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Catalytic Reactions Involving Palladium(II) Salts Supported on Amberlyst

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Palladium(II) salts supported on Amberlyst-A21 have been characterised by elemental analyses, infrared and electronic spectra, thermal analysis and Mössbauer measurements. The catalytic properties of these materials have been studied for ester interchange involving vinylacetate and vinyl propionate and the reaction of ethylene and oxygen in acetic acid; the results are compared with a previous study.

Introduction

In recent years there has been considerable interest in the synthesis and application of "heterogenised" homogeneous catalysts [1]. These species, usually consisting of a catalytically active transition metal complex anchored to a polymeric support, combine many of the advantages of homogeneous and heterogeneous catalysts. Much of the earlier work in this area was carried out by Haag and Whitehurst [2].

The difficulty in obtaining detailed structural information about the metal sites in complexes with polymeric ligands has often been noted. Elemental analyses, which are difficult to interpret, and infrared spectra, which are usually poorly resolved, have been the main techniques used to characterise these complexes. In an attempt to further elucidate the structure of some of these polymeric complexes we have re-examined a system of Haag and Whitehurst and been able to look at some catalysts by a range of physical techniques and have compared these species with analogous monomeric complexes. Our efforts have been moderately successful and are reported here.

Experimental

Solvents and reagents used were of the best grade available. Amberlyst-A21 (from British Drug Houses Ltd) was used after milling and sintering to a uniform 200–300 mesh; Na_2PdCl_4 was generously loaned by Johnson, Matthey Co. Ltd.

Infrared spectra were obtained using Perkin-Elmer 137, 257 and 621 instruments. Samples for infrared spectral analysis usually required ball-milling and pressing as KBr discs. Solid u.v./visible reflectance spectra were obtained on Optika D.B. 325 and Beckman Acta MIV instruments. Differential thermal analyses (DTA) in the range 373–773K were obtained using a Du Pont 900 Thermal Analyser fitted with a low temperature head. ^{119}Sn-Mössbauer spectra were obtained with the help of Dr R.V. Parish. Gas liquid chromatographic analyses of the products obtained in catalytic runs were carried out using a Pye-Series 104 gas chromatograph equipped with 7′ glass columns of Poropak P, Q and neopentylglycol adipate on Celite with helium as carrier gas.

Preparation of Polymer-bound Catalyst A

A solution of Na_2PdCl_4 (2.1 g) and NaCl (5.0 g) in water (65 cm^3) was added to a suspension of Amberlyst-A21 resin (12.8 g) in water (35 cm^3). This mixture was stirred overnight at room temperature and the resulting pale yellow compound (catalyst A) was recovered by filtration and washed with water, ethanol and ether (30 cm^3 each) and then dried at 110 °C for 2 hr. The filtrate was colourless. Yield 14.7 g.

Preparation of Polymer-bound Catalyst B

Catalyst A (2.0 g) was stirred with an excess of $SnCl_2$ (2.0 g) in water (100 cm^3) for 1 hr, after which the dark brown product was filtered, washed with water, ethanol and ether (30 cm^3) and dried at 100 °C. Yield 3.8 g.

Preparation of Polymer-bound Catalyst C

(i) An excess of NaNCS (3.0 g) in solution in water (200 cm^3) was stirred with catalyst A for 1 hr, after which the orange solid was filtered, washed with water, ethanol and ether (30 cm^3) and dried at 100 °C. Yield 1.0 g.

(ii) A blood-red solution of $Na_2[Pd(SCN)_4]$ was prepared *in situ* by adding an excess of NaNCS to a solution of Na_2PdCl_4 (1.47 g) in water (65 cm^3). This was stirred overnight at room temperature with a suspension of Amberlyst-A21 resin (9 g) and NaNCS (6 g) in water (35 cm^3), and then the orange product was filtered, washed with water, ethanol and ether (30 cm^3) and dried at 100 °C. Yield 10.2 g.

Dehydration Procedures

In order to improve the analytical and spectral interpretation a number of dehydration procedures were attempted. The most effective proved to be heating the compounds *in vacuo* at 100 °C and subsequently extracting the displaced water with methanol and then further drying.

