

Hydrogenation of Cinnamaldehyde Using Catalysts Prepared from Supported Palladium Phosphine Complexes

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The liquid phase hydrogenation of cinnamaldehyde has been studied using catalysts prepared from the binuclear palladium complexes $[\text{Pd}_2\text{X}_4(\text{PR}_3)_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{or I}; \text{R} = \text{Me}, \text{Et}, \text{and Pr}^i \text{ or Bu for } \text{X} = \text{Br only}$) on silica, and the results have been compared with the performance of a standard Pd/SiO_2 catalyst prepared from $\text{Pd}(\text{NO}_3)_2$ and with that of the unsupported molecular complexes. When $\text{X} = \text{Br}$, cinnamaldehyde is rapidly hydrogenated selectively to hydrocinnamaldehyde and no further reaction occurs. When $\text{X} = \text{I}$, the reactions are extremely slow but are again limited to hydrocinnamaldehyde formation. The catalysts prepared from the chloride-containing precursors behave differently, and some phenyl propanol is formed along with hydrocinnamaldehyde. However, the reaction mechanisms are different from that which operates with the silica-supported palladium catalyst. The rates of the reactions are dependent on the nature of the phosphine substituent, but the selectivities are dependent primarily on the halide. Hydrogenation reactions on all of the catalysts prepared from the binuclear complexes proceed only after an induction period during which partial reduction and/or surface reconstruction of the supported complexes occur. This contrasts with the performance of the standard Pd/SiO_2 catalysts for cinnamaldehyde hydrogenation, which proceeds without any induction period. The reactions of all of these catalysts are thought to take place on a hydrocarbonaceous overlayer which is formed rapidly from unsaturated aldehydes and alcohols. Hydrogenations of cinnamaldehyde using the unsupported complexes in solution proceed at much lower rates, but reveal the same selectivities observed with their silica-supported counterparts. © 1996

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INTRODUCTION

Many palladium complexes are known to behave as homogeneous hydrogenation catalysts. These include palladium(II) compounds with nitrogen donor atoms (1–7), of which *ortho*-metallated examples with Pd–C bonds appear most versatile, palladium(II) complexes of S,N-bidentate ligands (8), and palladium(0) diimine compounds (9). Complexes with phosphine ligands have also been extensively examined, including some binuclear species

$[\text{Pd}_2\text{X}_4(\text{PR}_3)_2]$ (10) and several other monophosphine–palladium derivatives which also have a 1:1 P to Pd ratio (6, 11), bis(phosphine) complexes $[\text{PdX}_2(\text{PR}_3)_2]$ (10, 12), and complexes of bidentate (13–15) and terdentate (16, 17) phosphorus ligands. In a number of cases, mixtures of tertiary phosphines with complexes of palladium(II) or palladium(0) have been employed as homogeneous hydrogenation catalysts, and while the active species are almost certainly Pd– PR_3 derivatives, their identities remain unresolved (18, 19).

The applicability, activity, and selectivity of these catalysts vary considerably. They are believed to operate via Pd(H) and Pd(substrate) intermediate complexes, and in a number of cases IR and NMR spectroscopic evidence for Pd–H intermediates has been reported (6, 9, 16, 17). Interestingly, both addition of N-donors to palladium phosphine catalysts and addition of phosphines to palladium nitrogen catalysts cause deactivation (20, 21), suggesting that the availability of coordination sites is of critical importance (14). In some cases induction periods have been noted (2), and the identity of the catalysing species is sometimes obscure (22). In addition, all suffer from the usual drawback of homogeneous catalysis, that of catalyst separation.

A number of attempts have been made to prepare heterogeneous catalysts by supporting molecular palladium complexes. The use of organic polymer-based benzyl-diphenylphosphine (23) or isocyanopropylpolyacrylate (24) as ligands produced heterogeneous analogues of $[\text{PdCl}_2(\text{PR}_3)_2]$ and $[\text{PdCl}_2(\text{CNR})_2]$, respectively. In both cases the polymer-based materials were more active than their monomeric analogues as hydrogenation catalysts (the latter comparing well with commercial Pd/C catalysts) while retaining many of the desirable features of their homogeneous counterparts, such as high selectivity. Likewise, catalysts prepared by contacting solutions of chloropalladium amine complexes with alumina, silica, MgO, BaSO₄, CaCO₃, or zeolites also led to materials with enhanced activity (25), which were quite stable to poisons such as H₂O, PPh₃, or thiophene and performed well after repeated use. Treatment of SiO₂/hydrosilane with $[\text{Pd}(\text{PPh}_3)_4]$ and acetic acid produced immobilised catalysts which specifically

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reduced alkynes to *Z*-alkenes (26). A third type of "heterogenised" palladium-based molecular catalyst takes advantage of the protection offered by intercalating and anchoring the complexes into the layers of pillared clays like montmorillonite (27) or into the pores of zeolites (28): both offer enhanced catalyst stability.

