,H_2O$. Two sets of morphologies of these products have been found. 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. Direct reduction of vanadyl phosphate dihydrate with ethanol or isobutyl alcohol[33], and general with C_2–C_4 alcohols[34], was the basis for the study of vanadium phosphate catalyst precursors.

3.3. Intercalation of Amines

3.3.1. Intercalation of Aliphatic Amines

The intercalates of the composition $VOPO_4 \cdot x\,C_nH_{2n+1}NH_2$ (x = 1.68–2.02) were obtained by the direct reaction of anhydrous vanadyl phosphate and aliphatic amines with nonbranched chains C_1 to C_{10} (ref.[35]). The basal spacings increase by about 0.14 nm be lengthening the chain from n (even) to $n + 1$, and by about 0.31 nm from n (odd) to $n + 1$. This alternation indicates the bilayer arrangements of the molecules, which are inclined at the angle of 55° to the layer of host for the shortest chains. This angle increases with increasing number of the carbon atoms in the chain.

Aliphatic amines from C_4 to C_{16} have been intercalated into $VOPO_4 \cdot 2\,H_2O$ and $NbOPO_4 \cdot 3\,H_2O$ (ref.[23]). The dependence of the basal spacing increase on the number of the carbon atoms is nearly linear and the interlayer distance indicates that the angle between the carbon chain and the plane of the layer is about 60° for the chains up to C_{11}. Longer chains have perpendicular orientation. The composition of $VOPO_4 \cdot 1.5\,RNH_2$ has been found for these intercalates.

3.3.2. Intercalation of Aromatic Amines

These reactions rank among Lewis acid-base reactions with respect to their initial step. Aromatic amines are in vanadyl phosphate dihydrate partially protonized, the vanadium(V) atom can subsequently function as an oxidant and intercalative polymerization can occur.

Three types of intercalation compounds were prepared by reaction of $VOPO_4 \cdot 2\,H_2O$ with aniline[36]. Water molecules, neutral aniline molecules, protonated aniline ions and polymerized aniline were taken up into the interlayer space. Water in the host and solvent plays an important role. Under the moist conditions, the product which includes water molecules, protonated aniline ions and polyaniline in the interlayer space is formed. At the beginning of the reaction a small amount of aniline molecules is intercalated, and subsequent intercalation of them results in polymerization. By the reaction with neat aniline, products with aniline/vanadium ratio 1.8–2.1 were obtained, basal spacing 1.48 nm. These products contained only a very small amount of polyaniline. The ratios of H_2O/V and total aniline/V ranged from 1.7 to 2.4 and from 1.0 to 1.4, respectively, for the products obtained by the interaction of vanadyl phosphate dihydrate with aniline dissolved in tetrahydrofuran. In accordance with this fact, the basal spacing varied in the range from 1.33 to 1.65 nm, depending on the amount of water and aniline present as polyaniline in the interlayer space.

It was shown[36] that aniline molecules inserted into the $VOPO_4$ interlayer space caused the reduction of vanadium(V) to vanadium(IV) which was followed by transformation of a part of aniline molecules as $PhNH_3^+$ cation. Similarly, powdered $VOPO_4 \cdot 2\,H_2O$ suspended in excess of neat aniline gives intercalation compounds $VOPO_4 \cdot x\,H_2O \cdot y\,C_6H_5NH_3^+$ ($0.6 < x < 1.1$; $0.5 < y < 1.0$) with the vanadium atom reduced[37]. Two phases were observed ($d = 1.5$ nm, $d = 0.9$ nm) during intercalation. The compounds with $y > 0.7$ lead to polymerization of the cation by the addition of Cu^{2+} ion to afford polyaniline. Vanadyl phosphate dihydrate powder when suspended in a solution of $C_6H_5NH_3^+Cl^-$ in ethanol gives the compound intercalated with both anilinium cation and polyaniline. The vanadium(V) atoms of the $VOPO_4$ layer are expected to cause the oxidative polymerization of the $PhNH_3^+$ ion forming polyaniline in the interlayer space.

