

Characterization and catalytic activity of novel palladium-incorporated vanadium phosphates

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Abstract

Palladium has been introduced into the layered vanadyl hydrogen phosphate hemihydrate $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ in different ways depending upon the medium of preparation. In aqueous medium, the introduction of palladium leads to the formation of a new phase containing mixed valent vanadium whereas in the preparation in organic medium, the palladium appears to substitute into the lattice of the parent compound. The palladium-incorporated compounds have been found to be catalytically active, both for oxidative coupling as well as for hydrogenation reactions, with the activity and selectivity varying quite markedly with the mode of incorporation. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The design of novel microporous materials that can function as new catalysts has been an area of tremendous interest in both the academic and industrial communities. In this context, a more recent trend [1,2] in zeolite and molecular sieve catalysis has been the deposition of metals into the microporous voids to yield shape selective monofunctional (metal) or bifunctional (metal, acid site) catalysts.

We have shown [3–6] that the incorporation of metal ions into the catalytically important layered vanadium phosphates leads both to novel structural changes as well as interesting shape selective catalysis. These metal-incorporated vanadium phosphates have some similarity with the metal-incorporated zeolites, in the sense that they both contain metal active cen-

ters confined within pores (in the case of zeolites) or layers (as in the case of the vanadium phosphates). However, unlike, the metal containing zeolites, the metal-incorporated vanadium phosphates contain active metal centers within a parent *oxidation* rather than an *acidic* catalyst and therefore constitute a new and interesting class of compounds. The vanadium phosphates, it may be pointed out are important oxidation catalysts and the vanadyl hydrogen phosphate $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ is the precursor [7] for the catalyst used for the commercially important and scientifically fascinating 14 electron selective oxidation of butane to maleic anhydride. In this context, it would be particularly interesting to introduce oxidation centers within the parent VPO oxidation catalyst. Accordingly, in the present work we report the incorporation of palladium in different ways and in different oxidation states into the vanadyl hydrogen phosphate $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ and demonstrate that these palladium-incorporated

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compounds function as interesting catalysts for both selective oxidation and hydrogenation reactions with the catalytic activity varying quite markedly with the mode of incorporation of the palladium.

2. Experimental

2.1. Synthesis

Palladium was incorporated into the parent $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ phase prepared in both organic and aqueous media since the medium of preparation is known to affect the morphology of the phase obtained [8]. Palladium was introduced into the parent vanadyl hydrogen phosphate in organic medium by reduction of a slurry of vanadium pentoxide and palladium nitrate with benzyl alcohol and isobutanol followed by the addition of a stoichiometric amount of phosphoric acid [9]. The P:V:Pd ratio was 1:1:0.2. Typically 1.818 g of V_2O_5 powder was dispersed into 40 ml of isobutyl alcohol into which 7 ml of benzyl alcohol was added along with 0.941 g of $\text{Pd}(\text{NO}_3)_2$. The mixture was refluxed for 3 h and stirred at room temperature for 16 h. Subsequently, 2.306 g of 85% H_3PO_4 was added and the reaction mixture was again refluxed for 2 h under continuous stirring. The bluish black slurry was filtered and the residue thoroughly washed with isobutyl alcohol. The material was then dried at 120°C for 16 h.

In the case of the preparation in aqueous medium [10], the reductant used was hydroxylamine hydrochloride but the P:V:Pd ratio was the same. In this case, 1.818 g of finely powdered V_2O_5 was dispersed in an aqueous solution 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 H_2O) into which 2.306 g of 85% H_3PO_4 and 0.941 g $\text{Pd}(\text{NO}_3)_2$ were added. The mixture was stirred at 80°C for 1 h and the green slurry obtained was carefully evaporated to a pasty mass, which was heated in an air oven at 120°C for 16 h. The dark green solid thus obtained was ground and thoroughly washed with hot water till it was free from residual chloride and the solid dried at 120°C for 16 h. The palladium compounds prepared in organic and aqueous media were coded as Pd_{org} and Pd_{aq} and their respective yields were 109 and 58% in relation to the parent compounds. The parent compounds (without any palladium) were

also prepared in organic and aqueous media using the procedures given above and were coded as P_{org} and P_{aq} , respectively.