We describe in this work the activities and selectivities of catalysts prepared from $[\text{Pd}_2\text{X}_4(\text{PR}_3)_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$; $\text{R} = \text{Me}$ or Et) and $[\text{Pd}_2\text{Br}_4(\text{PR}'_3)_2]$ ($\text{R}' = \text{Me}, \text{Et}, \text{Pr}^i, \text{or Bu}$) on silica, using the hydrogenation of cinnamaldehyde as a model reaction.

EXPERIMENTAL

The palladium complexes were prepared by standard methods and their identities and purities were checked by microanalyses, melting points, ^1H and ^{31}P NMR spectroscopy, and IR spectroscopy (29–36). Gasil 35M silica was supplied by Crosfield and dried at 100°C for 3 h before use. Gasil 35M has a surface area of $320 \text{ m}^2 \text{ g}^{-1}$, a pore volume of 1.2 ml g^{-1} and a mean particle size of $4.0 \mu\text{m}$. Gas chromatography (GC) analyses were carried out on a Philips PU4500 gas chromatograph fitted with a Phase Separations 2 m glass column of 5% carbowax 20M on chromosorb W (mesh size 80–100 μm) and a flame ionisation detector.

Preparation of the Catalyst Precursors

Precursors with a 5% w/w Pd loading were prepared by stirring a solution of the palladium complex in ethanol or ethanol/chloroform with Gasil 35M silica for 24 h and then removing the solvent with a rotary evaporator at room temperature followed by pumping at high vacuum. The stoichiometry of each of these yellow or orange materials was checked by C, H, halide, and P microanalyses.

Catalyst Activation and Hydrogenation

Under a helium atmosphere, 0.5 g of the catalyst precursor and 25 ml of decahydronaphthalene (decalin) were treated with 0.25 ml of cinnamaldehyde, and the temperature was raised to 135°C . Hydrogen gas was bubbled through the liquid at 1 atm pressure at a rate of 70 ml min^{-1} . The catalyst rapidly turned black. Aliquots of the reaction mixture were removed at intervals, and were subjected to GC analysis after filtration. Additional experiments were carried out at 95°C in order to follow the activities and selectivities during the initial stages of the reaction. The hydrogenations of hydrocinnamaldehyde (0.25 ml) and cinnamyl alcohol at 135°C were also investigated in a similar manner using selected catalysts.

The hydrogenation of cinnamaldehyde using the homogeneous analogues of the binuclear palladium complexes were carried out under identical conditions to those for the heterogeneous catalysts, using the same weights of complexes.

Preparation of the Standard Pd/SiO₂ Catalysts

These catalysts were prepared by impregnating Gasil 35M silica with sufficient $[\text{Pd}(\text{NO}_3)_2]$ in water to give 5% Pd loading, removing the solvent after 24 h using a rotary evaporator, and then pumping at high vacuum as before. The catalysts were calcined in flowing air (60 ml min^{-1}) at 200°C for 3 h and reduced in H_2 (60 ml min^{-1}) at 200°C for 18 h in the reactor prior to the hydrogenation reactions.

RESULTS

Preparation of the Catalysts

The catalyst precursors were made by impregnating solutions of the palladium complexes onto the silica to give a 5% w/w loading of palladium. C, H, halogen, and phosphorus microanalyses on these yellow or orange materials indicated that the palladium complexes retained their integrity on the silica. The analytical values for hydrogen were all about 0.5% higher than calculated, and these discrepancies were assigned to the presence of surface silanol groups on the silica.

