Novel Compounds of Nickel Intercalated/Substituted into the Vanadyl Orthophosphate $VOHPO_4{\cdot}0.5H_2O$ and their Catalytic Activity

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Nickel incorporated into the vanadyl orthophosphate $VOHPO_4{\cdot}0.5H_2O$ appears to intercalate in aqueous medium and substitute into the lattice of the parent compound in organic medium; these nickel compounds show different catalytic activity.

The intercalation chemistry of the layered vanadyl orthophosphate $VOHPO_4{\cdot}0.5H_2O$, which is the precursor for the commercially important catalyst for the selective oxidation of butane to maleic anhydride,[1] has not been studied although the vanadium(v) phosphates such as $VOPO_4{\cdot}2H_2O$ have been shown to give rise to interesting intercalation reactions.[2] We have recently reported[3] the novel and diverse effects on the structure of $VOHPO_4{\cdot}0.5H_2O$ brought about by the incorporation of zinc ions. This study had raised the interesting possibility of incorporating catalytically active metal ions into the $VOHPO_4{\cdot}0.5H_2O$ structure and then using these compounds as novel catalysts. We describe herein the preparation, characterization and catalytic activity of novel compounds prepared by incorporating nickel ions into the vanadyl hydrogen phosphate in both aqueous and organic media.

The $VOHPO_4{\cdot}0.5H_2O$ was prepared in aqueous medium[4] by 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 ($P:V = 1:1$) while the nickel compound was prepared by adding a stoichiometric amount of $NiCl_2$ ($P:V:Ni = 1:1:0.2$) to the V_2O_5 slurry during the preparation procedure and the final product was

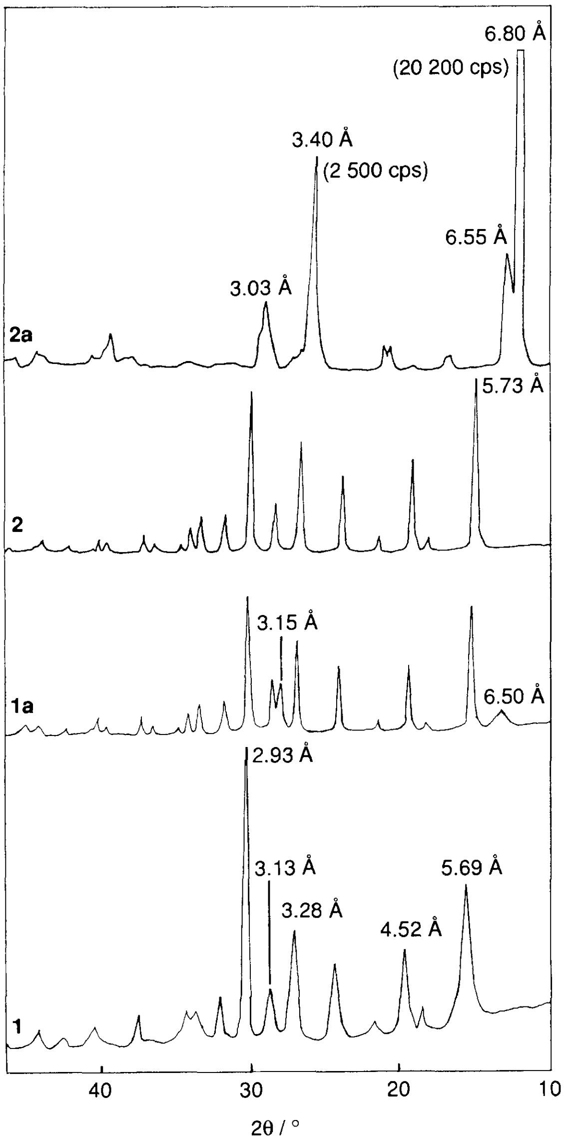

Fig. 1 XRD patterns of $VOHPO_4{\cdot}0.5H_2O$ prepared in organic **1** and aqueous **2** media and their corresponding nickel compounds **1a** and **2a**