A wide range of stoichiometries and interlayer distances was found for composites formed by the interaction of $VOPO_4 \cdot 2\,H_2O$ and aniline in its solution in anhydrous EtOH or 95% EtOH (ref.[38]). The products obtained from anhydrous EtOH contain only

small amounts of polyaniline. Benzidine gives two benzidinium (Bz^+) charge transfer complexes: $VOPO_4 \cdot (Bz)_{0.5} \cdot 2 \, H_2O$ (anhydrous EtOH) and $VOPO_4 \cdot (Bz)_{0.7} \cdot 3.5 \, H_2O$ (95% EtOH) with interlayer distance lower (0.705 and 0.665 nm, respectively) than in α-$VOPO_4 \cdot 2 \, H_2O$ alone. The interlayer "pocket" orientation with layer shifting and turbostraticity to accommodate Bz^+ cations is suggested.

3.4. Intercalation of Heterocyclic N- and S-Donors

Vanadyl phosphate dihydrate reacts with pyridine, 4-phenylpyridine (4-Phpy) and 4,4′-bipyridyl (4,4′-bpy) to give $VOPO_4 \cdot (py)$, $VOPO_4 \cdot (4\text{-Phpy})$, and $VOPO_4 \cdot (4,4'\text{-bpy})_{0.5}$ (ref.[39]). Anhydrous host reacts very slowly. The pyridine molecules replace either a coordinated water molecule in $VOPO_4 \cdot 2 \, H_2O$ or vanadyl oxygen from an adjacent layer in the anhydrous hosts. In the intercalates, the pyridine molecules are perpendicular to the layers and little or no reduction of the V(V) centers occurs. The reactions with 4-substituted pyridines are much more slower than with pyridine itself. The 0.46 nm expansion observed when going from $VOPO_4 \cdot (py)$ to $VOPO_4 \cdot (4\text{-Phpy})$ corresponds closely to the difference in the lengths of the ligands (0.44 nm). Intercalation compounds of α-$VOPO_4 \cdot 2 \, H_2O$ with pyridine, 4-methylpyridine, and 4-phenylpyridine have been synthesized by two orders of magnitude more quickly using microwave dielectric loss heating effects than with conventional thermal methods[40]. The samples retain a high degree of crystallinity and therefore can be readily characterized by powder X-ray crystallographic techniques.

The intercalation compound obtained on the reaction of $VOPO_4 \cdot 2 \, H_2O$ with 2,2′-dithiodipyridine (2,2′-pySSpy) in ethanol for 10 days contains 2,2′-pySSpy, ethanol and water molecules in the interlayer space[41]. The long axis direction of the present monoprotonated 2,2′-pySSpy molecule is arranged approximately perpendicular to the two-dimensional $VOPO_4$ sheet.

Vanadyl phosphate dihydrate reacts with imidazole (Im) in anhydrous EtOH (ref.[42]) to give a layered compound (basal spacing 1.03 nm), whereas in 95% EtOH it gives a phase with basal spacing 0.88 nm. Both compounds have formula $VOPO_4 \cdot (Im)_{1.0} \cdot n \, H_2O$ (where n is 0.6 and 0.2, respectively).

Under mild conditions (anhydrous EtOH, 25 °C), pyrazole (Prz), pyrazine (Pyzn) and phenazine (Phzn) intercalate into α-$VOPO_4 \cdot 2 \, H_2O$ as protonated, non-coordinated amines[38]. The interlayer distance in the intercalate $VOPO_4 \cdot (Pyzn)_{0.46} \cdot (H_2O)_{0.78}$ suggests that a bilayer is formed first, followed by a "nestled" structure in which the Pyzn lies horizontally in the pockets generated by corner-attached $VOPO_4$ units. Pyrazole in $VOPO_4 \cdot (Prz)_{0.28} \cdot (H_2O)_{1.44}$ appears to adopt a similar gross orientation. The low interlayer distance (0.763 nm) in $VOPO_4 \cdot (Phzn)_{0.07} \cdot (H_2O)_{1.75}$ was explained by assuming that phenazine molecules lie deep in channels and that the layers slide with respect to one another to form such channels. A layer expansion (with respect to anhydrous $VOPO_4$) of 0.9 nm in the intercalate with 2,2′-bipyridine (2,2′-bpy) of the composition

$VOPO_4 \cdot (2,2'\text{-bpy})_{0.55} \cdot (H_2O)_{1.57}$ suggests a vertical orientation within the layers *via* an NH···O=V interaction and without pocket lodgment. Pyrrole almost completely polymerizes on direct intercalation into α-$VOPO_4 \cdot 2\ H_2O$, giving "nestled" polymer composites with several stoichiometries and differing polypyrrole oxidation levels.