2.2. Analysis

The average oxidation state of vanadium in these materials was determined by redox titration [10] 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 sulfate using diphenylamine as indicator. The average oxidation state was then expressed as $5 - (V_1/V_2)$. X-ray diffraction patterns were run on a Philips X-ray diffractometer using $\text{Cu K}\alpha$ radiation and infrared spectra were recorded on a Perkin-Elmer 1760X FT-IR spectrometer with the sample dispersed in KBr pellets. To eliminate any interference from KBr, the single beam spectrum of the sample was ratioed to a background spectrum of a pure KBr pellet. 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 $150\text{ cm}^3/\text{min}$ and a heating rate of $10^\circ\text{C}/\text{min}$. X-ray photoelectron spectra (XPS) were recorded on a VG ESCA LAB MkII spectrometer using the C 1s line (285.0 eV) for calibration.

3. Results and discussion

3.1. Characterization of palladium-incorporated vanadium phosphate

Analysis by atomic absorption spectroscopy showed that Pd_{org} and Pd_{aq} contained 13.6 and 0.61% palladium, respectively. In the case of Pd_{org} , the total palladium incorporated is present in two different forms as is evident from the fact that when the sample is dissolved in conc. HCl, some black particles remained undissolved. This solution on analysis gave a palladium content of 5.8%. In another experiment, the solid was completely solubilized using aqua-regia and the palladium content of this solution was found to be 13.6%. In essence therefore the total palladium in Pd_{org} comprised of 5.8 and 7.8% of a HCl-soluble and

HCl-insoluble species, respectively. Since VPO compounds are completely soluble in conc. HCl, it can be assumed from the analysis results that in Pd_{org}, 5.8% palladium is incorporated into the parent compound and the remaining 7.8% palladium is present in a different form. Determination of the average vanadium oxidation states of these compounds showed that Pd_{org} had an average vanadium oxidation state of +4.0 whereas the corresponding value for Pd_{aq} was +4.65 indicating the presence of mixed valent vanadium species.

3.1.1. X-ray diffraction

The X-ray diffraction (XRD) patterns (Fig. 1) of the two palladium-incorporated compounds Pd_{org} and Pd_{aq} are quite different from each other. The pattern of Pd_{org} is essentially similar to that reported for the parent compound VOHPO₄·0.5H₂O with an additional broad line corresponding to a *d* value of 2.25 Å. This agrees well with the *d* value for the 100% line in the XRD pattern of metallic palladium [11] and the width of the peak indicates that the crystallite size is small. This, in conjunction with chemical analysis data, suggests that the palladium in Pd_{org} is partly substituted into the lattice without causing any observable distortion and partly reduced to metallic palladium. On the other hand, the XRD pattern of Pd_{aq} is completely different from that of the parent compound with a reduction in the total number of reflections and with pronounced selective ordering along the *c*-axis. The XRD pattern of Pd_{aq} can be indexed for a tetragonal system with *a* = *b* = 9.24 Å and *c* = 7.04 Å whereas the parent vanadyl hydrogen phosphate is orthorhombic [12].

3.1.2. X-ray photoelectron spectroscopy

The XPS of Pd_{org} in the Pd 3d binding energy (BE) region (Fig. 2a) shows a broad peak which can be curve-fitted with four peaks corresponding to two each for the Pd 3d_{5/2} and Pd 3d_{3/2} states. The two Pd 3d_{5/2} peaks have BE of 338.6 and 336.5 eV. The BE of the 3d_{5/2} state of Pd²⁺ species is reported [13] to be in the region 338.0–338.2 eV and consequently the slightly higher BE of 338.6 eV of the major peak in the XPS of Pd_{org} is indicative of a higher effective positive charge on the palladium. This would once again suggest that the palladium is incorporated into the lattice of the parent vanadyl hydrogen phosphate.

