



Novel platinum incorporated vanadium phosphates and their catalytic activity

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Received 8 October 2002; accepted 2 December 2002

Abstract

Platinum has been incorporated into the layered vanadyl hydrogen phosphate $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ in different ways depending upon the medium of its preparation. The phase obtained by the introduction of platinum during the synthesis of $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ in aqueous medium is a new crystalline phase with mixed-valent vanadium containing Pt^{2+} species. This phase forms a novel hydrogen insertion compound involving hydrogen spillover from the incorporated platinum onto the VPO matrix. On the other hand, the incorporation of platinum during the synthesis of the hemihydrate in organic medium gives rise to a phase containing both metallic platinum and an amorphous Pt^{2+} containing VPO phase. Both these platinum incorporated phases have been found to be active catalysts for reduction and oxidation reactions such as the hydrogenation of nitrobenzene and the oxidation of tetrahydrofuran with the activity varying quite markedly with the mode of incorporation. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Vanadium phosphates; Platinum incorporation; Characterisation; Hydrogen insertion compound; Catalytic activity

1. Introduction

Selective functionalisation of alkanes is an important objective from both industrial and fundamental aspects. Vanadium phosphorus oxides are the only known catalysts to be used commercially for the functionalisation of an alkane, namely the selective oxidation of *n*-butane to maleic anhydride [1]. In addition, VPO phases have also shown promise as catalysts for the selective oxidation of other alkanes such as propane and pentane and for the ammoxidation of alkyl aromatics. Vanadium phosphates exhibit

a very fascinating and complex structural diversity, wherein depending upon the interlinkage between vanadyl octahedra and phosphate tetrahedra various different phases are formed. These phases are layered compounds and are therefore amenable for intercalation reactions. The incorporation of metal ions can modify the physicochemical characteristics of these catalytically important vanadium phosphates. In this context, we have shown earlier [2] that the introduction of different metal ions into the $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ phase leads both to novel structural changes as well as interesting shape selective catalysis with the catalytic activity varying quite markedly with the mode of incorporation.

The catalytic oxyfunctionalisation of hydrocarbons, particularly alkanes, has also been achieved

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[3] in homogeneous medium using metal salts, particularly those of platinum, as catalysts. It has been shown [4], for instance, that unactivated C–H bonds were attacked by Pt(II), whereas C–H bonds α to an oxygen were attacked by metallic Pt. In addition, oxidation reactions such as that of THF proceed in a very facile manner without an induction period when both metallic Pt and Pt(II) are present. In this context, it would be particularly interesting to incorporate Pt ions into the $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ phase and investigate its catalytic activity, with the dual hope of enhancing the oxidising capability of Pt^{2+} by incorporating it within an oxidation catalyst and also exploring the possibility of heterogenising catalytically important homogeneous systems.

In the present work, therefore we demonstrate the formation of VPO phases in which Pt is incorporated in different modes and in different oxidation states. Also, one of the Pt incorporated phases forms a novel hydrogen insertion compound and both the phases prepared are active catalysts for hydrogenation as well as oxidation reactions with widely differing activity.

2. Experimental

2.1. Syntheses

Since it is known [5] that the morphology of the precursor is strongly dependent upon the medium of preparation, platinum was incorporated into the $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ phase in both organic and aqueous media. For the incorporation of Pt into $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ in organic medium, H_2PtCl_6 was dispersed into a slurry of V_2O_5 and benzyl alcohol-isobutanol followed by the addition of a stoichiometric amount of 85% phosphoric acid [6]. The P:V:Pt ratio was 1:1:0.2. Typically, 1.818 g of V_2O_5 was dispersed in a mixture of 40 ml isobutyl alcohol and 7 ml benzyl alcohol and 2.072 g of H_2PtCl_6 . The mixture was refluxed for 3 h and then stirred at room temperature for 16 h. Subsequently, 2.306 g 85% H_3PO_4 was added and the reaction mixture was again refluxed for 2 h. The black slurry was filtered and the residue thoroughly washed with isobutyl alcohol and dried at 120 °C in an air oven. In the case of the preparation in aqueous medium, 1.818 g of

V_2O_5 powder was dispersed in an aqueous solution [7] of $\text{NH}_2\text{OH} \cdot \text{HCl}$ (1.390 g $\text{NH}_2\text{OH} \cdot \text{HCl}$ dissolved in 40 ml of distilled water) and 2.072 g of H_2PtCl_6 and 2.306 g of 85% H_3PO_4 (P:V:Pt = 1:1:0.2) and heated to 80 °C for 1 h. The green slurry obtained was evaporated to dryness and heated overnight to 120 °C. The dried mass was washed with hot water and dried in an air oven at 120 °C. The platinum incorporated compounds prepared in organic and aqueous media were coded as Pt_{org} and Pt_{aq} , respectively. The parent compounds were also prepared in organic and aqueous medium using the procedures given above and were coded as P_{org} and P_{aq} , respectively.

