Novel Modifications of the Structure of the Layered Vanadyl Hydrogenphosphate $VO(HPO_4)\cdot0.5H_2O$†

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The addition of metal ions such as Zn^{2+}, Ni^{2+} and Pd^{2+} during the preparation of the layered vanadyl hydrogenphosphate $VO(HPO_4)\cdot0.5H_2O$ in aqueous media led to the formation of a new phase which is very different from that of the parent compound. This phase, which appears to be structurally similar to the vanadium(V) phosphate $VO(PO_4)\cdot2H_2O$, is a mixed-valent vanadium compound with an expanded *c*-axis spacing in which the incorporated metal ions, in their divalent state, appear to be lodged in the interlayer region.

The solid state chemistry of vanadium phosphates is very interesting and diverse because vanadium can exist in more than one oxidation state and also because of the variety of ways in which the phosphate tetrahedra and vanadyl octahedra can be interlinked to give layered structures which are amenable to intercalation reactions. In this context, the vanadium(V) phosphates such as $VO(PO_4)\cdot2H_2O$ have been shown to undergo intercalation with various donor ligands such as pyridine and ferrocene[1] as well as redox intercalation reactions[2] where a fraction of the V^V is reduced to V^{IV} and compensating cations are incorporated into the interlayer region. Both these types of intercalation lead to a change in the basal spacing with retention of the structure of the host lattice. In contrast, the intercalation reactions of the vanadium(IV) phosphates have not been studied although there is a report[3] on the intercalation of alcohols into vanadyl alkylphosphates. Amongst the vanadium(IV) phosphates the compound $VO(HPO_4)\cdot0.5H_2O$ is known to be the precursor for the catalyst used for the commercially important and scientifically fascinating selective oxidation of butane to maleic anhydride.[4] However, the possibility of this interesting layered compound being a host for intercalating ions and molecules has not been explored.

We have recently reported the variation in the morphology[5] of $VO(HPO_4)\cdot0.5H_2O$ with the medium of preparation as well as the diverse effects[6] of incorporating metal ions into this compound prepared in different media. We describe here the very novel modifications of the structure of the vanadyl orthophosphate hemihydrate on addition of metal ions during its preparation in aqueous media.

Experimental

The $VO(HPO_4)\cdot0.5H_2O$ was prepared by a published method[7] involving the reduction of an aqueous slurry of V_2O_5 with $NH_2OH\cdot HCl$ followed by the addition of a stoichiometric amount of 85% orthophosphoric acid (P : V = 1 : 1) and heating to 80 °C for 1 h. The reaction mixture was then evaporated to dryness, heated overnight at 130 °C, boiled with water for 10 min, filtered and then dried. In the preparation of the intercalation compounds, the relevant metal salt [$ZnCl_2$, $NiCl_2$ or $Pd(NO_3)_2$] was added to the V_2O_5 slurry in the atomic ratio P : V : M = 1 : 1 : 0.2. The parent vanadyl hydrogenphosphate is denoted as **1** and the zinc, nickel and palladium compounds as **2**, **3** and **4**, respectively. For comparison, a sample of $VO(PO_4)\cdot2H_2O$ **5** was prepared[1c] by refluxing stoichiometric amounts of V_2O_5 with phosphoric acid for 16 h. The yellow crystalline solid isolated was washed sparingly with water and ethanol and dried by suction in air. The amount of metal ion incorporated in each compound was determined by atomic absorption spectroscopy and the average oxidation state determined by redox titrations[7] wherein about 0.1 g of the compound was dissolved in 2 mol dm^{-3} H_2SO_4 (100 cm^3) at 80 °C. The vanadium(IV) content was then determined by titration (V_1) with 0.1 mol dm^{-3} $KMnO_4$ and the vanadium(V) content by titration (V_2) with 0.1 mol dm^{-3} ammonium iron(II) sulfate using diphenylamine as indicator. The average oxidation state was then expressed as $5 - (V_1/V_2)$. X-Ray diffraction (XRD) patterns were run on a Philips X-ray diffractometer using Cu-Kα radiation and infrared spectra were recorded on a Nicolet 710 FTIR spectrometer. The differential scanning calorimetry (DSC) experiments were conducted using a Mettler DSC 20 system with a TC 11 TA processor in an atmosphere of nitrogen at a flow rate of 150 cm^3 min^{-1} and at a heating rate of 10 °C min^{-1}. X-Ray photoelectron spectra were recorded on a VG ESCA MKII spectrometer using the C ls line (285.0 eV) as the internal standard.