Finely powdered $VOPO_4 \cdot 2\ H_2O$ suspended in an ethanol solution containing 3-methyl- or 3,4-dimethylpyrrole leads to the intercalative polymerization of these pyrrole derivatives through the 2,5-coupling to yield $VOPO_4 \cdot (H_2O)_{1.4} \cdot (C_2H_5OH)_{0.2} \cdot (methylpyrrole)_{0.65}$ and $VOPO_4 \cdot (H_2O)_{1.8} \cdot (C_2H_5OH)_{0.2} \cdot (dimethylpyrrole)_{0.6}$ (refs[43,44]).

An intercalate have been prepared by 15-day's reaction of acetone solution of tetrathiafulvalene (TTF) with vanadyl phosphate dihydrate at room temperature[45]. The product has a composition $VOPO_4 \cdot (TTF)_{0.25} \cdot (H_2O)$. The supposed layered structure has not been confirmed by XRD. The system is probably more complex than a simple intercalate. Infrared spectrum indicates the presence of the TTF^+ cation in this material. Electrical properties of the product have been studied.

3.5. Intercalation of Carboxylic Acids and Their Derivatives

3.5.1. Intercalation of Carboxylic Acids

Layered complexes $VOXO_4 \cdot RCOOH$ (X = P, As, S, and RCOOH is formic, acetic, propionic or butyric acid) have been prepared[46] either by the intercalation reaction of the anhydrous host with a carboxylic acid or by the exchange reactions of the hydrates $VOXO_4 \cdot x\ H_2O$ or the intercalates $VOXO_4 \cdot 2\ C_2H_5OH$ with acids in the presence of a dehydrating agent. The basal spacing is changed by about 0.18 nm when going from the complexes with formic acid to those with acetic acid, and the change is the same (0.2 nm) when going from propionic to butyric acid for all three hosts. On the other hand, when replacing acetic acid by propionic acid an increase of only 0.02–0.04 in the basal spacing has been found. 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.

3.5.2. Intercalation of Amides

The layered compound $VOPO_4 \cdot 2\ H_2O$ interacts with primary and tertiary amides causing either dehydration or intercalation reactions, or sometimes both[47] to form $VOPO_4 \cdot (HCONH_2)_{1.6}$, $VOPO_4 \cdot (CH_3CONH_2)_{0.1} \cdot (H_2O)_{1.8}$, $VOPO_4 \cdot (DMF)_{0.82}$ (DMF = dimethylformamide), and $VOPO_4 \cdot [CH_3CON(CH_3)_2]_{0.34} \cdot (H_2O)_{0.25}$. The molecules with larger molecule sizes (butyramide and benzamide) are not intercalated, however, much

the temperature or contact time may be increased. The tetragonal lattice structure of the starting solid is preserved and amide intercalation occurs without any appreciable reduction in the host lattice. 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. Vanadyl phosphate $VOPO_4 \cdot 2\,H_2O$ is less reactive than arsenate $VOAsO_4 \cdot 3\,H_2O$ at room temperature. Various amides can be also intercalated by the layered mixed niobyl–vanadyl phosphate[48].

3.5.3. Intercalation of Glycine

Glycine-intercalated vanadyl ($VOPO_4 \cdot NH_2CH_2COOH$) and niobyl ($NbOPO_4 \cdot (NH_2CH_2-COOH)_{0.85} \cdot (H_2O)_{0.45}$) phosphates were prepared by shaking of the reaction mixture at room temperature and by refluxing of starting compounds, respectively[49]. The intercalates retain the layered structure of parent phosphates with basal spacing corresponding to perpendicular arrangement of glycine chains in the interlayer space. IR spectra confirm the presence of glycine molecules in the intercalates as zwitterionic species. Similarly to those observed for anhydrous $VOPO_4$ (ref.[50]), 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.