Catalytic Screening

Ester interchange between vinyl acetate and propionic acid

1 g samples of catalyst were stirred with vinyl acetate (10 cm^3) and propionic acid (50 cm^3) at constant temperature in the range 50–70 °C. Samples of the reaction mixture were analysed by g.l.c.

Preparation of vinyl acetate from ethylene, oxygen and acetic acid

Oxygen (5 cm^3/min) and ethylene (15 cm^3/min) were bubbled through a reactor containing acetic acid (15.6 g) and catalyst (3.0 g). The reactor was maintained at a temperature of 110 °C and the effluents were passed into a cold trap from which samples of the products were removed and analysed by g.l.c.

Analyses

These were obtained by this Department's Microanalytical Service. Palladium was estimated by ashing or by a dimethylglyoxime gravimetric route. Results: Amberlyst-A21: C, 48.9; H, 6.9; O, 38.5; N, 5.7; Pd, 0.0%. Catalyst A: C, 62.9; H, 6.8; O, 5.8; N, 4.3; Cl, 9.2; Pd, 11.1%. Catalyst B: C, 30.6; H, 4.4; O, 14.8; N, 2.5; Cl, 13.1; Pd, 11.1%. Catalyst C: Route (i): C, 72.3; H, 7.8; O, 1.6; N, 7.7; S, 5.2; Cl, 0.0; Pd 5.4%. Route (ii): C, 71.8; H, 7.7; O, 2.8; N, 7.4; S, 4.9; Cl, 0.0; Pd, 5.2%.

Infrared Spectra

The main absorptions consist of:

Amberlyst-A21: 3400 (vs), 3010 (m), 2850 (ms), 2760 (m), 1735 (vs), 1505 (s), 1450 (vs), 1440 (s), 1425 (m), 1403 (w), 1360 (s), 1300 (s), 1255 (s), 1211 (ms), 1166 (ms), 1146 (ms), 1110 (ms), 1090 (m), 1070 (m), 1030 (m), 1015 (s), 970 (m), 900 (s), 810 (ms), 719 (vs), 555 (w), 329 (w), 315 (w), 300 (w), 282 (w), 270 (w), 265 (w), 255 (w), 246 (w), 238 (w), 212 (w), 203 (w).

Catalyst A: 3400 (vs), 3015 (s), 2920 (vs), 2860 (s), 2810 (ms), 2770 (s), 1750 (m), 1632 (vs), 1582 (vs), 1552 (s), 1510 (s), 1455 (s), 1441 (ms), 1425 (m), 1408 (m), 1361 (ms), 1300 (s), 1255 (s), 1210 (m), 1170 (ms), 1150 (ms), 1110 (m), 1095 (m), 1035 (ms), 1020 (s), 985 (m), 970 (m), 940 (m), 920 (m), 890 (m), 855 (s), 845 (m), 810 (s), 765 (m), 720 (s), 702 (m), 550 (m), 330 (mw), 315 (mw), 288 (w), 272 (w), 270 (w), 261 (w), 250 (w), 239 (w), 230 (w), 215 (w), 200 (w).

Catalyst B: (Range 200–400 cm^{-1}) 330 (w), 320 (w), 310 (w), 300 (w), 288 (w), 273 (w), 262 (w), 250 (w), 241 (w), 230 (w), 200 (w).

Catalyst C: 3400 (vs), 3020 (m), 3009 (m), 2985 (m), 2920 (vs), 2850 (m), 2815 (m), 2785 (m), 2700 (mw), 2090 (vs), 2040 (s), 1630 (m), 1608 (s), 1580 (m), 1555 (m), 1509 (m), 1465 (m), 1455 (ms), 1440 (m), 1425 (m), 1420 (m), 1405 (m), 1360 (m), 1321 (mw), 1260 (m), 1210 (m), 1170 (m), 1150 (m), 1132 (m), 1110 (mw), 1092 (mw), 1070 (mw), 1039 (m), 1015 (ms), 1005 (m), 985 (m), 970 (ms), 940 (m), 915 (mw), 890 (w), 855 (ms), 810 (ms), 745 (mw), 720 (s), 702 (m), 670 (w), 650 (w), 550 (m), 500 (w), 345 (w), 340 (w), 330 (w), 320 (w), 308 (w), 293 (w), 285 (w), 272 (w), 260 (w), 250 (w), 240 (w), 229 (w), 200 (m).