2.2. Characterisation

The average oxidation state of vanadium in these materials was determined by redox titration [7], wherein about 0.1 g of the material was dissolved in 100 cm^3 of 2 mol dm^{-3} H_2SO_4 at 80 °C. The vanadium(IV) content was 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} ferrous ammonium sulphate using diphenylamine as indicator. The average oxidation state was then expressed as $5 - (V_1/V_2)$. Chemical analysis of the samples was performed with an ICP-AES PS 3000 UV Leeman Labs, Inc., USA inductively coupled plasma spectrometer. X-ray diffraction patterns were run on a GE X-ray diffractometer using $\text{Cu K}\alpha$ radiation and a 2θ scanning rate of 2° min^{-1} . The infrared spectra were recorded on a Perkin-Elmer 1760X FTIR spectrometer with the sample dispersed in KBr pellets. To eliminate any interference from KBr, the ratio of single beam spectrum of the sample to a background spectrum of a pure KBr pellet was taken. X-ray photoelectron spectra (XPS) were recorded on a VG ESCA LAB MkII spectrometer using the C 1s line (285.0 eV) for calibration. The thermogravimetric analysis (TGA) experiments were conducted using a Mettler TG 50 system in an atmosphere of nitrogen at a flow rate of 150 $\text{cm}^3 \text{min}^{-1}$ and at a heating rate of 10 °C min^{-1} . Temperature-programmed reduction profiles (from room temperature to 1000 °C) were obtained with a TPD/TPR-2900 micromeritics (USA) instrument using 5% H_2/Ar mixture with a flow rate of 50 $\text{cm}^3 \text{min}^{-1}$ and a heating rate of 10 °C min^{-1} .

3. Results and discussion

3.1. Characterisation of platinum incorporated vanadium phosphates

Analysis by ICP showed that Pt_{org} and Pt_{aq} contained 13.3 and 0.57% platinum, respectively. In the case of Pt_{org}, the total platinum incorporated is present in two different forms as is evident from the fact that when the sample was dissolved in conc. HCl, it went completely into solution which on analysis gave a Pt content of 13.3%. However, when the sample was dissolved in 1:1 H₂SO₄ some black particles remained undissolved. Analysis of this solution after filtration gave a platinum content of 2.8%, whereas the analysis of the black undissolved component showed it to be pure metallic platinum. In essence, therefore, Pt_{org} contains 10.5% metallic platinum and 2.8% of another platinum species. Determination of the average vanadium oxidation states of these compounds showed that Pt_{org} had an average vanadium oxidation state of +4.0, whereas the corresponding value for Pt_{aq} was +4.65 indicating the presence of mixed-valent vanadium species.

3.1.1. X-ray diffraction (XRD)

The XRD pattern (Fig. 1) of Pt_{org} shows that the sample is generally amorphous in nature with a broad line corresponding to a *d* value of 2.27 Å which agrees with the *d* value for the 100% line of metallic Pt. In contrast, the XRD pattern of Pt_{aq} is entirely different from that of the parent compound with a reduction in the total number of reflections. This phase has an expanded *c*-axis spacing with a *d* value of 6.8 Å and the predominant intensity of this line indicates pronounced selective ordering along this axis.

3.1.2. FT-IR

The infrared spectrum (Fig. 2) of Pt_{aq} is different from that of the parent compound with two broad bands at 3547 and 3153 cm⁻¹ in the O–H stretching region instead of a single band at 3368 cm⁻¹ in the parent compound. Also, in the P–O, V–O stretching region, Pt_{aq} shows peaks at 1088, 1035, 997 (weak), 966, 908 cm⁻¹ which do not correspond with those of the parent compound which has bands at 1202, 1132, 1102, 1050, 975, 928 cm⁻¹. Assignment of the individual bands of Pt_{aq} in the 1500–400 cm⁻¹ region

is difficult due to the mixing of the V–O and P–O modes. However, the band at 1035 cm⁻¹, which is not present in the vanadium(IV) containing parent compound, strongly suggests the presence of V⁵⁺ species since the $\nu_{V^{5+}=O}$ in the vanadium(V) containing VOPO₄·2H₂O has been reported [8] at 1036 cm⁻¹. In addition, the strong band at 966 cm⁻¹ can be assigned to the stretching vibration of the V⁴⁺=O moiety since it occurs at 975 cm⁻¹ in the parent compound. The infrared data, therefore, suggests that Pt_{aq} contains mixed-valent vanadium in agreement with its vanadium oxidation state value of +4.65.