On the other hand, the BE of the other peak at 336.5 instead of 335.0 eV expected for Pd⁰ (and observed for the Pd/C sample) corroborates the observation from XRD data that the palladium is present as very small crystallites. It has been reported [14] that for palladium dispersed on different supports, the BE of the Pd 3d_{5/2} state increases quite markedly with decreasing particle size with a BE of 336.5 eV corresponding to a particle size of approximately 1 nm. In contrast, Pd_{aq} with a peak at 338.2 eV appears to contain only Pd²⁺ species. On the other hand in the V 2p_{3/2} BE region Pd_{org}, with a BE of 516.9 eV contains only V⁴⁺ species whereas in the case of Pd_{aq} the broad peak observed (Fig. 2b) can be resolved into two components with BEs of 517.0 and 518.1 eV which can be attributed to V⁴⁺ and V⁵⁺ species, respectively [15]. This is in keeping with the average vanadium oxidation state value of +4.65 obtained in the case of Pd_{aq}.

3.1.3. Differential scanning calorimetry

The DSC pattern (Fig. 3) of Pd_{org} shows an endotherm at 443 °C which is believed [16] to be due to the transformation of the orthophosphate to the pyrophosphate involving condensation of P–OH groups of two adjacent layers. In comparison, the DSC pattern of the parent compound P_{org} prepared under identical conditions in organic medium shows an endotherm at 447 °C. The DSC pattern of Pd_{aq} on the other hand shows only two endotherms at 123 and 182 °C, respectively and no endotherm is observed in the 400–500 °C region indicating that the transformation to the pyrophosphate does not take place. This was confirmed by XRD data which showed that the sample of Pd_{aq} heated at 450 °C in a nitrogen atmosphere was X-ray amorphous, whereas Pd_{org} on heating to 450 °C gave the pyrophosphate phase.

3.1.4. FT-IR

The infrared spectrum (Fig. 4) of Pd_{org} is very similar to that of the parent compound but the spectrum of Pd_{aq} is completely different. In the OH stretching region, the IR spectrum of Pd_{aq} has bands at 3547 and 3153 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, Pd_{aq} shows broad unresolved peaks at 1075, 934 and 903 cm⁻¹ which do not correspond with those of the parent compound.