Electronic Spectra

Data are contained in Table I.

Differential Thermal Analysis

Data are contained in Figure 1.

TABLE I. U.V.–Visible Spectra of the Catalysts.

Sample	Peak Maxima (kK)			
Resin	36.0	28.5		20.1
Catalyst A	35.5	29.0		20.0
Catalyst B	39.0	35.1	31.0	23.2
Catalyst C	37.0	32.0	28.0	25.0
$Pd(en)Cl_2$	37.7	34.2	26.6	21.2

TABLE II. Results of Ester Interchange Reaction at 75 °C.

Sample	Time (min)	Acetic Acid/Vinyl Acetate				Vinyl Propionate/Acetic Acid			
		Resin	A	B	C	Resin	A	B	C
	0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	20	0.000	0.025	0.059	0.000	0.000	0.060	0.015	0.000
	40	0.000	0.032	0.062	0.002	0.000	0.060	0.20	0.000
	60	0.000	0.034	0.067	0.002	0.000	0.060	0.26	0.000
	80	0.000	0.047	0.082	0.003	0.000	0.060	0.27	0.000

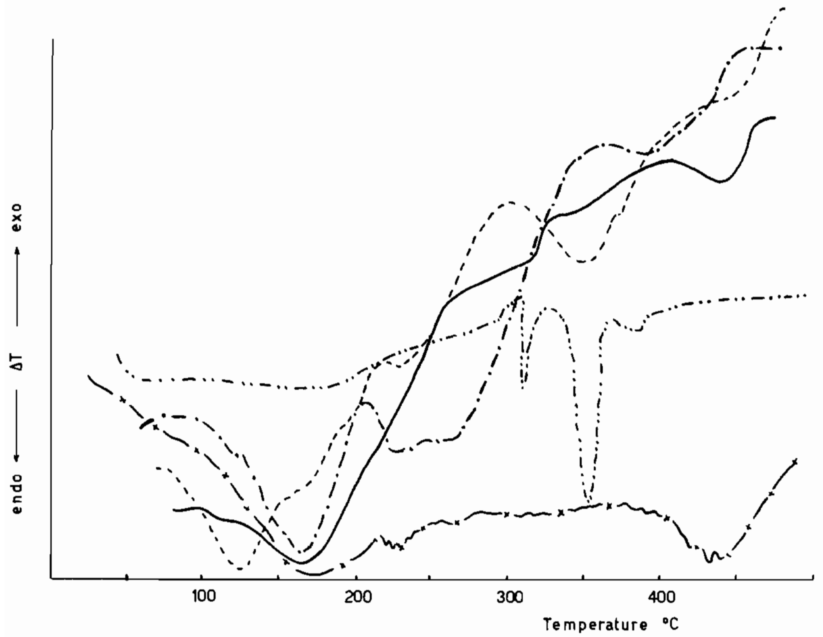


Figure 1. DTA traces of catalysts A, B, C, of amberlyst-A21 resin, and of the complex $PdenCl_2$. Amberlyst-A21 resin ———, Catalyst A -----, B —·—·—, C —x—x—, complex $PdenCl_2$ —··—··—.

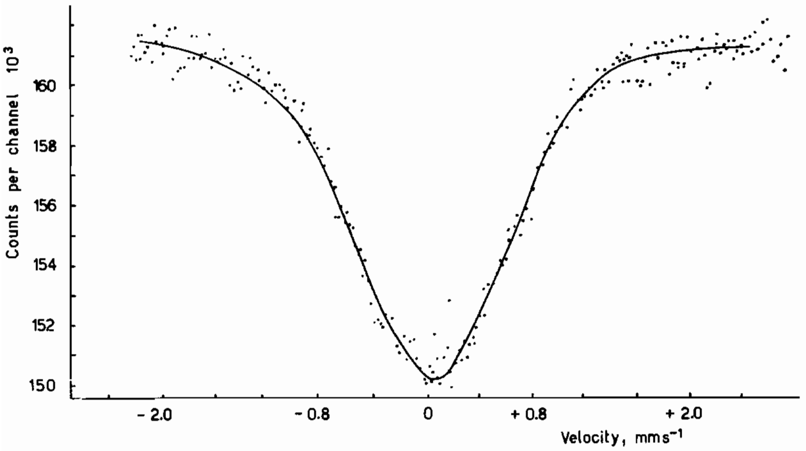


Figure 2. Mössbauer spectrum of catalyst B.