3.6. Intercalation of Complex Compounds

3.6.1. Intercalation of Ferrocene and Its Substituted Derivatives

Intercalation of ferrocene from acetone medium into $VOPO_4 \cdot 2\,H_2O$ undergoes as a redox topotactic reaction[51]. An increase in of the basal spacing indicates that ferrocene forms molecular monolayers between the slabs of the host structure. Sterical arguments based on the size of the ferrocene molecule suggest that the guest lies with its fivefold symmetry axis parallel to the host layers. The observed IR absorption bands of intercalates correspond to vibration modes of the ferricinium ion. The content of ferricinium is relatively low (0.11 to 0.12 mol of guest per one mole of host) and the water content decreases with the contact time. Corresponding part of vanadium atoms is reduced during reaction. The bulky [(dimethylamino)methyl]ferrocene was not intercalated into vanadyl phosphate dihydrate.

The mixed intercalate $VOPO_4 \cdot H_2O \cdot C_2H_5OH$ suspended in ethanolic solution of ferrocene (Fc) and stirred for one week at ambient temperature leads to the $VOPO_4 \cdot H_2O \cdot (Fc^+)_{0.35}$ intercalate[52]. An increase in of basal spacing corresponds to an arrangement in which cyclopentadienyl rings are parallel to the sheets of the host. The same basal spacing was found for a compound with a lower content of ferricinium ion $VOPO_4 \cdot H_2O \cdot (Fc^+)_{0.21}$. By standing at room temperature, the basal spacing of this compound and of the intercalate with 1,1′-dimethylferrocene ($VOPO_4 \cdot (Me_2Fc^+)_{0.21}$) change after 30 day, so that the arrangement of the guest molecules corresponds to the form with the cyclopentadienyl rings perpendicular to the layers. The fivefold symmetry axis parallel to the sheets of layers is generally assumed for the metallocene intercalates of lamellar inorganic solids[53]. The space expansion of the $EtFc^+$- and n-$BuFc^+$-$VOPO_4$ compounds correspond to this form. However, $VOPO_4 \cdot H_2O \cdot (Fc^+)_{0.35}$ does not change the primary interlayer spacing to form an arrangement with cyclopentadienyl planes perpendicular to the layers.

The alkyl-bridged biferrocene compounds can be also intercalated into the interlayer space of the layered $VOPO_4$ through the redox reaction between the ferrocene center and the vanadium(V) atom[54]. The long-axis direction of these guest molecules is arranged approximately parallel to the sheet of the host lattice (Fig. 4). Both Fc centers are oxidized to form the Fc^+ moieties in $VOPO_4 \cdot H_2O \cdot (Fc^+CH_2CH_2Fc^+)_{0.15}$. On the other hand, in the intercalate $VOPO_4 \cdot H_2O \cdot (Fc^+CH_2Fc)_{0.12}$, one of the Fc centers of $FcCH_2Fc$ is not oxidized in the molecule where one Fc center approaches one vanadium site and the other Fc center cannot be located in proximity of another vanadium site.

3.6.2. Intercalation of Rhodium Carbonyl

Vanadyl phosphate dihydrate forms an intercalate with a $Rh_2(CO)_4Cl_2$ solution in tetrahydrofuran under argon at ambient conditions for 12 days[55]. The interlayer distance of the layered dark green solid prepared is 0.92 nm. The FTIR spectrum shows a broad band with distinct components centered at 2 098 and 2 107 cm^{-1}. The position of these
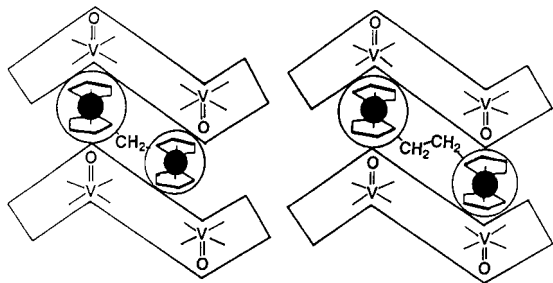