Results

Analysis and Average Oxidation State.—Compounds **2**–**4** were found to contain 0.41% (by weight) of zinc, 0.15% nickel and 0.61% palladium respectively under identical reaction conditions. This indicated that the amount of foreign metal ion incorporated into the parent compound is a small percentage of the total amount of metal salt taken in the reaction mixture.

The average oxidation state of vanadium in the parent compound **1** was found to be +4.03 indicating the presence of only vanadium(IV) species. In contrast compounds **2**–**4** had an average vanadium oxidation state of +4.6 suggesting the presence of mixed-valent vanadium with a predominance of vanadium(V).

X-Ray Diffraction.—The XRD pattern (Fig. 1) of compound **1** corresponds closely with that reported[8] for $VO(HPO_4)\cdot0.5H_2O$. In the case of the intercalates, **2**–**4** however, it is clear that the patterns are completely different from that of the parent compound but interestingly somewhat similar to that of $VO(PO_4)\cdot2H_2O$ **5**. Compared to the parent compound, there appears to be a significant loss of crystallinity upon intercalation as evident from the decreased number of observable Bragg reflections. Also, the very strong intensity of the (001) reflection indicates preferred orientation along the *c* axis. All the

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† *Non-SI unit employed:* eV ≈ 1.60×10^{-19} J.

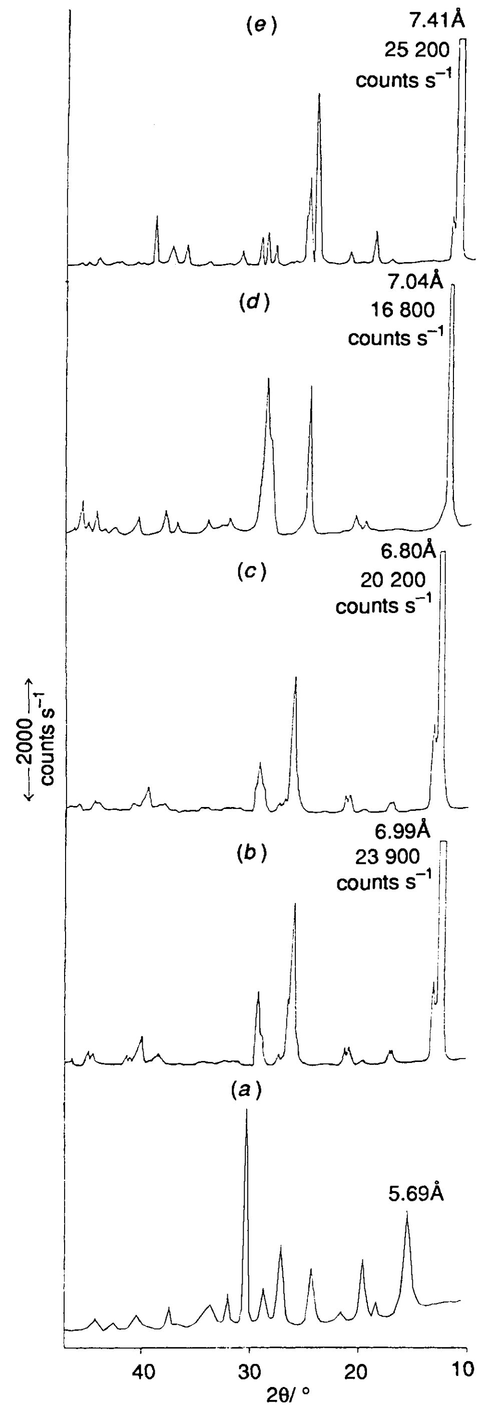

Fig. 1 The XRD patterns of compounds **1**–**5** [(*a*)–(*e*)]

three intercalates have similar XRD patterns with the *c* axis interlayer distance however varying with the metal ion from 6.80 Å in the nickel compound to 7.04 Å in the palladium intercalate.