The infrared spectrum of Pt_{org} on the other hand is relatively less resolved in both the O–H stretching and P–O, V–O stretching regions which is in keeping with its amorphous nature. In the O–H stretching region, it shows a broad absorption in the 3550–3200 cm⁻¹ region as in the case of Pt_{aq} although the bands are better resolved in the latter case. In the P–O, V–O stretching region also with bands at 1154, 1063, 964, and 909 cm⁻¹, the spectrum of Pt_{org} is different from that of the parent compound but similar in structure to that of Pt_{aq} although the band positions are different. It is evident that Pt_{org} though amorphous, is a vanadium phosphate phase in which the V–P–O connectivity is dissimilar to that of the parent VOHPO₄·0.5H₂O phase but is similar to that of Pt_{aq}.

3.1.3. X-ray photoelectron spectroscopy (XPS)

The XPS (Fig. 3) of Pt_{org} in the 4f binding energy region shows a broad peak which can be curve fitted with four peaks corresponding to two each for the Pt 4f_{5/2} and Pt 4f_{7/2} states. The BE of the 4f_{7/2} state of Pt⁴⁺, Pt²⁺ and Pt⁰ species are reported to be 75.0, 73.0 and 70.9 eV, respectively [9]. In Pt_{org}, two Pt 4f_{7/2} peaks with BE's of 71.5 and 73.0 eV are observed of which the former can be attributed to metallic Pt in agreement with the XRD data and the latter peak at 73.0 eV can be assigned to Pt²⁺ species. The slightly higher BE of the metallic Pt in Pt_{org} is probably due to its small particle size since it is known that the BE increases with decreasing particle size as in the case of metallic Pd dispersed on different supports [10]. The small crystallite size of metallic Pt is also evident from the broad peak due to it, in the XRD pattern of Pt_{org}. In contrast, Pt_{aq} in the Pt 4f region shows two peaks at 73.2 and 76.6 eV which can be attributed to the 4f_{7/2} and 4f_{5/2} states of Pt²⁺ species.