washed repeatedly with water to remove unreacted nickel chloride. In the preparations in organic medium[5] the reductant, as well as the solvent, was a mixture of benzyl alcohol and isobutyl alcohol but the reactants were in the same ratio as for the aqueous preparations. The $VOHPO_4{\cdot}0.5H_2O$ prepared in organic and aqueous media are coded as **1** and **2**, respectively, whereas the corresponding nickel compounds are coded as **1a** and **2a**. Samples **1a** and **2a** were found to contain 3.95 and 0.15% nickel, respectively. Determination of the average oxidation state of vanadium by redox titration[4] showed that **1**, **2** and **1a** had an average vanadium oxidation state close to +4.0 whereas for **2a**, the corresponding value was 4.65 indicating the presence of substantial amounts of V^{5+} species in contrast to the other three compounds which contain vanadium exclusively in the +4 state.

The X-ray diffraction (XRD) patterns (Fig. 1) of **1** and **2** are similar and correspond closely with that reported[5] for $VOHPO_4.0.5H_2O$ although the peaks in **1** are a little broader indicating poorer crystallinity in comparison to **2**. In the case of the nickel compound prepared in organic medium, although there are additional lines corresponding to d values of 6.50 and 3.15 Å, the XRD pattern is essentially similar to that of the parent compound indicating that the incorporation of 3.95% nickel has little effect on the structure of $VOHPO_4{\cdot}0.5H_2O$. However, in the case of **2a**, the presence of just 0.15% nickel induces a changeover to a new V–P–O phase with an expanded basal spacing of 6.8 Å and with a pronounced selective enhancement in the intensity of the (001) line.

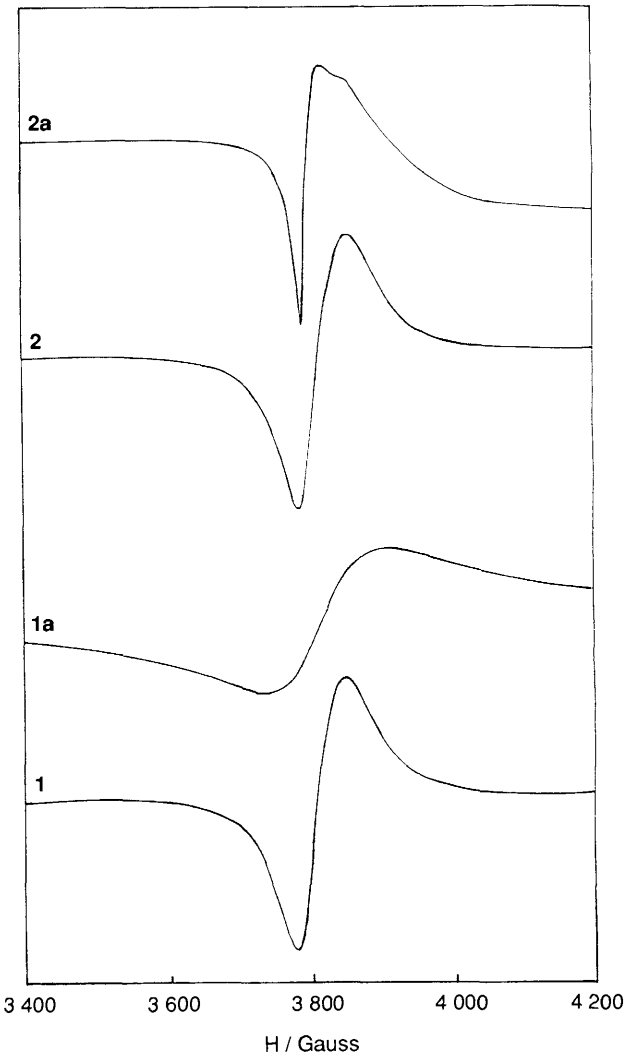

Fig. 2 EPR spectra (at room temp. of $VOHPO_4{\cdot}0.5H_2O$ prepared in organic **1** and aqueous **2** media and their corresponding nickel compounds **1a** and **2a**

The IR spectrum of **1**, **2** and **1a** correspond closely with that reported[5] for $VOHPO_4{\cdot}0.5H_2O$ whereas the spectrum of **2a** is completely different from that of the parent compound. This is in accordance with the XRD data. The spectrum of **2a** in the O–H stretching and bending regions shows the presence of additional water molecules and in the V–O, P–O stretching region, there are strong bands at 1171, 1082, 1032, 1011, 960 and 902 cm^{-1} which do not, however, correspond with those of the parent compound.