The catalyst precursors did not change in appearance upon the introduction of the solvent or the cinnamaldehyde substrate, even at temperatures up to 135°C . (A separate solution reaction between $[\text{Pd}_2\text{Cl}_4(\text{PMe}_3)_2]$ and cinnamaldehyde showed no evidence for reaction, the palladium complex being recovered intact). The introduction of hydrogen gas, however, immediately caused the materials to turn black, even at temperatures as low as 70°C , producing the active catalysts.

Catalytic Activity

The hydrogenation of cinnamaldehyde can give rise to three likely products, namely hydrocinnamaldehyde, cinnamyl alcohol, and phenylpropanol. No cinnamyl alcohol, $\text{PhCH}=\text{CHCH}_2\text{OH}$, was detected as a product of any of our experiments. Table 1 lists the results of the liquid phase hydrogenations of cinnamaldehyde at 1 atm pressure and 135°C by catalysts prepared from the supported molecular complexes $[\text{Pd}_2\text{X}_4(\text{PR}_3)_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$; $\text{R} = \text{Me}$ or Et) and $[\text{Pd}_2\text{Br}_4(\text{PR}'_3)_2]$ ($\text{R}' = \text{Me}, \text{Et}, \text{Pr}^i, \text{or Bu}$). All of the results were reproducible. The performance of the standard Pd/SiO₂ catalyst is included in the table for comparison. The results are presented as a percent conversion of cinnamaldehyde and selectivity to either hydrocinnamaldehyde or phenylpropanol. The SiO₂ itself and $[\text{PMe}_3\text{H}]\text{Br}$ on silica were confirmed to be catalytically inactive under the same conditions.

The nature of the halide had the largest effect on both the activity and the product selectivity in the hydrogenation of cinnamaldehyde over the catalysts prepared from the supported halogen-bridged binuclear compounds. The catalysts from the chloro-complexes $[\text{Pd}_2\text{Cl}_4(\text{PR}_3)_2]$ ($\text{R} = \text{Me}$

TABLE 1

Hydrogenation of Cinnamaldehyde at 135°C over Supported Palladium Catalysts

Catalyst Precursor	Time on Line (h)	Conversion (%)	Product HC ^a (mol%)	Selectivity PP ^b (mol%)
Pd ₂ Cl ₄ (PMe ₃) ₂ /SiO ₂	1	29	25	4
	2.5	35	31	4
	4	53	42	5
	24	79	47	32
Pd ₂ Br ₄ (PMe ₃) ₂ /SiO ₂	0.5	27	27	0
	1	100	100	0
	24	100	100	0
Pd ₂ I ₄ (PMe ₃) ₂ /SiO ₂	1	1	1	0
	2.5	3	3	0
	4	4	4	0
	24	6	6	0
Pd ₂ Cl ₄ (PEt ₃) ₂ /SiO ₂	0.5	100	29	71
	3	100	28	72
	24	100	23	77
Pd ₂ Br ₄ (PEt ₃) ₂ /SiO ₂	0.5	76	76	0
	3	100	100	0
	24	100	100	0
	48	100	100	0
Pd ₂ I ₄ (PEt ₃) ₂ /SiO ₂	48	6	6	0
Pd ₂ Br ₄ (PPr ₃) ₂ /SiO ₂	0.5	100	100	0
	48	100	100	0
Pd ₂ Br ₄ (PBu ₃) ₂ /SiO ₂	0.5	96	96	0
	1	100	100	0
	48	100	100	0
Pd(NO ₃) ₂ /SiO ₂	0.25	81	81	0
	0.5	100	99	1
	0.75	100	98	2
	1	100	91	9
	2.5	100	78	22
	3	100	71	29
	4	100	62	38
	24	100	16	84
48	100	0	100	

^a HC = hydrocinnamaldehyde.^b PP = phenylpropanol.

or Et) hydrogenated cinnamaldehyde to both hydrocinnamaldehyde and phenylpropanol. Conversion to phenylpropanol did not appear to take place sequentially from hydrocinnamaldehyde, however, since even after 24 h some hydrocinnamaldehyde remained (Table 1). This conclusion was supported by independent experiments on hydrocinnamaldehyde itself. Neither catalyst reduced it to phenylpropanol, even after prolonged exposure under these conditions. The catalysts slowly deactivated during use.