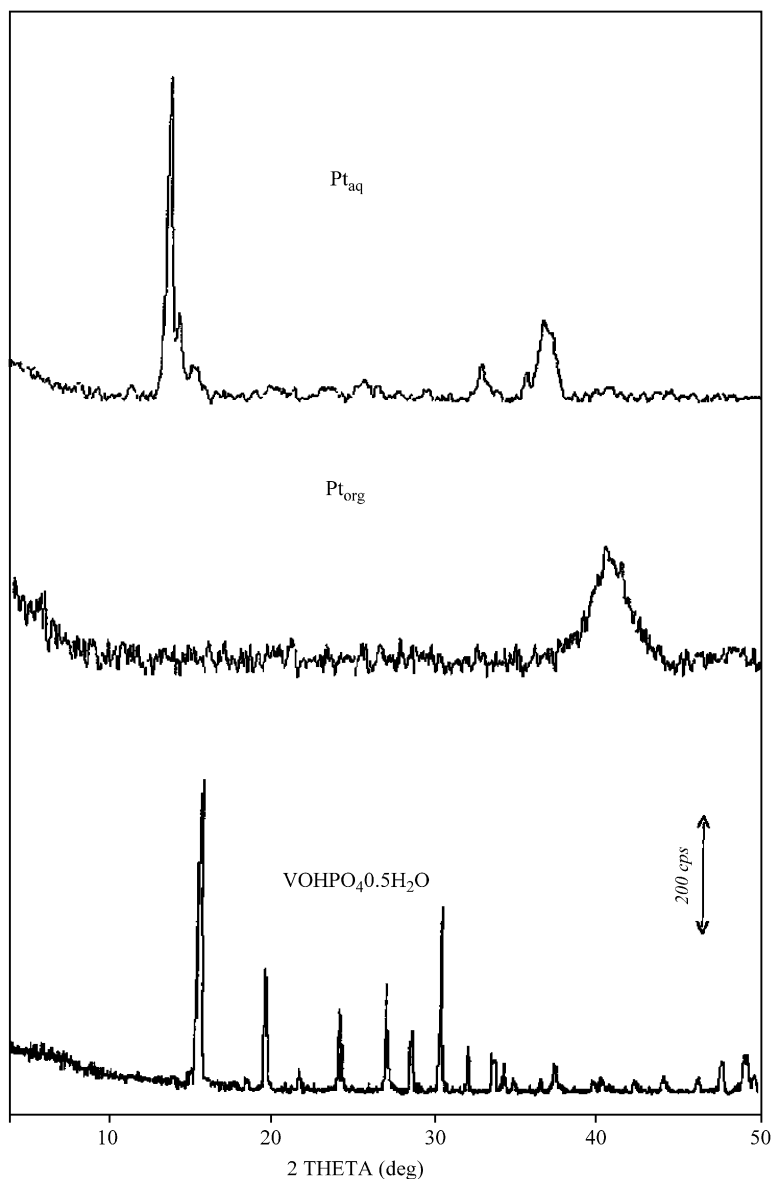


Fig. 1. XRD patterns of $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ and platinum incorporated compounds prepared in organic (Pt_{org}) and aqueous media (Pt_{aq}).

On the other hand, in the $\text{V}_{2p_{3/2}}$ BE region, Pt_{org} has a single peak with BE of 516.9 eV which is indicative of the presence of V^{4+} species only, whereas in the case of Pt_{aq} the broad peak observed can be resolved into two components with BE's of 517.0 and 518.1 eV which can be attributed to V^{4+} and V^{5+} species, respectively [11]. This further confirms the presence of mixed valency of vanadium in Pt_{aq} .

3.1.4. Thermogravimetric analysis (TGA)

The TGA pattern (Fig. 4) of Pt_{org} shows a weight loss at 56 °C and another broad peak centred at 277 °C, which can be ascribed to the loss of water molecules held in the interlayer and bound to the lattice vanadium, respectively. There is however no weight loss in the 400–500 °C temperature region, indicating that the transformation to the pyrophosphate, as in the parent

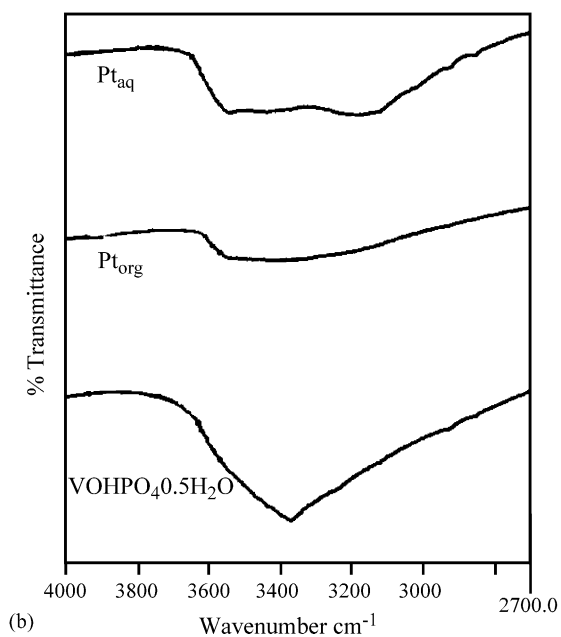
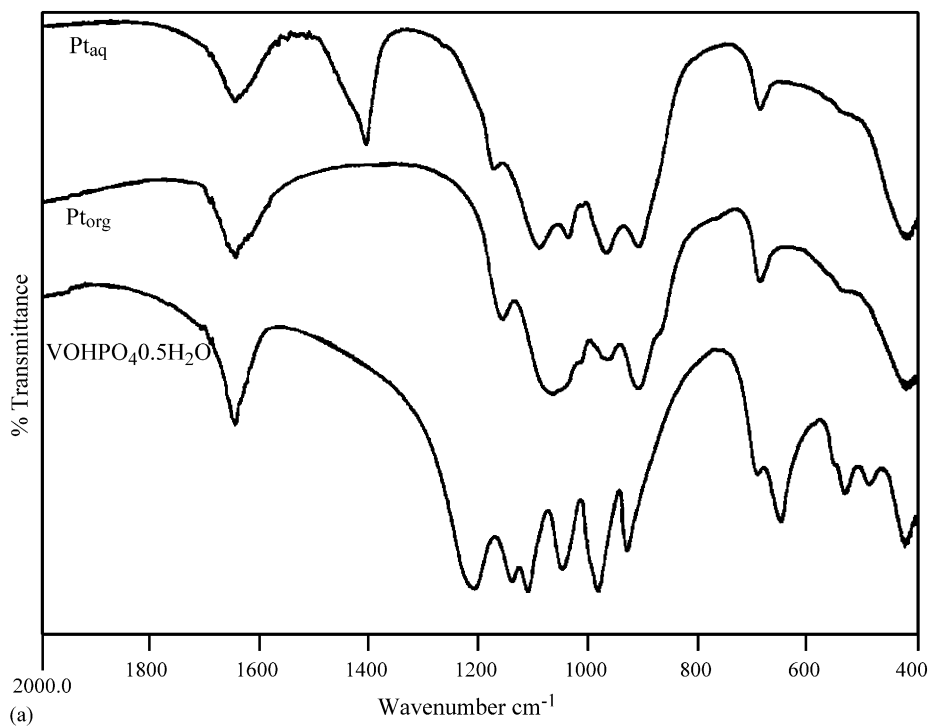