Fig. 4

Schematic arrangement of the alkylene-bridged biferrocene molecules in the α_I-$VOPO_4$ interlayer space

bands is indicative of a Rh(I) rather than a Rh(III) carbonyl species in the intercalated compound. The catalytic activity and shape selectivity exhibited by the rhodium carbonyl species intercalated into a host compound with oxidation centers raises a very attractive possibility of such intercalated carbonyl species acting as novel catalysts.

4. REDOX INTERCALATIONS

4.1. Redox Intercalation of Ammonium Ions

Due to the possibility of reducing vanadium atom, the intercalates of alkylammonium ions into $VOXO_4 \cdot n\ H_2O$ (X = P, As) were prepared by the reaction of alkylammonium iodides with host in acetone solution[56]. The course of this reaction can be represented by the following equation

$$VOPO_4 \cdot 2\ H_2O + x\ RNH_3I = (RNH_3)_x V_x^{IV} V_{1-x}^{V} OPO_4 \cdot y\ H_2O + (x/2)\ I_2 + (2 - y)\ H_2O\ , \quad (A)$$
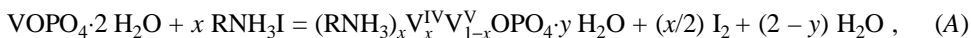
where R = $PhCH_2$ or C_nH_{2n+1} (n = 3 to 8), and x = 0.4 to 0.6. In this way, a fraction of V(V) is reduced by the iodide to V(IV) which produces a charge deficiency in the host lattice subsequently compensated by the organic cations. The starting material retains its layered arrangement but with distorted PO_4 tetrahedra due to V(V) → V(IV) transformations, and with an increase in the basal spacing. The "pillar" arrangement of the alkyl chains in the interlayer space is assumed.

The mechanism of redox intercalation reactions between alkylammonium iodides and the layered host $VOPO_4 \cdot 2\ H_2O$ has been investigated by synthesis of mixed- and single-ion intercalates, by ion exchange experiments, and by EPR study of *in situ* reactions[57]. Intercalation was found to occur first at the edge of crystallites. With alkyl chains of butyl and longer, intercalation of ions was seen to proceed throughout the interlayer galleries, resulting in a bilayer arrangement, with the chains making an average angle of 39° to the host layers. Smaller ions were not intercalated to any great degree, with 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.

Some ferrocenylalkylammonium iodides $[Fe^{II}(C_5H_5)\{C_5H_4(CH_2)_nNR_2R'\}]^+I^-$ (n = 1 or 2; R, R' = H or Me), benzyldimethyl- and benzyltrimethylammonium iodides[58] react with $VOPO_4 \cdot H_2O \cdot EtOH$ suspended in ethanol to afford intercalation compounds of $VOPO_4 \cdot H_2O$ with 0.45 $[Fe^{II}(C_5H_5)(C_5H_4CH_2NHMe_2)]^+$ (**A**), 0.20 $[Fe^{II}(C_5H_5)(C_5H_4CH_2NMe_3)]^+$ (**B**), 0.43 $[Fe^{II}(C_5H_5)(C_5H_4–CH_2CH_2NH_3)]^+$ (**C**), 0.17 $[Fe^{III}(C_5H_5)(C_5H_4CH_2CH_2NMe_3)]^{2+}$ (**D**), 0.54 $[PhCH_2NHMe_2]^+$ (**G**), and 0.45 $[PhCH_2NMe_3]^+$ (**H**). Ferrocenylalkylammonium