This behaviour can be contrasted with that of a standard 5% Pd/SiO₂ catalyst prepared by calcination and reduction of supported [Pd(NO₃)₂]. Phenylpropanol was formed in 100% yield by hydrogenation of the hydrocinnamaldehyde,

formed in turn from the hydrogenation of the cinnamaldehyde substrate. It is of interest to note that the performance of a catalyst prepared by impregnation of [Pd₂Cl₄(PMe₃)₂] on SiO₂ (5% Pd) followed by calcination at 400°C and reduction at 200°C before use was indistinguishable from that of the standard 5% Pd/SiO₂ catalyst, indicating that under those somewhat extreme conditions effectively all of the halide and phosphine had been removed from the palladium.

The catalysts prepared from the bromo-bridged compounds, [Pd₂Br₄(PR₃)₂], showed remarkable selectivity. They all hydrogenated cinnamaldehyde rapidly and completely to hydrocinnamaldehyde and no further reaction then occurred. The iodide-containing catalysts from [Pd₂I₄(PR₃)₂] (*R* = Me or Et) were equally selective but acted very slowly, both of them producing only 6% hydrocinnamaldehyde over a 48 h time period under the same conditions. In an extended cinnamaldehyde hydrogenation reaction carried out with the catalyst prepared from [Pd₂I₄(PMe₃)₂]/SiO₂, only 10% of the cinnamaldehyde was hydrogenated after 200 h, hydrocinnamaldehyde again being the only product formed. This selectivity indicates that the halide is retained as an integral part of the catalysts. The activity differences between bromides and iodides may simply be steric in origin. As with the chloride catalysts, a marked deactivation was apparent in these catalysts with repeated use.

Experiments using a catalyst precursor prepared simply by grinding together sufficient [Pd₂Br₄(PMe₃)₂] and silica to give a 5% Pd loading also produced an active catalyst that was 100% selective to hydrocinnamaldehyde. Somewhat counterintuitively, these reactions proceeded faster than those of the catalysts prepared by prior impregnation of the complex onto the support. These differences presumably arise from differences in the particle size of the active palladium-containing species on the surface, since microanalyses indicated that the complexes retained their integrity when impregnated onto the supports.

Although the nature of the halide present produced the largest influence on the behaviour of the catalyst, it was apparent that the tertiary phosphine ligands also played a critical role. Thus catalysts prepared by grinding together crystals of PdBr₂ with silica (5% Pd loading) or from the standard Pd/SiO₂ catalyst modified by [NBu₄]Br produced phenylpropanol as well as hydrocinnamaldehyde, although the amount of phenylpropanol was considerably less than that from the use of the unmodified Pd/SiO₂ catalyst. This suggests that the presence of phosphine is also important in promoting the selectivity to hydrocinnamaldehyde, and possibly that intimate contact of the halide with each of the Pd atoms prior to catalyst formation and use is important.

The nature of the alkyl groups on the tertiary phosphines affected the rates but not the selectivities of the catalysts prepared from the silica-supported [Pd₂Br₄(PR₃)₂]

(Table 1). This may be predominantly a steric effect, since it was observed that the rate of conversion of cinnamaldehyde to hydrocinnamaldehyde increased with increasing cone-angle size of the phosphine (37). Differences in the electronic effects of this selection of phosphines are small (37). Thus, after the hydrogenation reactions had proceeded for 30 min, the yields of hydrocinnamaldehyde were 27, 76, 96, and 100 mol% for $R = \text{Me}$, Et, PBU_3^n and PPR_3^i , respectively. A similar promoting effect of the phosphine on the catalytic activity was observed for catalysts prepared from the chloride complexes, $[\text{Pd}_2\text{Cl}_4(\text{PR}_3)_2]$ (see Table 1).

The activities of selected catalysts prepared from the supported chloro- and bromo-bridged palladium complexes were determined at the lower temperature of 95°C in either decalin or heptane solvents so that the progress of the reactions could be followed in more detail. These catalytic runs showed no apparent dependence on the solvent used and displayed the same trends in selectivity as their higher temperature counterparts, albeit at the expected lower rates of reaction.