Fig. 2. (a) FTIR spectra of the parent and platinum incorporated compounds in the OH stretching region. (b) FTIR spectra of the parent and platinum incorporated compounds in the P–O, V–O stretching region.

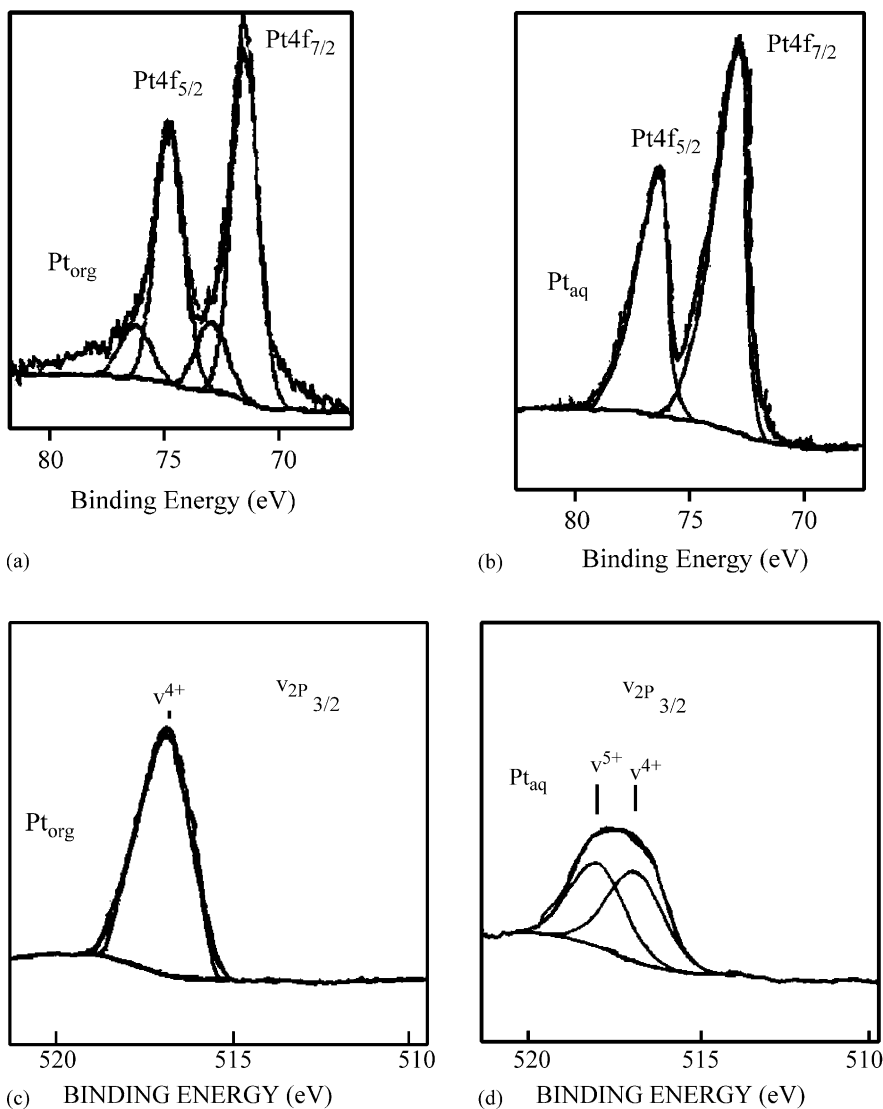


Fig. 3. XPS of platinum incorporated compounds: (a) Pt 4f region of Pt_{org}; (b) Pt 4f region of Pt_{aq}; (c) V 2p_{3/2} region of Pt_{org}; (d) V 2p_{3/2} region of Pt_{aq}.

compound, does not take place. However, the broadness of the peak corresponding presumably to the loss of lattice bound water once again indicates the amorphous nature of this compound. In the case of Pt_{aq} on the other hand, two weight loss peaks at 61 and 182 °C are observed, but there is no loss in the 400–500 °C region indicating once again that the transformation to the pyrophosphate does not take place. The fact that

no pyrophosphate was obtained on heating either Pt_{org} or Pt_{aq} to 450 °C in nitrogen was confirmed by the XRD patterns of these samples which showed the materials to be X-ray amorphous. The peaks at 61 and 182 °C would then, correspond to the loss of interlayer and lattice bound water. However, the sharpness of the peaks in contrast to those in the case of Pt_{org} is in keeping with the crystalline nature of this compound.

