Evidence for a hydrogen insertion compound of novel palladium incorporated vanadyl hydrogen phosphates

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Palladium is shown to be incorporated into the vanadyl hydrogen phosphate phase $VOHPO_4{\cdot}0.5H_2O$ in different ways depending on the medium used for preparation; temperature programmed reduction (TPR) studies provide evidence for the formation of a hydrogen insertion compound of one of these palladium incorporated vanadyl phosphates.

Vanadium phosphates have attracted a lot of attention in recent years both because of their catalytic activity and their wide structural diversity.[1] We have recently shown[2] that metal ions and molecular species can be introduced into layered vanadyl phosphates in different ways and the incorporated species were found to be catalytically active and in some cases, exhibited shape-selective catalysis.[2e] In the present work therefore we have prepared and characterized novel compounds containing palladium incorporated in different ways into a vanadyl hydrogen phosphate phase. The TPR studies of these compounds while confirming the different modes of incorporation of palladium into the VPO matrix, provide evidence for the formation of a hydrogen insertion complex of one of the palladium incorporated vanadium phosphates. Such hydrogen insertion compounds of vanadium oxides have been reported but are not known for vanadium phosphates.

The parent vanadyl hydrogen phosphate $VOHPO_4{\cdot}0.5H_2O$ was prepared in both organic and aqueous media since the medium used for preparation is known[2c] to affect the morphology of the phase obtained. In organic medium,[4] $VOHPO_4{\cdot}0.5H_2O$ was prepared by reduction of V_2O_5 with benzyl alcohol in isobutyl alcohol followed by the addition of a stochiometric amount of phosphoric acid (P : V = 1 : 1). For the preparation of the corresponding palladium inserted compound, a stochiometric amount of $Pd(NO_3)_2$ (P : V : Pd = 1 : 1 : 0.2) was added to the V_2O_5 slurry during the preparation procedure. For preparation in aqueous solution,[5] the reductant was $NH_2OH{\cdot}HCl$ but the reactants were in the same ratio as for the organic preparations. In the preparation of the palladium inserted compounds in both organic and aqueous media, the final products were washed repeatedly with water to remove unreacted palladium nitrate. The parent compounds prepared in organic and aqueous media are denoted as **1** and **2** respectively. The palladium incorporated compounds **1a** and **2a** were found to contain 13.6 and 0.61% palladium respectively. Determination of the average oxidation state of vanadium by redox titration[5] showed that **1**, **2** and **1a** had an average vanadium oxidation state of +4.0 whereas for **2a** the corresponding value was +4.65 indicating the presence of both V^{4+} and V^{5+} species.

The XRD patterns (Fig. 1) of **1** and **2** correspond closely with that reported[4] for $VOHPO_4{\cdot}0.5H_2O$ although the peaks in **1** are a little broader indicating poorer crystallinity in comparison to **2**. In the case of the palladium incorporated compound prepared in an organic medium (**1a**), the XRD pattern though essentially similar to that of the parent compound has additional broad lines corresponding to *d* values of 2.25 and 1.95 Å which correspond[6] to the 100 and 40% lines respectively of metallic palladium. In contrast, the XRD pattern of **2a** is completely different from that of the parent compound with a reduction in the total number of reflections. This new phase has an expanded *c* axis spacing of 7.04 Å compared to 5.71 Å in the parent compound and the X-ray powder pattern can be indexed for a tetragonal system with $a = b = 9.24$ and $c = 7.04$ Å.

The IR spectra of **1**, **1a** and **2** are similar and correspond closely with that reported[4] for $VOHPO_4{\cdot}0.5H_2O$ but the spectra of **2a** is completely different from that of the parent compound. In the OH stretching region the IR spectrum of **2a** has bands at