The hydrogenation of cinnamaldehyde over the catalyst prepared from $[\text{Pd}_2\text{Cl}_4(\text{PEt}_3)_2]/\text{SiO}_2$ is shown in Fig. 1. The reaction had an induction period of about 40 min before conversion of cinnamaldehyde to hydrocinnamaldehyde at an appreciable rate was observed. Hydrogenation to hydrocinnamaldehyde was then quite rapid until at high conversions the process became reactant limited. Phenylpropanol was not detected until a significant concentration of hydrocinnamaldehyde was formed. This phenylpropanol did not appear to originate from the hydrocinnamaldehyde, however, since the yield did not increase at the ex-

pense of the hydrocinnamaldehyde. Separate experiments confirmed that there was no reaction between hydrocinnamaldehyde and hydrogen over the catalyst prepared from $[\text{Pd}_2\text{Cl}_4(\text{PMe}_3)_2]/\text{SiO}_2$. Interestingly, another separate experiment with this catalyst showed that cinnamyl alcohol was partly hydrogenated to phenylpropanol and partly isomerised to hydrocinnamaldehyde.

Figure 2 shows the plots of mol fraction against time obtained for the hydrogenation of cinnamaldehyde at 95°C over the catalysts prepared from $[\text{Pd}_2\text{Br}_4(\text{PMe}_3)_2]/\text{SiO}_2$ and $[\text{Pd}_2\text{Br}_4(\text{PEt}_3)_2]/\text{SiO}_2$. Both catalysts remained 100% selective to hydrocinnamaldehyde at the lower temperature. An induction period was again apparent during which the conversion to hydrocinnamaldehyde was very slow. This was followed by rapid hydrogenation of the unsaturated aldehyde to hydrocinnamaldehyde. The hydrogenation of cinnamaldehyde was faster with the catalyst formed from $[\text{Pd}_2\text{Br}_4(\text{PEt}_3)_2]/\text{SiO}_2$ than that from $[\text{Pd}_2\text{Br}_4(\text{PMe}_3)_2]/\text{SiO}_2$. Thus, 100% conversion to hydrocinnamaldehyde occurred after 180 min for the catalyst formed from the triethylphosphine complex, whereas the reaction slowed down considerably after 180 min for the catalyst formed from $[\text{Pd}_2\text{Br}_4(\text{PMe}_3)_2]/\text{SiO}_2$. Even after 72 h on line only 83% of the cinnamaldehyde had been hydrogenated to hydrocinnamaldehyde at this temperature and the reaction had effectively stopped.

Separate experiments in which the hydrogenation of hydrocinnamaldehyde and cinnamyl alcohol was studied over the catalysts prepared from the bromo complexes again showed that hydrocinnamaldehyde was not hydrogenated over these catalysts whereas cinnamyl alcohol was readily

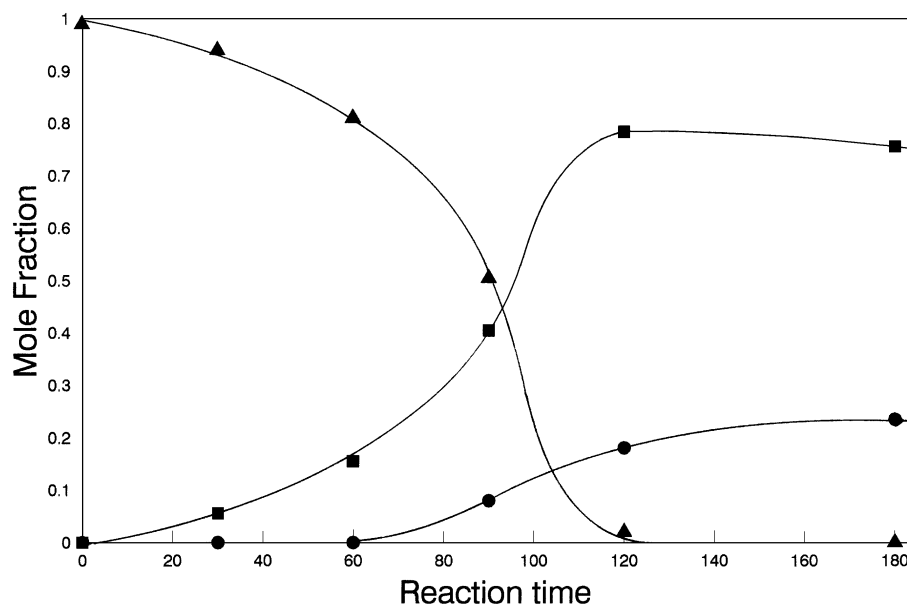


FIG. 1. Mole fraction vs time in minutes for the catalyst derived from $[\text{Pd}_2\text{Cl}_4(\text{PEt}_3)_2]/\text{SiO}_2$ and used in the hydrogenation of cinnamaldehyde in decalin at 95°C . Hydrocinnamaldehyde, ■; cinnamaldehyde, ▲; phenylpropanol, ●.