It would appear from the XRD patterns therefore that compounds **2**–**4** cannot be regarded as intercalates of the parent compound $VO(HPO_4)\cdot 0.5H_2O$ but instead belong to an altogether different phase which appears to be similar to that of $VO(PO_4)\cdot 2H_2O$.

Fourier-transform IR Spectra.—It is evident that the infrared spectra (Fig. 2) of compounds **2**–**4** though similar to each other are very different from that of the parent compound **1**. The reduced crystallinity of these compounds is also evident from the broadening of the bands due to the P–O and V–O stretching vibrations in the region 1200–800 cm^{-1}.

In the O–H stretching region the band at 3365 cm^{-1} of the parent compound is due to the P–O–H groups believed[9] to be projecting into the interlayer regions of the layered vanadyl orthophosphate, and the overlapping band, appearing as a shoulder at 3547 cm^{-1}, is associated with the water molecule the oxygen atom of which is part of two face-sharing octahedra. In contrast, compounds **2**–**4** show two distinct bands at about 3550 and 3160 cm^{-1}. The higher wavenumber band can be assigned to water molecules bound to vanadium (*i.e.* $V–OH_2$) and that at around 3160 cm^{-1} to non-bonded water molecules residing in the interlayer region. The spectra of **2**–**4** are comparable with that of $VO(PO_4)\cdot 2H_2O$ in which the bands at 3570 and 3406 cm^{-1} have been assigned[2a] to water molecules bound to vanadium and to those in the interlayer respectively. It is also significant that the band at 3365 cm^{-1} due to P–OH groups in **1** is absent in the cases of **2**–**4**. The topotactic transformation of **1** to the pyrophosphate is believed[8,9] to involve condensation of P–OH groups of adjacent layers and it may therefore be expected that such transformations should not be possible in the case of compounds **2**–**4**.

The bending mode of water occurs as a sharp peak at 1637 cm^{-1} for compound **1** [Fig. 2(*b*)] and is indicative of a single type of water molecule. In contrast, compounds **2**–**4** like $VO(PO_4)\cdot 2H_2O$ have broad bands suggesting once again the presence of weakly bound water molecules (in the interlayer) in addition to water molecules bound to vanadium.

In the 1500–400 cm^{-1} region [Fig. 2(*b*)] the assignment of the bands is difficult due to the mixing of the V–O and P–O modes, but the fact that the spectra of compounds **2**–**4** are less resolved and different from that of the parent compound **1** but similar to that of $VO(PO_4)\cdot 2H_2O$ is quite evident. The $V^{IV}=O$ vibration in **1** occurs at 976 cm^{-1} which is absent from compounds **2**–**4**. However, since the intercalates contain mixed-valent vanadium, the shoulder at 995 cm^{-1} for **2**–**4** can probably be assigned to the $V^{IV}=O$ stretch with the blue shift of 19 cm^{-1} being due to the reduced interaction of the vanadyl oxygen with the adjacent layer as a result of the larger basal spacing in **2**–**4** as compared to that in **1**. At the same time the shoulder at 1036 cm^{-1} in the case of $VO(PO_4)\cdot 2H_2O$ has been attributed[2a] to the $V^V=O$ stretch and accordingly the distinct shoulder at around 1033 cm^{-1} in the spectra of **2**–**4** can be similarly assigned.