The differential scanning calorimetry (DSC) patterns of **1** and **2** in a N_2 atmosphere show endotherms at 443 and 431 °C, respectively, which correspond to the topotactic transformation of the orthophosphate to the pyrophosphate.[6] In the case of **1a** the transformation takes place at a higher temperature of 465 °C whereas for **2a**, only two endotherms at 65 and 193 °C are present but no endotherm is observed in the 400–500 °C region indicating that the transformation to the pyrophosphate does not take place.

The EPR spectra (Fig. 2) of **1** and **2** are similar and show an isotropic signal [g = 1.97, linewidth 75 G (G = 10^{-4} T)] typical[7] of $(VO)^{2+}$ species. In the case of **1a**, however, the observed broadening (linewidth 155 G) is probably due to rapid spin relaxation arising from magnetic exchange interactions between the paramagnetic V^{4+} and the incorporated Ni^{2+} ions and suggests that the nickel ions are probably substituted into the lattice of the parent compound. In the case of **2a**, the observed anisotropic signal is in keeping with the XRD pattern of the compound which shows pronounced selective ordering along the *c*-axis. Also, the narrowing of the signal, indicative of a less efficient relaxation process, suggests that the paramagnetic centres in **2a** are more isolated and separated than in the parent compound. This agrees with the observation that **2a** with an average oxidation state of 4.65 has a substantial amount of V^{5+} ions, which could shield the paramagnetic V^{4+} centres from each other.

From all the above evidence it appears that the nickel incorporated into the layered $VOHPO_4 \cdot 0.5H_2O$ in organic medium is not lodged in the interlayer region, since there is no change in the basal spacing nor does it affect the structure of the parent compound. However, the EPR evidence suggests that the Ni^{2+} ions are probably substituted into the lattice and since the size of the Ni^{2+} ions (0.69 Å) is comparable with that of V^{4+} (0.63 Å) the substitution of 3.95% nickel does not cause any appreciable distortion in the structure. However, in the case of the compound prepared in aqueous medium, the nickel ions appear to be intercalated and the presence of just 0.15% nickel causes the structure of the parent compound to change to a new V–P–O phase with the incorporated ions being selectively oriented along the *c*-axis. The new VPO phase has an expanded basal spacing compared to the parent molecule and contains mixed valent vanadium.

Since the compounds **1a** and **2a** appeared to have nickel ions incorporated in different ways into a VPO matrix, the catalytic activity of nickel in these compounds was investigated. In the catalytic hydrogenation of cyclohexene to cyclohexane at 80 °C and 100 psi hydrogen pressure, practically no conversion was observed in the case of **1a** or **2a** even after 5 h. On the other hand, for the nickel catalysed dehydrogenation of amines to nitriles[8] it was found that on stirring an aqueous solution of the catalyst (0.020 mmol Ni) with benzylamine (4.00 mmol) in CH_2Cl_2 (10 ml) and an aqueous solution (50 ml) of $K_2S_2O_8$–NaOH (10:20 mmol), for 6 h at room temperature, 92% of benzonitrile was obtained in the case of **1a**, whereas no conversion to the benzonitrile was observed in the case of **2a**. The hydrogenation studies confirm that nickel is present in both **1a** and **2a** as Ni^{2+} ions which are not reduced under the conditions of the experiment. On the other hand, the dehydrogenation studies show that the Ni^{2+} ions in **1a** are catalytically active whereas those in **2a** appear to be inaccessible to reactant molecules.

It is evident, therefore, that the incorporation of nickel ions into the vanadyl orthophosphate $VOHPO_4 \cdot 0.5H_2O$ in different media leads not only to novel modifications in the structure of the parent compound, but also gives rise to different catalytic behaviour of the incorporated ion.

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