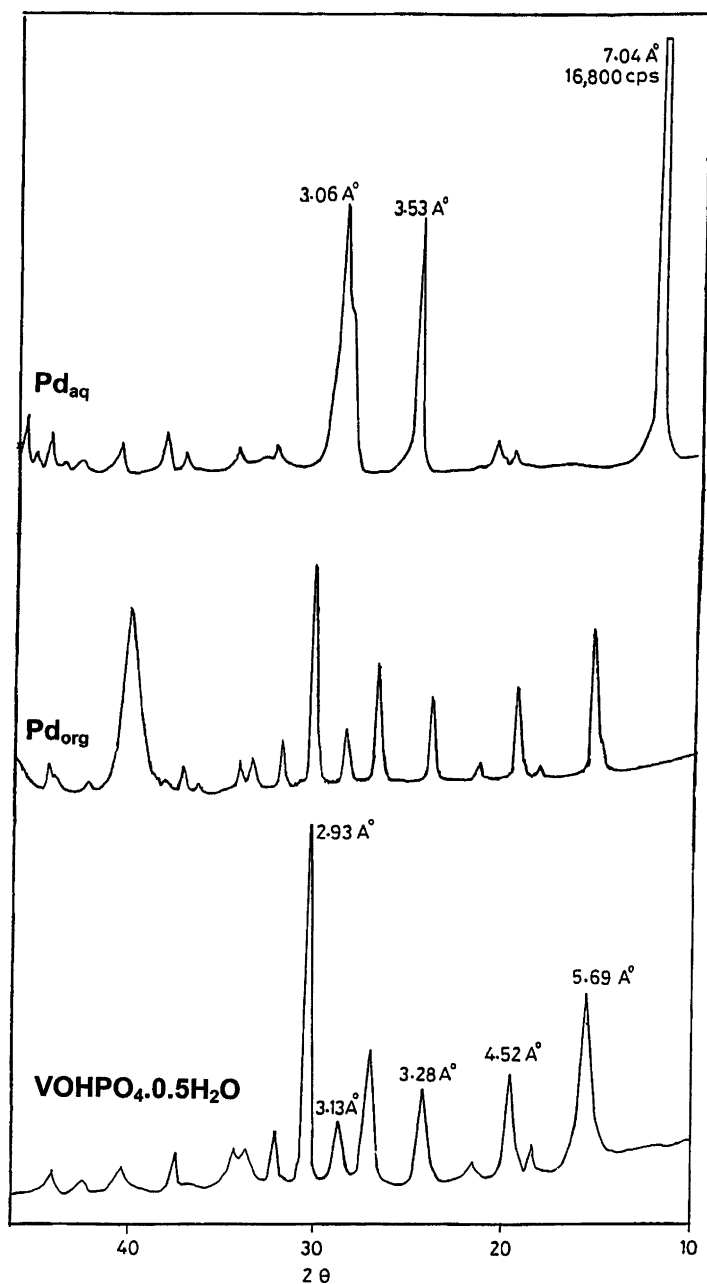


Fig. 1. XRD patterns of $VOHPO_4 \cdot 0.5H_2O$ and of the palladium-incorporated compounds prepared in organic (Pd_{org}) and aqueous media (Pd_{aq}).

From all the evidence presented above, it would appear that in Pd_{aq} , the incorporated palladium is lodged in the interlayer region of a new layered structure whereas the palladium in Pd_{org} is partially substituted

into the framework of the parent vanadyl hydrogen phosphate as Pd^{2+} and partially present as small crystallites of metallic palladium dispersed in the VPO lattice.

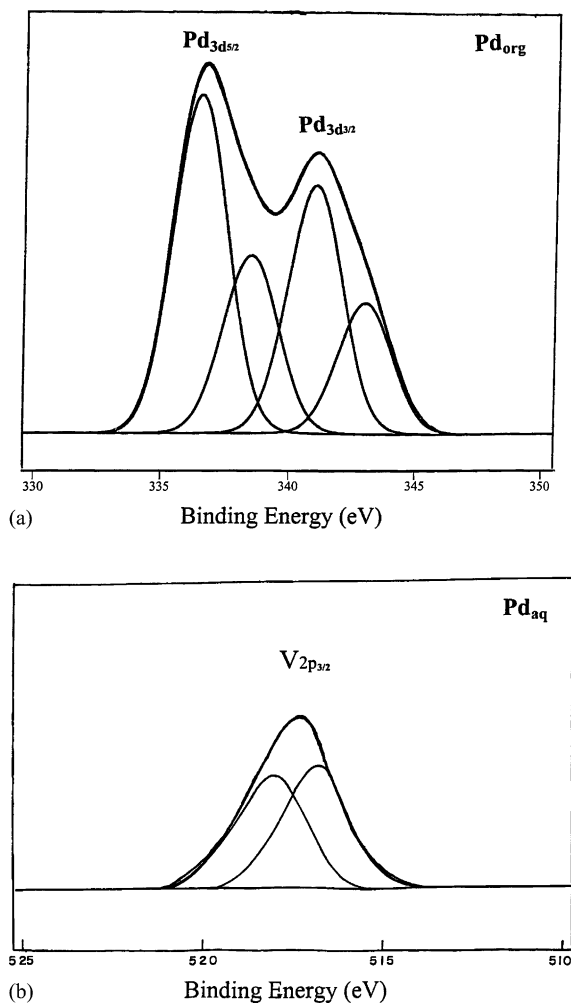


Fig. 2. XPS of the palladium-incorporated compounds (a) Pd 3d BE region of Pd_{org}; (b) V 2p BE region of Pd_{aq}.

3.2. Catalytic activity

Since compounds Pd_{org} and Pd_{aq} contain palladium in different oxidation states incorporated in different ways into the layered vanadyl hydrogen phosphate, the catalytic activity of palladium in these compounds was evaluated.