chlorides, $[Fe^{II}(C_5H_5)(C_5H_4CH_2NHMe_2)]^+Cl^-$ and $[Fe^{II}(C_5H_5)(C_5H_4CH_2CH_2NH_3)]^+Cl^-$, were also intercalated to give compounds of $VOPO_4 \cdot H_2O$ with 0.29 $[Fe^{III}(C_5H_5)(C_5H_4CH_2NHMe_2^+Cl^-)]$ (**E**) and 0.18 $[Fe^{III}(C_5H_5)(C_5H_4CH_2CH_2NH_3^+Cl^-)]$ (**F**). The intercalation compounds comprise layered $VOPO_4$ moieties having both the vanadium(IV) and (V) states and the ferrocenylalkyl-, benzyldimethyl-, and benzyltrimethyl-lammonium cations as well as ferrocenium-substituted alkylammonium chlorides in the interlayer space. The ferrocenylalkylammonium iodides can reduce the vanadium(V) in the $VOPO_4$ sheet by the iodide ion and ferrocenylalkylammonium cation is intercalated to give charge compensation (**A–D**); the ferrocenyl center remains non-oxidized because it is well separated from vanadium(V) site (**A–C**). In contrast, ferrocenyl compounds with alkylammonium chloride moieties are intercalated into the $VOPO_4$ interlayer through oxidation of the ferrocenyl centers (**E**, **F**). The long interlayer distances of compounds **A**, **C**, and **G** suggest large expansions of the interlayer spaces caused by a close proximity of the ammonium groups to the vanadium(IV) site, the long-axis direction of the guest molecules being arranged approximately perpendicular to the two-dimensional sheet of the $VOPO_4$. This arrangement is close to the molecular arrangements of some alkylammonium–$VOPO_4$ intercalation compounds[23]. However, the interlayer distances of the other compounds indicate that the long-axis direction of the guest moieties (in the interlayer space) may be arranged approximately parallel to the swelling $VOPO_4$ sheet. In compound **B** the NMe_3^+ group approaches the vanadium(IV) site, the ferrocenyl center being located somewhat apart from another vanadium(V) site and remaining non-oxidized. On the other hand, both the NMe_3^+ group and the ferrocenyl center of **D** can be located in close proximity to the vanadium sites as estimated from the crystal structure of the $VOPO_4$ sheet and the shape of the guest molecule. This may cause oxidation of the ferrocenyl center.

A layered compound of the composition $VOPO_4 \cdot H_2O \cdot [Co(C_5H_5)_2^+]_{0.52}$ was obtained when a suspension of $VOPO_4 \cdot H_2O \cdot C_2H_5OH$ in ethanol–acetonitrile (1 : 1) containing excess amounts of an equimolar mixture of $[Co(C_5H_5)_2][PF_6]$ and $[NBu_4^n]I$ was stirred for a week at room temperature[52]. In this reaction the $VOPO_4$ moieties were reduced by the iodide ion to include the $[Co(C_5H_5)_2]^+$ cation.

4.2. Redox Intercalation of Mono- and Divalent Metal Cations into VOPO4·2 H2O

The reaction of crystalline α-$VOPO_4 \cdot 2\ H_2O$ with an ethanolic solution of an iodide of Li, Na, K, Rb, Cs, Mg, Mn, Co, Ni or Zn, which is rapid and spontaneous at room temperature, is a redox process[59] analogous to the reaction with ammonium iodide. The vanadium(V) is reduced to vanadium(IV) by iodide, releasing iodine, and the cations enter into the interlayer space simultaneously. The structure of the host layers is preserved during the reaction but the distance between adjacent $(VOPO_4)_\infty$ layers decreases. This decrease is due to stronger interactions between the positively charged species in the interlayer space and the negatively charged sheets of $VOPO_4$ with re-

duced vanadium atoms. The products are often composed from more phases, which differ by the basal spacing. The content of these phases depends on the amount of the metal intercalated. Thermal analyses and IR spectra show that it is not possible, like in $VOPO_4 \cdot 2\,H_2O$, to make a distinction between the two types of water in intercalates of the type $M_x^I V_x^{IV} V_{1-x}^V OPO_4 \cdot y\,H_2O$ (ref.[60]). The water molecules are not coordinated to vanadium, but they must be surrounding the intercalated cation. Interlayer coordination environment of iron, cobalt, and nickel in intercalation compounds of approximate stoichiometries $Fe_{0.4}VOPO_4 \cdot 3\,H_2O$, $Co_{0.2}VOPO_4 \cdot 2\,H_2O$ and $Ni_{0.2}VOPO_4 \cdot 2\,H_2O$ have been studied[61]. The EXAFS results indicate that Fe^{3+} and Co^{2+} ions have four oxygen nearest neighbors, whereas Ni^{2+} ion has six oxygen nearest neighbors.