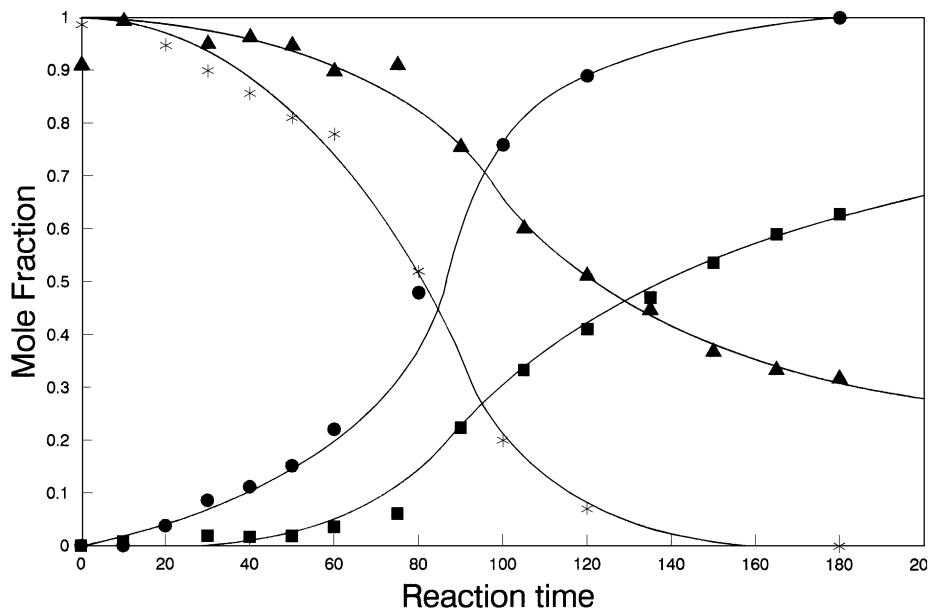


FIG. 2. Mole fraction vs time in minutes for the hydrogenations of cinnamaldehyde in decalin at 95°C over the catalysts prepared from silica-supported $[\text{Pd}_2\text{Br}_4(\text{PMe}_3)_2]$ (Cat. 1) and $[\text{Pd}_2\text{Br}_4(\text{PEt}_3)_2]$ (Cat. 2). Hydrocinnamaldehyde (Cat. 1), ■; cinnamaldehyde (Cat. 1), ▲; hydrocinnamaldehyde (Cat. 2), ●; cinnamaldehyde (Cat. 2), *.

hydrogenated to phenylpropanol, this time with negligible isomerisation to hydrocinnamaldehyde. Thus, while cinnamyl alcohol could conceivably be an intermediate in the catalysis by the chloro-bridged complexes, it is clearly not produced when the bromo-bridged complexes are used since no phenylpropanol is observed among the products.

Figure 3 shows the results obtained for the hydrogenation of cinnamaldehyde over the standard Pd/SiO₂ catalyst

at 95°C. With this catalyst no induction period was observed and cinnamaldehyde was rapidly and completely hydrogenated to hydrocinnamaldehyde. No phenylpropanol was detected until virtually all of the cinnamaldehyde had been hydrogenated to hydrocinnamaldehyde, suggesting that this reaction followed a sequential pathway in which cinnamaldehyde is converted to hydrocinnamaldehyde, which is desorbed from the surface before being readsorbed onto