3.2.1. Oxidative coupling of furan with ethylacrylate

One area of modern chemistry that has attracted a tremendous amount of interest is the activation of the C–H bond by transition metal compounds either

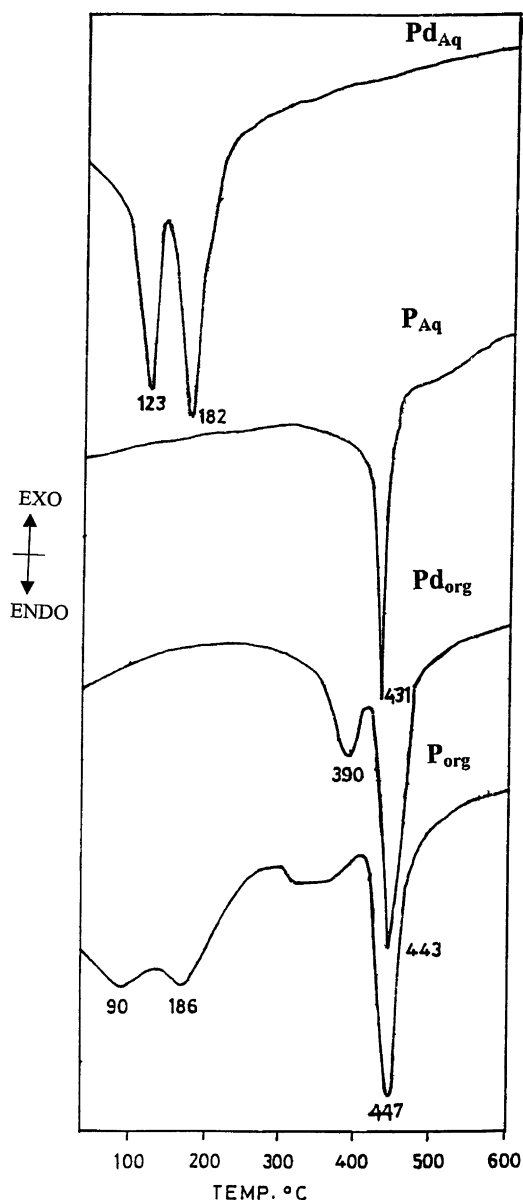


Fig. 3. DSC of the parent and palladium-incorporated compounds (heating rate, 10 °C/min and nitrogen flow of 150 ml/min).

through electrophilic substitution or oxidative addition of the metal center [17–19]. In this context, palladium acetate and acetic acid along with copper acetate or butyl perbenzoate as the re-oxidant has been reported to catalyze the oxidative coupling of aromatic compounds with olefins through direct activation of both