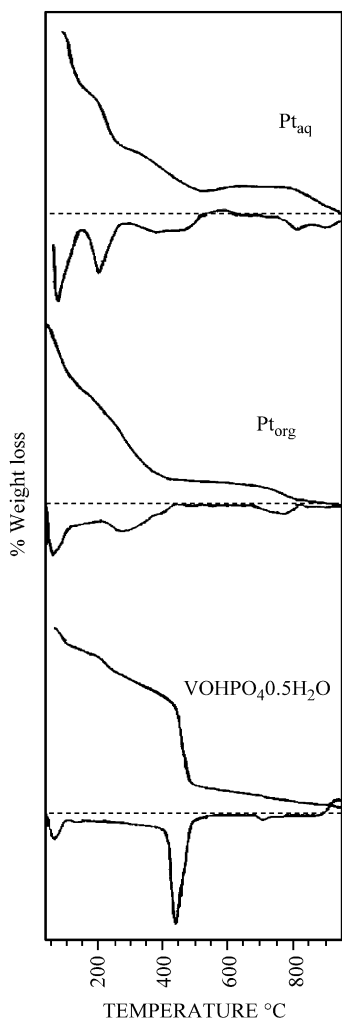


Fig. 4. TGA of parent and platinum incorporated compounds (heating rate $10^{\circ}\text{C min}^{-1}$ and nitrogen flow of 150 ml min^{-1}).

3.1.5. Temperature-programmed reduction (TPR)

The TPR profile (Fig. 5) of Pt_{org} shows a peak at 104°C which is probably due to the adsorption of hydrogen on the metallic Pt shown to be present from both XRD and XPS studies. The subsequent peak at 370°C with a weak shoulder at 280°C would then correspond to the reduction of Pt^{2+} present in Pt_{org} as evident from XPS data. H_2PtCl_6 has been reported [12] to undergo reduction at around 160°C , whereas PtCl_2 reduces in the region of 70°C . On the other hand, Pt^{2+} supported on zeolites or on alumina has been found [13] to reduce at a temperature of around

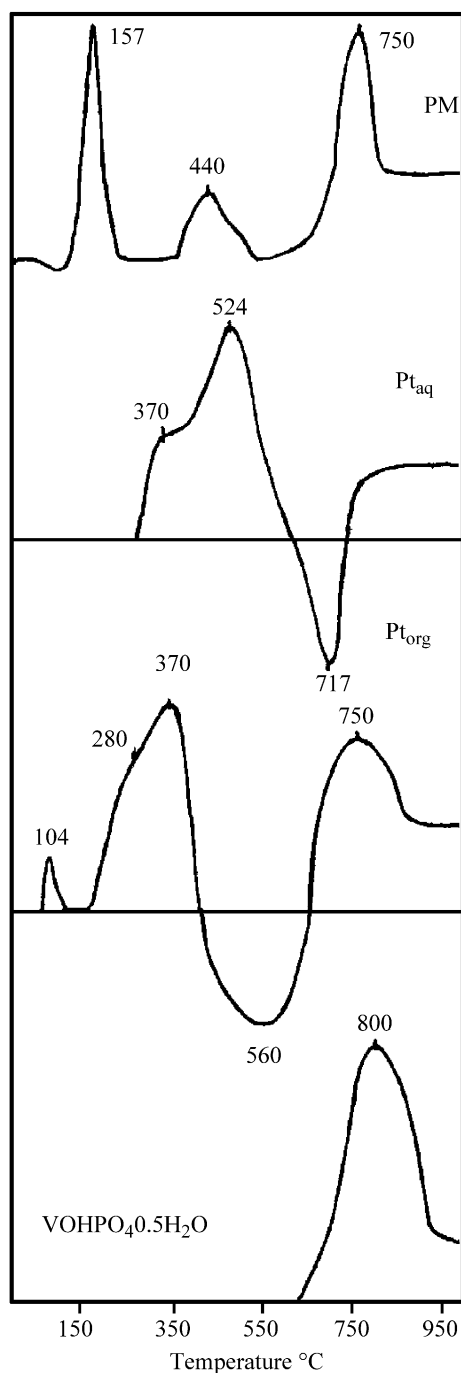


Fig. 5. TPR profiles of parent, platinum incorporated compounds and PM (physical mixture of H_2PtCl_6 and a mixed-valent VPO phase; heating rate of $10^{\circ}\text{C min}^{-1}$ and a flow of $50\text{ cm}^3\text{ min}^{-1}$ of 5 mol% H_2/Ar mixture).