Both EXAFS and XANES analyses suggest a complexed hydrated form for guest cations intercalated between $VOPO_4$ sheets[62]. The guest cation should be localized between two vanadyl groups of two adjacent layers; XANES spectroscopy indicates that the electron transferred in reduction is localized on a vanadium orbital. Though the lamellar morphology is preserved, the long-range order shown by X-ray powder diffraction is strongly affected by intercalation. However, the $VOPO_4$ framework is not much altered locally, the corrugation (V–O–P angles) may be changed or $VOPO_4$ sheets locally shifted to accommodate guest cations.

$VOPO_4 \cdot 2\,H_2O$ can be presented as a Brønsted acid $[VOPO_4 \cdot 2\,H_2O \leftrightarrow (HOVO)PO_4^- + H_3O^+]$ (ref.[63]) capable of yielding salts of the type $AHVPO_6$ (A = K, Rb, Cs, NH_4). The Lewis acid strength of the vanadyl(V) groups allows to prepare some sodium derivatives $Na_x V_x^{IV} V_{1-x}^V OPO_4 \cdot (2-x)\,H_2O$ in homogeneous (liquid) phase[64].

Redox intercalations of $VOPO_4 \cdot 2\,H_2O$ with acetone solutions of LiI, NaI, and KI were studied more in detail[65–68]. The time dependence of amount of the cation intercalated is exponential and the reaction rate increases with increasing temperature.

Gradual formation of several solid phases has been observed. These phases correspond to stages as is depicted in Fig. 5. Staging means a situation in the layer compounds in which certain galleries are filled, whereas others are empty[69]. The intercalate
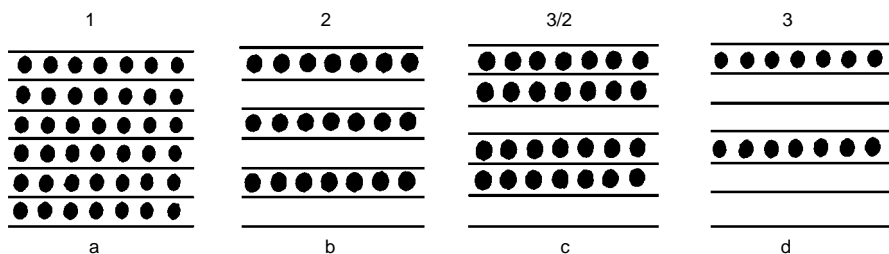

Fig. 5

Stages 3 (a), 2 (b), 3/2 (c), and 1 (d) of intercalated compounds. —— The layers of $(VOPO_4)_\infty$; ● the intercalated ions. Water molecules are omitted

forms sequences in which empty galleries and full galleries vary. The stages are numbered according to a number of the galleries in one sequence (empty ones plus full one). Two empty galleries and full one ($x = 0.33$) exist in stage 3, in stage 2 one empty gallery and the full gallery alternate ($x = 0.5$). Stage 1 consists only of the full galleries ($x = 1$).

In the case of sodium[66], stage 3 is formed first and only this phase is present in the system in a very short period; so it is not possible to observe the kinetics of its formation. A decrease in the stage 3 content is caused by stage 2 formation which is subsequently replaced by stage 1. Values of the sodium content, x_S, for all phases were determined by the multidimensional linear regression of the equation $x = \Sigma x_S w_S$, where x is total sodium content in the sample and w_S is a relative content of the single phase in the sample calculated from the equation $w_S = I_s(002)/\Sigma I_s(002)$. $I_s(002)$ is the intensity of the diffraction line (002) of the s-th phase. The water content determined by DTA remains constant up to $x = 0.5$, above this value, the water content decreases linearly.