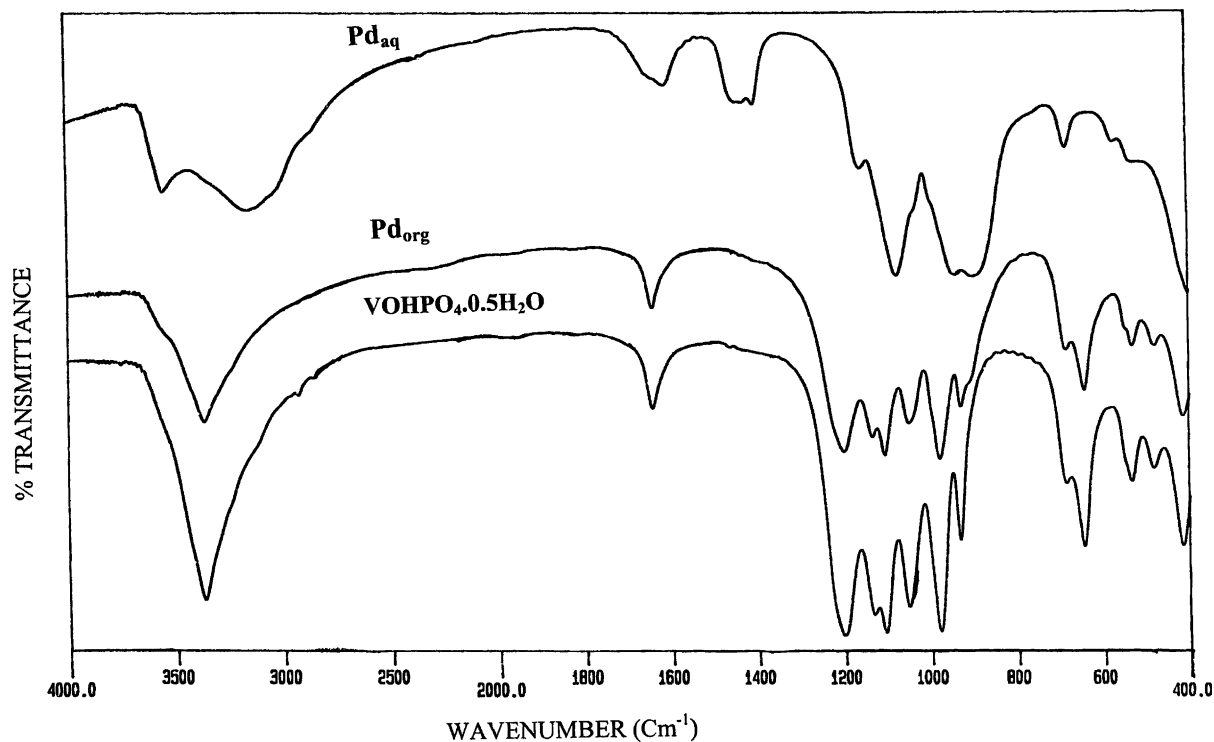


Fig. 4. FT-IR spectra of the parent and palladium-incorporated compounds.

the olefinic and aromatic C–H bonds. Consequently, since both Pd_{org} and Pd_{aq} contain Pd²⁺, the oxidative coupling reaction of furan with ethylacrylate was studied. It was observed (Table 1) that Pd_{org} and Pd_{aq} gave 32 and 13% of the monosubstituted product only compared to 11% of the monosubstituted and 5% of the disubstituted product in the case of palladium acetate used as the homogeneous catalyst. It is evident therefore that Pd_{org} in the *heterogeneous mode* gives selectively three times higher yield of the monosubstituted product as compared to the conventionally used homogeneous catalyst. Also, since neither Pd_{org} or Pd_{aq} gives the disubstituted product both these catalysts appear to display shape selectivity.

3.2.2. Hydrogenation of nitrobenzene to aniline

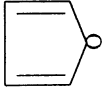
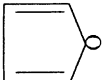
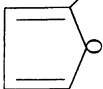


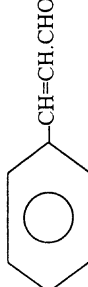
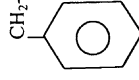
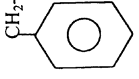
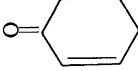
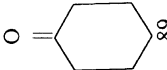
For the hydrogenation of nitrobenzene to aniline (Table 1) it is interesting that under conditions where a commercial Pd/C catalyst and Pd_{aq} gave conversions of 100 and 90%, respectively, the reaction with Pd_{org} as the catalyst *did not yield any aniline at all*.

Moreover, the rate of hydrogenation in the case of Pd_{aq} was very slow compared to the Pd/C catalyst. Thus, while 100% conversion to aniline was observed in the case of the Pd/C catalyst in only 0.5 h the corresponding conversion in the case of Pd_{aq} was only 6% and the conversions after 2 and 4 h were 48 and 90%, respectively.

3.2.3. Hydrogenation of cinnamaldehyde

In the hydrogenation of cinnamaldehyde (Table 1) while Pd/C gave the completely hydrogenated 3-phenylpropanol as the major product (76%), Pd_{aq} showed the reverse trend and the saturated aldehyde was obtained as the primary product (72%). In the case of Pd_{org} on the other hand an almost equimolecular mixture of the two hydrogenation products were obtained. No cinnamyl alcohol was detected as a product in any of the reactions. Interestingly, although an induction period of 1 h was necessary in the case of Pd/C as the catalyst, before any conversion of cinnamaldehyde took place, no such induction

Table 1
Catalytic activity of the palladium incorporated compounds^a

Reactants	Conditions	Catalyst	Products (%)
 + CH ₂ =CH.COOC ₂ H ₅	A	—	 C ₂ H ₅ OOC.CH=CH  CH=CH.COOC ₂ H ₅
		Pd _{org}	0
		Pd _{aq}	0
		Pd(OAc) ₂	5
	B	—	 —NH ₂
		Pd _{org}	0
		Pd _{aq}	90
	C	—	 CH ₂ -CH ₂ -CHO +  CH ₂ -CH ₂ -CH ₂ OH
		Pd _{org}	52
		Pd _{aq}	72
	D	—	 O
		Pd _{org}	89
		Pd _{aq}	98
		Pd/C	100