Thermal Studies.—The DSC patterns (Fig. 3) corroborate the data from the XRD and infrared studies. The parent orthophosphate **1** shows an endotherm at 431 °C which is known to be due to a topotactic transformation to the vanadyl pyrophosphate $(VO)_2P_2O_7$. This complicated transformation is postulated[8] to involve the concerted loss of two molecules of water, one of which is held by two face-sharing vanadium octahedra and the other resulting from the condensation of P–OH groups from adjacent layers. For compounds **2**–**4** however, the DSC patterns, like the XRD and infrared spectra, are completely different from that of **1**. The endotherm in the 400–450 °C region is absent indicating that the transformation to the pyrophosphate does not take place. At the same time there are endotherms at 209, 212 and 195 °C for **2**, **3** and **4** respectively which, in conjunction with the infrared data, can be ascribed to the loss of water bound to vanadium. The endotherms below 100 °C are due to the loss of water residing in the interlayer region. It is interesting that, compared to $VO(PO_4)\cdot 2H_2O$, the lattice-bound water ($V–OH_2$) in compounds **2**–**4** is lost at a higher temperature indicating that they are more strongly bound to the lattice.

Compound **1** after heating to 500 °C in a nitrogen atmosphere gave an infrared spectrum and XRD pattern corresponding[10] to the vanadyl pyrophosphate $(VO)_2P_2O_7$. In contrast, **2**–**4**, under similar conditions gave broad unresolved infrared spectra and were found to be X-ray amorphous, indicating loss of crystallinity on dehydration and confirming