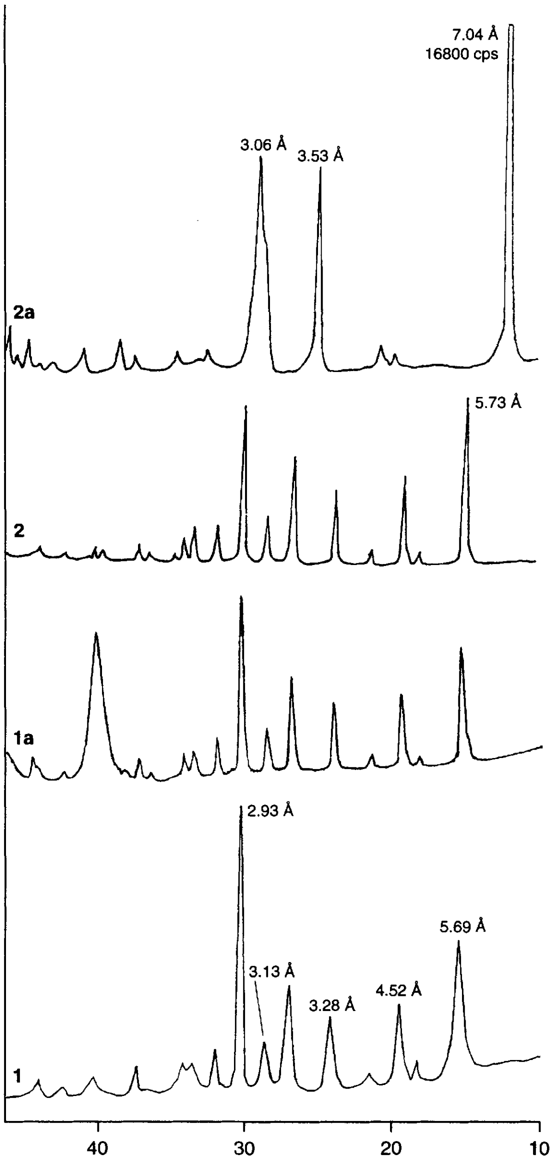

Fig. 1 XRD patterns of $VOHPO{\cdot}0.5H_2O$ prepared in organic (**1**) and aqueous media (**2**) and their corresponding palladium inserted compounds **1a** and **2a**

3550 and around 3160 cm^{-1} in contrast to a single band at 3365 cm^{-1} in the parent compound. Similarly in the V–O, P–O stretching region, **2a** shows two broad unresolved peaks at 1072 and 934 cm^{-1} which do not correspond with those of the parent compound.

The DSC patterns of **1** and **2** in an N_2 atmosphere show endotherms at 433 and 431 °C respectively which correspond to the topotactic transformation of the orthophosphate to the pyrophosphate.[7] In the case of **1a** this transformation takes place at 447 °C whereas for **2a** only two endotherms, at 123 and 182 °C, are present and no endotherm is observed in the region 400–500 indicating that the transformation to the pyrophosphate does not take place.

The TPR pattern of **1a** (Fig. 2) shows a desorption peak at 75 °C and adsorption peaks at 280 °C with a shoulder at 130 °C and a high-temperature peak at 730 °C. The desorption peak can be attributed to the release of hydrogen adsorbed at room temp. by the metallic palladium present in **1a** as indicated in the XRD pattern. The peak at 280 °C would then be due to the reduction of the Pd^{2+} species present in the lattice of the parent compound and the peak at 730 °C can be assigned[9] to the reduction of V^{4+} of the parent compound to V^{3+}. The TPR pattern of the parent $VOHPO_4{\cdot}0.5H_2O$ shows only one hydrogen adsorption peak at 760 °C corresponding to the reduction of V^{4+} to V^{3+}.