^a Condition A: 0.2 mmol furan + 0.2 mmol ethylacrylate + 0.4 mmol Cu(OAc)₂ + 2 ml dioxane + 0.5 ml acetic acid, heated in O₂ atmosphere for 5 h, Pd:substrate = 1:50; condition B: 20 ml methanol + 0.6 mmol substrate, stirring at RT under hydrogen atmosphere for 5 h, Pd:substrate = 1:100; condition C: 20 ml toluene + 0.6 mmol substrate, stirring at RT under hydrogen atmosphere for 4 h, Pd:substrate = 1:100; condition D: 20 ml THF + 0.4 mmol substrate at RT under hydrogen atmosphere for 1 h, Pd:substrate = 1:100.

period was required in the case of Pd_{org} and Pd_{aq}. Also, both the products dihydrocinnamaldehyde and 3-phenylpropanol were formed from the very beginning and were present in more-or-less the same ratio in which they are finally formed at the end of the reaction suggesting that both these products were formed by independent routes rather than the dihydrocinnamaldehyde being gradually further hydrogenated to 3-phenylpropanol.

3.2.4. Hydrogenation of 2-cyclohexen-1-one

In the hydrogenation of 2-cyclohexen-1-one, reduction of the carbon–oxygen double bond was not observed in any of the cases but facile hydrogenation of the ring double bond was found to occur in the case of all the three catalysts. Thus, almost total conversion to cyclohexanone was observed in 1 h in all the three cases. However, once again the initial rates were very different, with the reaction catalyzed by Pd_{org} showing only 13% conversion in 5 min in contrast to 44 and 60% in the case of Pd_{aq} and the Pd/C catalysts, respectively.

It is evident therefore that both the palladium-incorporated compounds Pd_{org} and Pd_{aq} show interesting catalysis for both oxidation and reduction reactions with the activity varying quite markedly with the mode of incorporation. The high activity of Pd_{org} for the oxidative coupling reaction is probably due to the presence of palladium in two different oxidation states since a Pd²⁺–Pd⁰ cycle is involved in the reaction. In fact a recent study [20] of the partial oxidation of methane to synthesis gas over a palladium-incorporated Y zeolite has shown that clusters of both Pd⁰ and Pd²⁺ co-existed in the zeolite lattice under catalytic operating conditions and functioned as the catalytic centers. On the other hand the rather remarkable lack of activity of Pd_{org} in the hydrogenation of nitrobenzene can be ascribed to the fact that the lattice-incorporated palladium would be difficult to reduce and the metallic palladium is present as very small crystallites. It is known [21] that the reduction of nitrobenzene on metal surfaces involves, as a first step, the transfer of an oxygen of the nitro group to the metal and the reduction of the resultant oxidized metal surface is a crucial step in the eventual reduction to the amine. This step has been reported to be strongly dependent on the metal particle size with the hydrogenation activity decreasing

dramatically with decreasing metal particle size. The Pd_{org} however like the Pd_{aq} sample is quite active for the hydrogenation of other substrates such as 2-cyclohexen-1-one and cinnamaldehyde.

4. Conclusions

In conclusion therefore, it is apparent that palladium is introduced into the same parent compound in very different ways depending upon the medium of preparation. These palladium-incorporated compounds are active catalysts for both oxidation and reduction reactions. In the case of Pd_{org}, the active sites for the oxidative coupling reaction appear to be the palladium-incorporated into the VPO lattice, whereas the hydrogenation activity can be attributed to the metallic palladium dispersed as small crystallites in the VPO matrix. On the other hand, the Pd²⁺ species incorporated in the interlayer region of Pd_{aq} appears to be responsible for both oxidation and reduction reactions presumably due to the easy reducibility of the palladium.

These palladium-incorporated compounds constitute a novel class which contain *oxidation* centers confined within a parent *oxidation* catalyst and have good potential for functioning also as novel selective oxidation catalysts. In particular, compound Pd_{org} is a particularly attractive candidate since it contains palladium in different oxidation states and the substitution of Pd²⁺ into the lattice of the parent compound most likely by replacing (VO)²⁺ species (to maintain charge neutrality) would cause oxygen vacancies which are known to be active sites for lattice oxygen mediated selective oxidation catalysis.

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