Mössbauer Spectra

The spectrum of catalyst B is shown in Figure 2. The observed isomer shift relative to a standard ^{57}Fe sample is 0.08 mm s^{-1}. The resonance is split into a broad unresolved doublet.

Catalysis of Ester Interchange Reaction

The relative amounts of vinyl acetate, acetic acid and vinyl propionate were measured and compared as ratios, Table II.

Reaction of Ethylene and Oxygen in Acetic Acid

The results of this reaction are presented in Table III.

TABLE III. Results of Oxidative Esterification of Ethylene.[a]

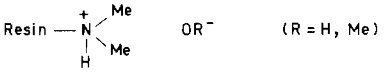
Sample	%Vinyl Acetate	%Aldehyde	Ratio ×100	Total Activity
Resin	0.0	0.0		0.0
Catalyst A	4.9	58.2	8.4	63.1
Catalyst B	12.5	29.6	42.2	42.1
Catalyst C	3.1	15.2	20.4	18.3

[a] Reaction for six hours at 110 °C.

Discussion

The singularly difficult problem encountered in attempts to characterise these catalysts is the presence of up to 50% water (by weight) in the resin. The various procedures adopted for dehydration proved to be either inefficient or water was merely replaced by another solvent, which presents similar problems.

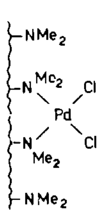
Amberlyst-A21 is an anion exchange resin containing pendant $-NMe_2$ groups. As such, it is feasible to postulate that some of the water molecules present in the resin may be associated with the amine groups through hydrogen bonds and perhaps through ionic interactions such as:



$\text{Resin}-\overset{+}{N}H(Me)_2 \quad OR^- \quad (R = H, Me)$

DTA and infrared spectral results appear to confirm both these hypotheses. The problem of water in these compounds is highlighted by the poorly resolved infrared spectra obtained and by the difficulty in the interpretation of elemental analyses. Infrared spectra were improved by the use of pressed disc techniques and vacuum cells.

The most satisfactory method for making use of the analytical data is merely to consider ratios of atoms not involving elements of water, *e.g.* Pd:Cl ratio in the case of catalysts A and B and Pd:S:N in the case of catalyst C. Whilst this sort of treatment does give some idea of stoichiometry (for instance, catalyst A has a Pd:Cl ratio of 1:2.5) it gives little idea of structure, but it is likely that the systems contain a mixture of coordination entities; for example the *cis*, (I), and *trans*, (II), structures can arise from chelation or monodentate donor behaviour of the polymeric ligands. The presence of the high chlorine content could be due to quaternised species such as (III). In order to help elucidate the structures present, catalyst C was synthesised, as the infrared spectra of thiocyanate complexes is quite well understood [3]. Two very strong bands at 2090 and 2040 cm^{-1} are observed, indicating the presence of N-bonded and ionic thiocyanate groups. On the basis of the infrared spectrum S-bonded and bridging thiocyanate can be discounted. As well as the presence of these ν(CN) vibrations, the absence of ν(Pd–S) vibrations in the region 314–280 cm^{-1} confirms that no Pd–S linkages exist. N-bonding is not to be expected in the presence of amine groups [4], but it may well be that steric factors force the NCS^- group to bond Pd–NCS (the NCS group is linear here) rather than Pd:SCN (where the SCN ~ 120°). The presence of large benzene rings and the coiling of the ligand backbone must introduce severe steric crowding.



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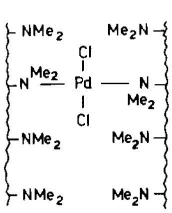

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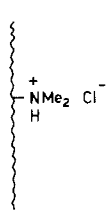


III

The DTA trace for catalyst A shows two thermal events at 350 °C and 327 °C which correspond well with the endo-peaks in the DTA trace of $[Pd(en)Cl_2]$, and we tentatively suggest that these are related to Pd–N or Pd–Cl bond rupture. The trace also shows the dehydration processes. The only other major features in the trace of catalyst A which differ from that of the resin are at 215 °C and 227 °C, and the latter peak is also observed in catalyst B. This may be due to some coordination rearrangement. The DTA trace of catalyst C is relatively featureless, with sample collapse probably occurring at *ca.* 215 °C.