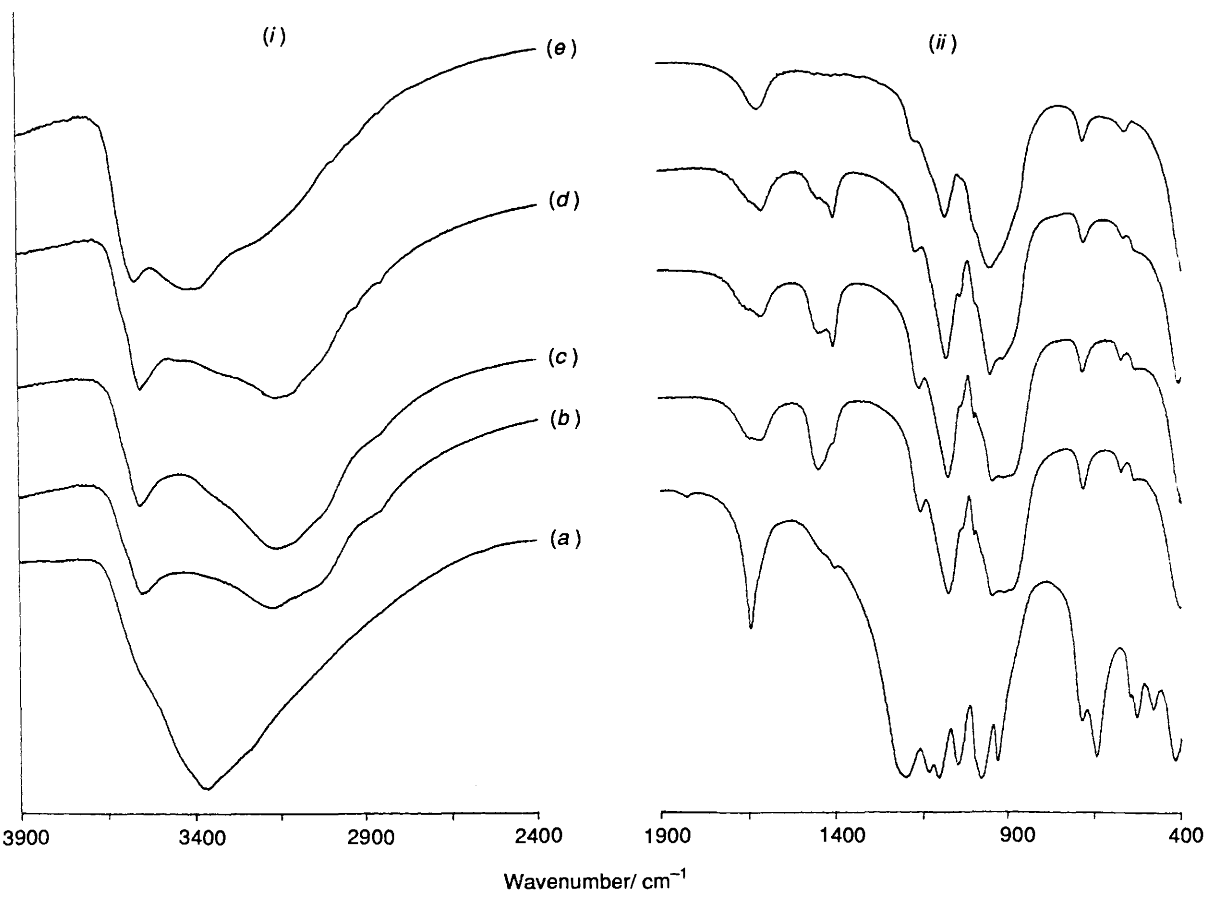

Fig. 2 The FTIR spectra of compounds 1–5 [(*a*)–(*e*)] in the O–H stretching region (*i*) and in the region 1900–400 cm^{-1} (*ii*)

that the transformation to the pyrophosphate does not take place.

X-Ray Photoelectron Spectra.—The X-ray photoelectron spectra in the vanadium 2p binding-energy (b.e.) region (Fig. 4) reveal that compound **1** has a sharp peak at 517.7 eV indicating that only vanadium(IV) species are present. On the other hand, **2**–**4** have a broad peak centred around 518.4 eV. The b.e. of the $2p_{\frac{3}{2}}$ state of V^V in $VO(PO_4)$ is reported[7] to be 519.0 eV. Consequently, the position and width of the vanadium peak for **2**–**4** strongly suggest the presence of both vanadium-(IV) and -(V) species. This corroborates the data on the average oxidation states of vanadium in these compounds.

At the same time the b.e.s of zinc ($2p_{\frac{3}{2}}$, 1022.6 eV) and palladium ($3d_{\frac{5}{2}}$, 338.3 eV) in compounds **2** and **4** respectively indicate that the incorporated metal ions are present only in the +2 oxidation state, which means that the oxidation state of the respective metals is retained during their incorporation into the vanadyl hydrogenphosphate. For compound **3** it was not possible to detect the presence of nickel by X-ray photoelectron spectroscopy probably because of the low concentration (0.15%) and also because the photoionisation cross-section of the $2p_{\frac{3}{2}}$ state of nickel is smaller than that of zinc and comparable with the $3d_{\frac{5}{2}}$ state of palladium.

Discussion

It is evident from all the studies presented here that compounds **2**–**4** have structural characteristics which are very different from those of the parent vanadyl hydrogenphosphate and are similar to those of the vanadium(V) phosphate $VO(PO_4)\cdot 2H_2O$.

The structure[11] of $VO(PO_4)\cdot 2H_2O$ consists of layers of PO_4 tetrahedra linked to distorted V^VO_6 octahedra by corner-sharing phosphate oxygens. The layers are held together only by a weak interaction of the apical vanadyl oxygen to the open square face of a vanadium pyramid in the adjacent layer. As a result of this weak interlayer bonding, intercalation of metal ions with retention of structure of the parent compound is possible and it has been suggested[2a] from extended X-ray absorption fine structure studies that the most probable location of the intercalated metal ions is a tetragonal pocket defined by four oxygens which are corner shared between vanadium octahedra and phosphate tetrahedra.