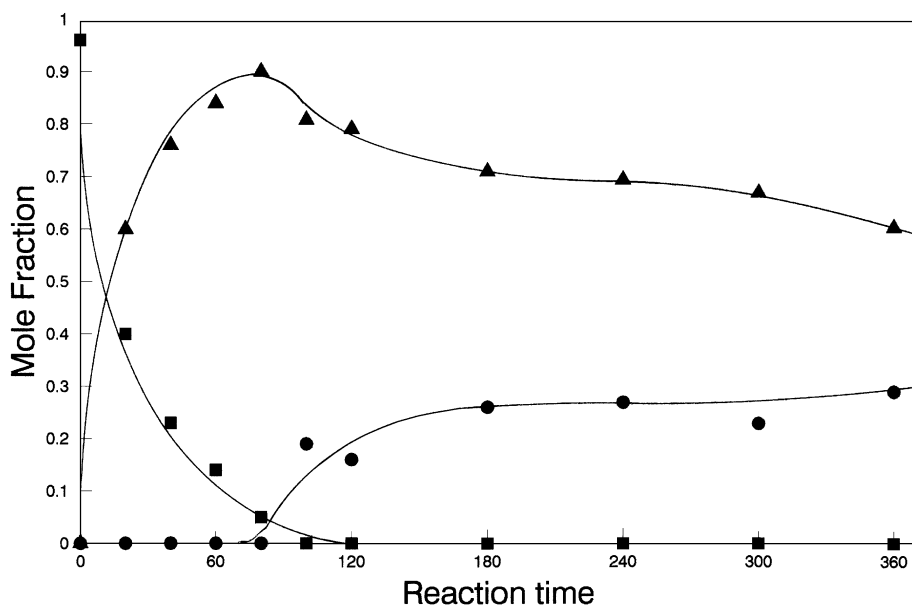


FIG. 3. Mole fraction vs time in minutes for Pd/SiO₂ used in the hydrogenation of cinnamaldehyde in decalin at 95°C. Cinnamaldehyde, ■; hydrocinnamaldehyde, ▲; phenylpropanol, ●.

the (now vacated) same sites and hydrogenated to phenylpropanol. Unsaturated alcohols are known to adsorb more strongly onto supported metals than on saturated aldehydes, in accordance with this interpretation (38).

Independent observations of the hydrogenations of hydrocinnamaldehyde and cinnamyl alcohol over the standard Pd/SiO₂ catalysts shed more light on the processes involved and on the nature of the catalyst surfaces. Hydrocinnamaldehyde was converted to phenylpropanol, but the reaction proceeded much more slowly than either the reduction of cinnamaldehyde to hydrocinnamaldehyde under the same conditions or the reduction of hydrocinnamaldehyde to phenylpropanol on the catalysts which had first reduced cinnamaldehyde to hydrocinnamaldehyde. Conversion was complete only after 48 h. Moreover, a distinct induction period was apparent before hydrogenation commenced, even at 135°C. It is clear from Fig. 3 that no induction period operates even at 95°C when cinnamaldehyde is used as substrate.

The hydrogenation reaction of cinnamyl alcohol over the Pd/SiO₂ catalyst, on the other hand, proceeds very rapidly to produce about 70% of phenylpropanol and 30% of hydrocinnamaldehyde. The reaction then continues much more slowly to convert the hydrocinnamaldehyde to phenylpropanol, with phenylpropanol accounting for 85% of the products after 48 h at 135°C. Figure 4 shows the early stages of this reaction at 95°C. The operation of an induction period is apparent before both the isomerisation and the hydrogenation reactions simultaneously commence. The processes appear to be independent, however, since the formation of hydrocinnamaldehyde slows consid-

erably after 1 h, but the formation of phenylpropanol from cinnamyl alcohol continues strongly for a longer period. The slow conversion of hydrocinnamaldehyde to phenylpropanol then ensues.

Finally, cinnamaldehyde hydrogenation reactions were also carried out at 135°C using unsupported [Pd₂Cl₄·(PMe₃)₂] and [Pd₂Br₄(PMe₃)₂], respectively, in decalin as a solvent. These catalysts turned black when placed in contact with hydrogen gas and formed a noncolloidal suspension of particles in the solution. Interestingly, the reactions proceeded with the same selectivities as their silica-supported counterparts, but with much lower activities despite the obvious heterogeneous nature of the material produced. The operation of an induction period with the bromide-derived catalyst was again clearly visible, but the reaction proceeded to only 55% in 3 h at 135°C. The progress on the chloride-derived catalyst was so slow even at 135°C that any such activation period was difficult to discern; the hydrogenation had progressed to only 8% in 3 h. It is of interest to note that the catalytic activities of a variety of complexes have been found to be enhanced when they have been "heterogenised" (23–25). In our case, at least, although the unsupported metal complexes clearly are not acting in the homogeneous phase they are much less active than the silica-supported materials.