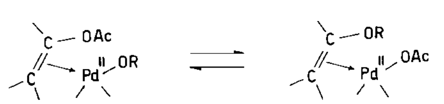
Published material [2] says little about the preparation, analysis and structure of catalyst B, save that it is more active in a Wacker-type reaction than is catalyst A. We have reprepared catalyst B and report here details of its infrared, electronic and Mössbauer spectra and its DTA results. We have also found catalyst B to be the most reactive catalyst in the reactions we have studied.

Catalysis

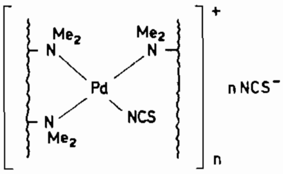
In the ester interchange reaction between vinyl acetate (VA) and propionic acid (HOPr) at 50 °C no vinyl propionate (VPr) was observed with any of the catalysts although there was some slight reaction over A and B as evidenced by changes in the ratio HAC/VA. At 75 °C vinyl propionate was observed in products from reactions catalysed by A and B. Catalyst C showed some reactivity at 75 °C (ratio HAC/VA) but the resin showed no activity at either temperature. The temperature at which vinyl propionate was detected (75 °C) is higher than that reported by Haag and Whitehurst [2] (50 °C) who tested only a catalyst similar to A in the ester interchange reaction.

The higher conversion to vinyl propionate over B (Table II) is presumably associated with the $SnCl_2$ treatment and might reflect synergism between Pd and Sn. On the other hand the lower activity of C as compared with A appears to be associated with replacement of Cl^- for SCN^-, and emphasises the similarity between supported transition metal catalysts and homogeneous catalysts in that activity is strongly dependent upon bonded ligands.

Presumably the ester interchange requires a series of reversible steps involving coordination of OR^- and VA to Pd(II) followed by interchange of OR^- and OAc^-, *e.g.*



This requires that coordination sites are available and accessible to incoming groups and presumably this is not so readily the case with SCN ligands as it is with Cl^- ligands. We propose (IV) as a most probable structure for the thiocyanate on the basis of I.R.



evidence. This structure involves strained stereochemistry and would not be expected to undergo ligand exchange readily and presumably would be a poor catalytic site. Other sites containing SCN^- groups must also be inactive or extremely small in number.

The oxidative esterification of ethylene was also a slow reaction (at 110 °C). Only the major products of reaction (acetone and vinyl acetate) were measured. Table III shows that catalysts A and B were considerably more active than C, and the resin was completely inactive. It seems likely that the reduced activity of catalyst C is again associated with the presence of SCN^- ligands and perhaps with difficulty in ligand replacement at the Pd(II) site.

If we consider the ratio of vinyl acetate to acetone as an approximate measure of catalyst selectivity, then B is clearly the most selective catalyst and this might be taken as evidence for synergism involving Pd and Sn. This type of oxidation typically involves Pd(II) in a redox process. The rate of reoxidation of Pd(0) to Pd(II) is a feature of the Wacker type processes which frequently involve Cu(II) to increase the rate Pd(0) → Pd(II). At this stage it is not possible to say whether Sn species are involved in a redox cycle, but this does not seem too likely if the only Sn species is SnO_2 (Mössbauer). Consequently the nature of any synergism requires further study.

The production of acetone requires water which is available as a reaction product

$$H_2C{=}CH_2 + \tfrac{1}{2}O_2 + HOAc \rightarrow CH_2{=}CHOOCCH_3 + H_2O$$

Acetone can then arise by direct hydrolysis of the vinyl acetate

$$\begin{array}{c} H_2O + CH_2{=}CHOOCR \rightleftharpoons CH_2{=}CHOH + RCOOH \\ \phantom{H_2O + CH_2{=}CHOOCR \rightleftharpoons} \downarrow \\ \phantom{H_2O + CH_2{=}CHOOCR \rightleftharpoons} CH_3CHO \end{array}$$

and it can also be formed by direct coordination of OH^- to Pd(II) as in the Wacker process. Further kinetic studies are required to differentiate between these routes and to explain product distributions.

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