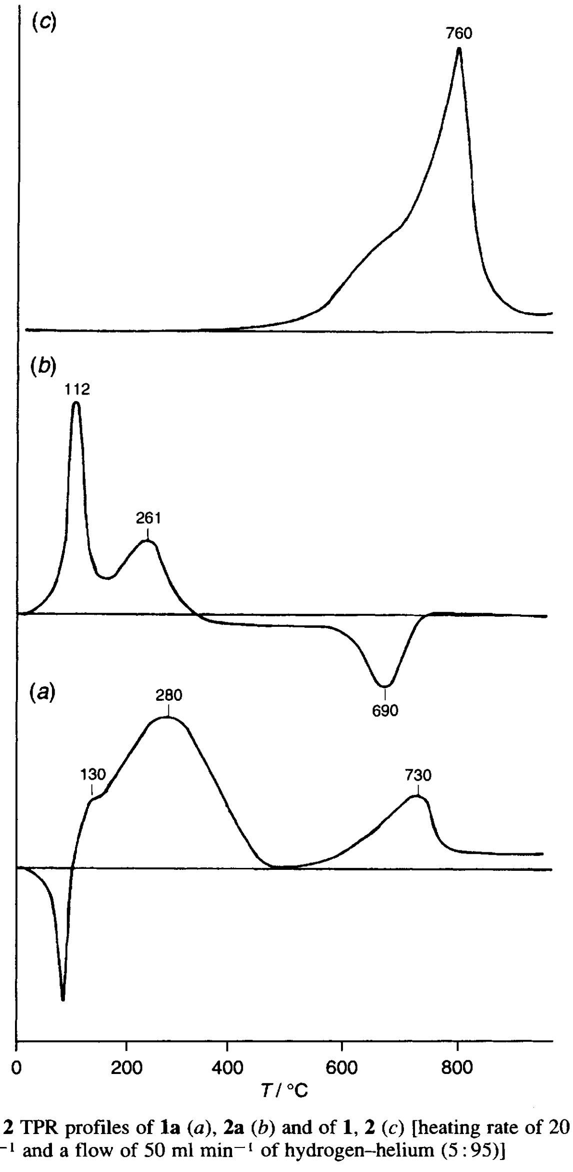

Fig. 2 TPR profiles of **1a** (*a*), **2a** (*b*) and of **1**, **2** (*c*) [heating rate of 20 °C min^{-1} and a flow of 50 ml min^{-1} of hydrogen–helium (5 : 95)]

In contrast, **2a** shows a very interesting TPR pattern wherein the peak at 112 °C can be ascribed to the reduction of the palladium species present in the interlayer. The lower temperature of reduction compared to **1a** confirms the observations from other studies that palladium is incorporated into **1a** and **2a** in very different ways. However, what is even more interesting is the observation of an adsorption peak at 261 °C followed by a desorption peak of similar area at 690 °C. The XPS of **2a** shows the presence of only one type of palladium species (Pd^{2+} with a BE of 338.1 eV for the $3d_{5/2}$ state). Accordingly, the adsorption peak at 112 °C in the TPR profile of **2a** would correspond to the reduction of the incorporated Pd^{2+} species. Infact, the XPS of a sample of **2a** subjected to the TPR experiment but heated isothermally for 0.5 h at 150 °C (that is just after the first adsorption peak at 112 °C) showed that the palladium (with a BE of 335.0 eV for the $3d_{5/2}$ state) was present exclusively as Pd^0. Consequently, the subsequent adsorption peak at 261 °C is not due to a reduction process and must be due to the formation of a hydrogen complex. In essence, it would appear that following the reduction of the incorporated palladium a hydrogen complex is formed which is stable up to *ca.* 600 °C and then decomposes to release hydrogen giving rise to the desorption peak at 690 °C. Hydrogen insertion compounds of mixed-valent vanadium oxides such as V_3O_7 and V_6O_{13} by hydrogen spillover using finely divided Pt catalyst have been reported[10] which however are formed only on heating for several weeks. There is to the best of our knowledge no report on such hydrogen insertion compounds of vanadium phosphates. It is interesting that no hydrogen insertion compound is formed in the case of **1a** although its palladium content is much higher.

It is evident from the above data that palladium is incorporated in very different ways into the $VOHPO{\cdot}0.5H_2O$ phase during its preparation in different media. In aqueous medium, the incorporation of 0.61% Pd^{2+} changes the structure of the parent compound to an altogether different phase in which the Pd^{2+} ions appear to be located in the interlayer region. The comparatively low reduction temperature of the incorporated palladium also points towards its location in the interlayer region. On the other hand, in an organic medium, palladium is partially reduced to the metal and partially introduced into the lattice of the parent compound. The fact that the incorporated Pd^{2+} ions are not lodged in the interlayer region is evident from the fact that there is no expansion in the basal spacing and the thermal transformation to the pyrophosphate, involving[11] condensation of P–OH groups between adjacent layers, does take place. The presence of both Pd^0 and Pd^{2+} is also indicated by the TPR profile and the higher reduction temperature of the palladium provides additional evidence in favour of the incorporated palladium being present in the lattice rather than in the interlayer. The facile formation of the hydrogen insertion compound in the case of **2a** is most likely due to hydrogen spillover wherein the incorporated palladium, after its reduction, catalyses the decomposition of molecular hydrogen. The fact that no hydrogen insertion compound is formed in the case of **1a** is probably due to the observation[10] that in insertion compounds of vanadium oxides the hydrogen prefers to co-ordinate with the oxygen attached to V^{5+} centres. In **1a**, which has the structure of the parent vanadium hydrogen phosphate, the vanadium is present exclusively as V^{4+} and the vanadyl oxygen is part of a strongly bound water molecule[11] and is therefore not available for co-ordination. The hydrogen insertion compound formed in the case of **2a** appears to have potential as a high temperature hydrogen sink since it adsorbs hydrogen at 261 °C and then releases it at 690 °C. On the other hand, the presence of palladium in the framework of the parent compound in the case of **1a** would suggest that for charge neutrality, the Pd^{2+} species would substitute the VO^{2+} moiety causing oxygen vacancies in the lattice. This along with the presence of palladium in mixed oxidation states should make **1a** a good candidate for lattice-oxygen mediated catalytic oxidation reactions. All these aspects of these novel compounds are being explored.

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Footnote

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