Similarly, during intercalation of lithium ions into $VOPO_4 \cdot 2\,H_2O$, four phases (stages) are formed[67,68]. In contrast to sodium, formation of a new phase is observed (with $x = 0.67$) between stages 2 and 1, which is out of definition of the stages. The most plausible structure of this stage is a sequence of two full galleries and one empty. Stage numbering, therefore, must be newly defined as a ratio of the number of all the galleries (empty plus full ones) to the number of full galleries in each sequence. The new stage mentioned is then denoted as a stage 3/2 (Fig. 5c). This stage has not been observed in non-graphite intercalation compounds so far. Numbering of the other stages is not changed in this way. The water content is the same in all four stages.

In comparison with sodium and lithium, the intercalation of potassium is a much slower process[65]. To achieve an almost fully intercalated product of $K_{0.97}VOPO_4 \cdot H_2O$, shaking of the reaction mixture at 40 °C for 1 600 h is required. The content of water is close to monohydrate as it was found out by DTA measurements for all intercalates prepared.

The conductance behaviour of the redox intercalates mentioned, measured by impedance spectroscopy, is very similar[65–68]. The value of conductivity decreases with increasing content of intercalated cation up to $x = 0.5$. At a higher content of guests, the conductivity remains almost constant. As follows from previous papers[21,70], the prevailing charge carriers in hydrates of vanadyl phosphate are positively charged. The only possible positively charged carriers are, in this case, protons formed by dissociation of interlayer water. The decrease in conductivity is explained by the fact that the highest density of the negative charge after intercalation of cation is localized at the vanadium(IV) atoms and intercalated positive charged species form counterparts of this negative charge. Therefore, intercalated cations unlike protons formed by dissociation of interlayer water are not mobile.

The reaction between $LiNO_3$ and $VOPO_4 \cdot 2\,H_2O$ in acetone medium besides being a redox process, proceeds by an acid-base mechanism[71]. The material obtained, $Li_{1.6}VOPO_4 \cdot 2\,H_2O$, is a non-homogeneous solid, which is converted to a crystalline solid if annealed at 450 °C. The existence of hydrated lithium ion within the intracrystalline space of lithium intercalate as well as the partial reduction of vanadium(V) to vanadium(IV) lead to a mixed ionic–electronic conductor. This fact is confirmed by the impedance spectroscopy.

In a series of papers, hydrothermal synthesis[72] and X-ray crystal structures have been reported for $Na_{0.5}VOPO_4 \cdot 2\,H_2O$, $K_{0.5}VOPO_4 \cdot 1.5\,H_2O$ (ref.[73]) as well as for the alkaline-earth metal compound $Sr_{0.5}VOPO_4 \cdot 2\,H_2O$ (ref.[74]). Systematic magnetic studies of this series, extended to $Rb_{0.5}VOPO_4 \cdot 1.5\,H_2O$, revealed surprising ferromagnetic couplings in the layers[75], which is in contradiction to magnetic measurements for the Na^+ compound synthesized by the iodide method[66].

4.3. Intercalation of Hydronium Ions

Hydronium ions cannot be intercalated into $VOPO_4$ by an analogous iodide procedure to that used for the above-mentioned cations because of solubility of the host lattice in acid[76]. The reaction can be carried out using a nonaqueous solution of a hydrogen-transfer agent such as hydroquinone forming $H_xVOPO_4 \cdot y\,H_2O$ ($0 < x < 1$) (ref.[65]). The water content (y is about 2.3) varied only little with the value of x. The products with $x < 0.26$ contain two phases whereas samples with $x > 0.26$ are apparently single phase. However, a plateau observed in the interlayer separation as a function of the composition strongly suggests that there exists a two-phase region centered at the composition of $x = 0.65$. By refluxing in butan-2-ol, the intercalation compound transforms to a blue layered crystalline phase which has formula $VO(HPO_4) \cdot 0.5\,H_2O$ (ref.[33]). Intercalation of hydronium ion from acetone solution of hydroquinone proceeds fast in comparison with intercalation of alkali metal ions. The content of water in hydronium intercalates is increased during intercalation. This is explained by the fact that the hydronium ions enter into the interlayer space as the species which are solvated by water.

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