280 °C. Consequently, the reduction of Pt^{2+} in Pt_{org} at the higher temperature of 370 °C would strongly suggest the presence of the Pt^{2+} in the VPO framework. Interestingly, the adsorption peak at 370 °C is followed by a broad desorption peak centred at 560 °C. This indicates that the adsorption peak due to the reduction of Pt^{2+} species is also associated with the simultaneous adsorption of hydrogen by the VPO matrix presumably after spillover from the reduced platinum. The desorption peak would then correspond to the release of hydrogen adsorbed on the VPO matrix and the broadness of the peak suggests that the hydrogen is non-specifically adsorbed. The final peak at 750 °C can be ascribed [14] to the reduction of V^{4+} and its reduction at a lower temperature compared to the parent compound is due to the presence of Pt which facilitates the reduction.

On the other hand, the TPR profile of Pt_{aq} quite expectedly does not show any adsorption at low temperature due to the absence of any metallic Pt in the sample. The first reduction peak at 370 °C can be assigned to the reduction of Pt^{2+} to Pt^0 with the high temperature of reduction once again suggesting that the Pt^{2+} species are present in the VPO framework. Interestingly, however, in this case, further adsorption takes place beyond 370 °C up to a peak temperature of 525 °C. This adsorption peak would appear to be, as in the case of Pt_{org} , due to the adsorption of hydrogen and its spillover, after dissociation on Pt, onto the VPO matrix with the adsorption even after the reduction of Pt^{2+} indicating the formation of a specific hydrogen compound unlike in the case of Pt_{org} . This is further supported by the presence of a sharp desorption peak at 717 °C which can be attributed to the decomposition of the well-defined hydrogen insertion compound. Moreover, the fact that no strong peak due to the reduction of V^{4+} species is observed as in all the other cases also supports the formation of a specific hydrogen insertion compound of the VPO phase. A similar behaviour was reported [14] by us earlier during the formation of a hydrogen insertion compound of a palladium incorporated vanadyl hydrogen phase. It was also shown that the presence of mixed valency of vanadium in the VPO phase was a pre-requisite for the formation of a hydrogen insertion compound. In the present case also, only Pt_{aq} , which has been shown to contain mixed-valent vanadium, forms a hydrogen insertion compound. How-

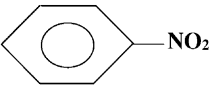
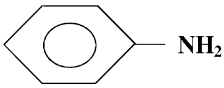
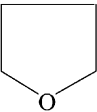
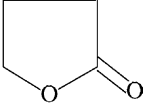
ever, to confirm whether mixed valency of vanadium is the only pre-requisite for the formation of a hydrogen insertion compound, the TPR of a sample (PM) containing a physical mixture of a mixed-valent VPO phase recently reported by us [15] and H_2PtCl_6 was recorded. This new mixed-valent phase, obtained by introducing a time delay between the onset of the reduction of V_2O_5 with hydroxylamine hydrochloride and the addition of phosphoric acid in the aqueous route preparation of $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$, has an average vanadium oxidation state of +4.65. It was also shown from XPS, ESR and UV-Vis studies, to contain both V^{4+} and V^{5+} species in keeping with its average vanadium oxidation state. The TPR pattern [15] of this phase showed peaks at 470 and 760 °C corresponding to the reduction of V^{5+} and V^{4+} species, respectively. On the other hand, the TPR pattern of the physical mixture of this mixed-valent phase and H_2PtCl_6 (sample PM) shows a peak at 157 °C corresponding to the reduction of Pt^{2+} species along with peaks at 440 and 750 °C which are due to the reduction of V^{5+} and V^{4+} species, respectively. However, it is clear that there are no peaks due to adsorption and subsequent desorption of hydrogen from the VPO matrix. This clearly establishes that the platinum has to be in the lattice of the mixed-valent vanadium phosphate phase for the VPO matrix to adsorb hydrogen spilt over from the reduced Pt as observed in Pt_{aq} and Pt_{org} .