In contrast, the structure[9] of $VO(HPO_4)\cdot 0.5H_2O$ consists of face-sharing VO_6 octahedra with the equatorial oxygens bound to phosphate tetrahedra. Also, unlike $VO(PO_4)\cdot 2H_2O$, the layers are held together by a tight network of hydrogen bonds. Each hydrogen atom of the water molecule bound to the two face-sharing octahedra is hydrogen bonded to an apical phosphate oxygen atom in an adjacent layer. In addition, the phosphate co-ordination sphere consists of an unshared OH group directed towards the interlayer space which is hydrogen bonded to the vanadyl oxygen atom of the next layer. The strong hydrogen-bonded network is reflected in the high temperature (≈450 °C) required for the loss of water from this compound. As a consequence of this interlayer hydrogen-bonding network, the tetragonal pockets available for intercalating metal ions in the case of $VO(PO_4)\cdot 2H_2O$ are blocked in $VO(HPO_4)\cdot 0.5H_2O$, and as evident from our studies it is therefore not capable of intercalating metal ions into its structure. What is however most interesting is that the presence of foreign metal ions during the synthesis of $VO(HPO_4)\cdot 0.5H_2O$ seems to induce the formation of an altogether different phase which is similar to that of $VO(PO_4)\cdot 2H_2O$ and is capable of accommodating metal ions into its interlayer. Our present results therefore provide the only example, that we are aware of, in the intercalation chemistry of layered compounds wherein the guest metal ions present during the synthesis of a layered

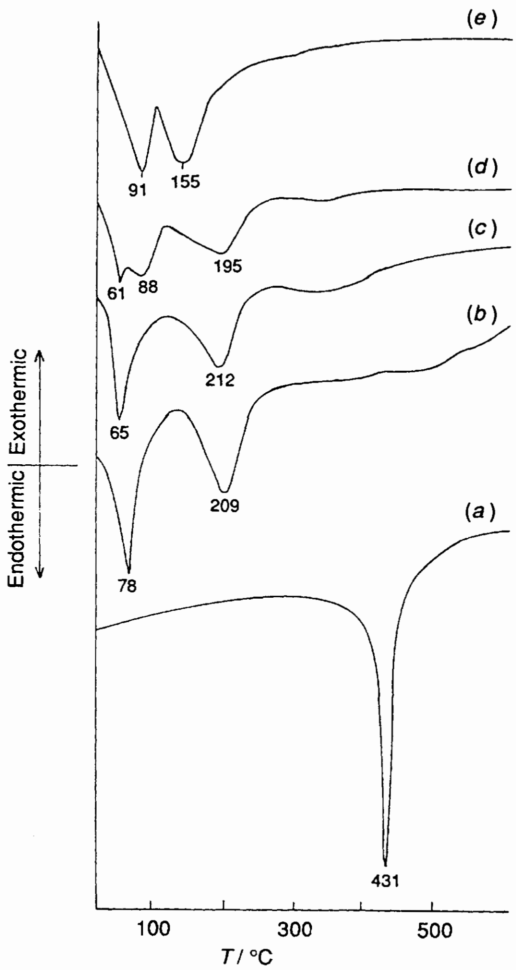

Fig. 3 The DSC patterns of compounds **1**–**5** [(*a*)–(*e*)] in a nitrogen atmosphere (150 cm^3 min^{-1}) and a heating rate of 10 °C min^{-1}

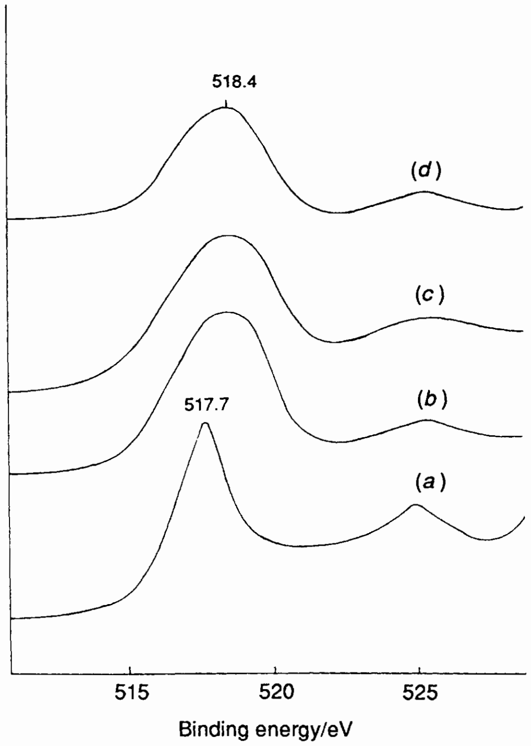

Fig. 4 X-Ray photoelectron spectra of compounds **1**–**4** [(*a*)–(*d*)] in the V $2p_{\frac{3}{2}}$ binding-energy region

compound incapable of intercalation induce the formation of a different host lattice which can accommodate the guest ions in the interlayer region. It is interesting that the same metal ions if present during the preparation of $VO(HPO_4)\cdot 0.5H_2O$ in an organic medium (involving reduction of V_2O_5 with benzyl alcohol in isobutyl alcohol followed by the addition of phosphoric acid) do not intercalate with change in structure of the parent compound but instead appear to substitute into the VPO framework.[6] This is probably because mixed-valent vanadium compounds are reported[12] to be formed in aqueous acidic media by the interaction of hydrated species like $[VO(H_2O)_5]^{2+}$ and $[VO_2(H_2O)_4]^+$ wherein one of the co-ordinated water molecules of the VO^{2+} aqua cation is substituted by one of the oxygens of the dioxovanadium(V) group. What is interesting however is that, under identical reaction conditions, in the absence of added foreign metal salts, the $VO(HPO_4)\cdot 0.5H_2O$ phase containing only vanadium(IV) species is formed in a facile manner. It is likely therefore that the added metal ions in their hydrated forms tend to stabilise the hydrated vanadium(V) species $[VO_2(H_2O)_4]^+$ which would otherwise have been reduced by the hydroxylamine hydrochloride.

Attempts to prepare single crystals of compounds **2**–**4** for a complete structural characterisation have so far been unsuccessful. It is however relevant that mixed-valent vanadium compounds such as $K_2V_3O_8$ are known[13] where the formal avarage oxidation state is +4.66 and the structure consists of infinite layers of VO_4 tetrahedra and VO_5 tetragonal pyramids sharing vertices. This type of layer network is similar to that present in $VO(PO_4)\cdot 2H_2O$ and it is therefore quite possible that the compounds **2**–**4** also have a layer structure similar to that of $K_2V_3O_8$ with the phosphate groups replacing the VO_4 tetrahedra.

Conclusion

It is evident from the present work that the presence of foreign metal ions such as Zn^{2+}, Ni^{2+} and Pd^{2+} in very small amounts of less than 1% during the preparation of $VO(HPO_4)\cdot 0.5H_2O$ in aqueous media leads to the formation of a new vanadium phosphate phase containing mixed-valent vanadium which appears to be structurally similar to $VO(PO_4)\cdot 2H_2O$. However, the $VO(PO_4)\cdot 2H_2O$ framework is structurally dissimilar from that of $VO(HPO_4)\cdot 0.5H_2O$. Consequently, the formation of a $VO(PO_4)\cdot 2H_2O$-like phase in the presence of foreign metal ions, under reaction conditions which otherwise lead to the formation of the $VO(HPO_4)\cdot 0.5H_2O$, is an interesting and novel aspect of the structurally fascinating and commercially important vanadium phosphates. Also, the presence of metal ions such as Pd^{2+} and Ni^{2+}, which are active catalysts for oxidation, within the layers of a VPO phase which itself has oxidation centres and a potential V^{IV}–V^{V} redox couple raises the possibility of these compounds being used as novel catalysts for selective oxidation. This is particularly so since it is generally believed[14] that a selective oxidation catalyst is composed of two oxides, one of which is responsible for activity and the other for selectivity with the latter property being due to certain ions in appropriate co-ordination rather than due to any defined phases in the catalyst.

Acknowledgements

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