It is quite evident that in Pt_{aq} a single type of Pt^{2+} species is incorporated into the framework of a vanadium phosphate phase which is different from that of the parent $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$. In contrast, Pt_{org} appears to be an amorphous vanadium phosphate phase containing 2.8% Pt^{2+} species incorporated into it along with 10.5% metallic Pt. Strong evidence for the incorporation of Pt into the lattice of both Pt_{aq} and Pt_{org} is provided by TPR data and the fact that Pt_{org} is X-ray amorphous is probably because of the introduction of 2.8% of the comparatively larger Pt^{2+} ion into the parent vanadium phosphate phase.

3.2. Catalytic activity

Since Pt was found to be incorporated in different ways and in different oxidation states in Pt_{aq} and Pt_{org} , the catalytic activity of these phases were evaluated for both oxidation and reduction reactions.

Table 1
Catalytic activity of the platinum incorporated compounds

Reactant	Condition	Catalyst	Product (%)
	A	–	
		Pt _{org}	74
		Pt _{aq}	33
		Pt/C	97
	B	–	
		Pt _{org}	13 (2 h); 48 (48 h)
		Pt _{aq}	0 (2 h); 18 (48 h)

Condition A: 2 mmol nitrobenzene + 15 ml methanol, stirring at RT under 300 psi hydrogen pressure for 3 h, substrate:Pt = 100:1. Condition B: 0.15 mmol THF + 0.5 ml H₂O, heated at 65 °C under O₂ atmosphere for 2 and 48 h, substrate:Pt = 20:1.

In the hydrogenation of nitrobenzene to aniline, Pt_{org} and Pt_{aq} were found to give conversions of 74 and 33%, respectively as compared to 97% conversion obtained in the case of Pt/C under exactly identical conditions (Table 1). The much lower conversion in the case of Pt_{aq} can be attributed to the lower reducibility of incorporated platinum. The relatively higher conversion obtained in the case of Pt_{org} on the other hand is most likely due to the metallic platinum present in it, since the component of platinum that is incorporated in the VPO matrix is also difficult to reduce as evident from TPR data. This would also explain the lower conversion in the case of Pt_{org} compared to Pt/C where the entire Pt is present in the metallic state.

The oxidation of an ether such as THF using the Pt incorporated phases as catalysts shows that conversions of 13 and 48% to *n*-butyrolactone were obtained in the case of Pt_{org} with reaction times of 2 and 48 h, respectively. In contrast, only 18% conversion to the lactone was obtained after 48 h reaction time in the case of Pt_{aq}. Although both the Pt incorporated phases contain Pt²⁺, the higher activity in the case of Pt_{org} can be attributed to the presence of metallic platinum also in that sample. It has in fact been reported [4] earlier that in the homogeneously catalysed oxidation of THF by Pt²⁺ salts the induction period was eliminated and the rate enhanced by the addition of metallic Pt. Our observation that Pt_{aq} which contains only Pt²⁺ gives no oxidation product even after 2 h and gives lower yield of the butyrolactone after 48 h as compared to

Pt_{org} which contains both Pt²⁺ and Pt⁰ is therefore in agreement with this earlier report.

For the hydrogenation and oxidation reactions described above, both parent compounds (P_{aq} and P_{org}) when used as catalysts did not show any activity.

4. Conclusions

It is apparent that Pt can be incorporated in very different ways into VOHPO₄·0.5H₂O depending upon the medium of preparation. Both these phases show very interesting TPR patterns indicating spillover of hydrogen dissociated on Pt, onto the VPO matrix. In Pt_{org}, the spilt over hydrogen appears to adsorb non-specifically onto the VPO matrix, whereas in Pt_{aq} a novel hydrogen insertion compound is formed. It is interesting that Pt is incorporated both into Pt_{org} and Pt_{aq} as Pt²⁺ and not as Pt⁴⁺ in keeping with our postulation earlier [2] that incorporation of metal ions into the VPO lattice involves replacement of the bivalent (VO)²⁺ species. The Pt_{aq} would represent a catalyst containing Pt²⁺ oxidation centres within a VPO matrix which functions as an oxidation catalyst. On the other hand, the Pt_{org} sample constitutes a novel catalytic phase containing Pt²⁺ species incorporated within an amorphous VPO matrix in combination with metallic platinum. Both these phases constitute a unique system comprising oxidation centres within an oxidation catalyst and with their demonstrated catalytic activity,

hold strong promise as novel heterogeneous catalysts for other oxidation and reduction reactions including reactions homogeneously catalysed by platinum salts.

Acknowledgements

One of the authors (SD) is grateful to the CSIR, India for the grant of a senior research fellowship.

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