DISCUSSION

The catalysts described in this work fall into three distinct behaviour profiles: (i) the standard palladium/silica catalyst; (ii) catalysts prepared from the binuclear bromo-

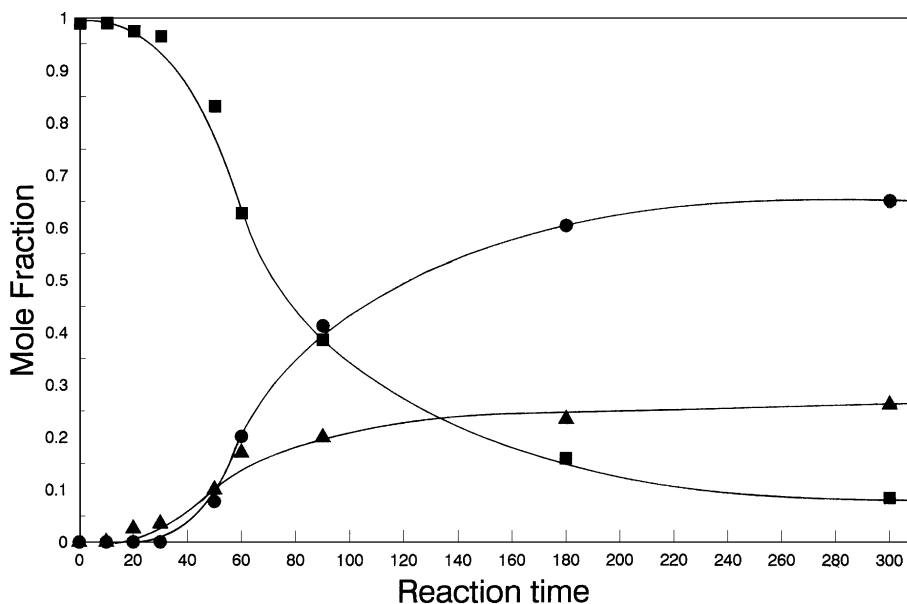


FIG. 4. Mole fraction vs time in minutes for Pd/SiO₂ used in the hydrogenation of cinnamyl alcohol in decalin at 95°C. Cinnamyl alcohol, ■; hydrocinnamaldehyde, ▲; phenylpropanol, ●.

and iodo-phosphine complexes; and (iii) those prepared from the chloro analogues. The Pd/SiO₂ catalysts are dealt with first. The hydrogenations of cinnamaldehyde, hydrocinnamaldehyde, and cinnamyl alcohol have each been examined over these catalysts. Cinnamaldehyde reacts sequentially to form hydrocinnamaldehyde and then phenylpropanol, most probably at the same sites, and with no observable induction period even at 95°C. Cinnamyl alcohol reacts after a short induction period (30 min at 95°C) both by isomerisation to produce hydrocinnamaldehyde and by hydrogenation to produce phenylpropanol. The rate of production of phenylpropanol at the early stages of the hydrogenation is greater than that from the hydrogenation of hydrocinnamaldehyde, either in the sequential process starting from cinnamaldehyde or independently on a fresh catalyst. The rate of production of hydrocinnamaldehyde from this substrate decays after about 1 h at 95°C and it is then steadily but slowly converted to phenylpropanol. The hydrogenation of hydrocinnamaldehyde to phenylpropanol over a fresh Pd/SiO₂ catalyst requires a long induction period (nearly 80 min at 135°C) before it slowly proceeds.

The differing induction periods can best be understood in terms of the greater affinity of palladium for C=C bonds than for C=O bonds (38, 39). Thus strong interactions with PhCH=CHCHO and PhCH=CHCH₂OH can lead to rapid surface activation, perhaps through the formation of a hydrocarbonaceous overlayer (40). The active sites formed from the contact of the fresh Pd/SiO₂ catalyst and hydrocinnamaldehyde, on the other hand, would be the results of a weaker interaction. They may simply be fewer in number or of a different type from those produced in the cinnamaldehyde reaction, catalysing the hydrogenation of hydrocinnamaldehyde to phenylpropanol but at a lower rate.

The isomerisation and hydrogenation reactions undergone by cinnamyl alcohol appear to proceed at different sites. While the two processes begin after a similar induction period, the production of hydrocinnamaldehyde falls away but formation of phenylpropanol continues. This must be the result of deactivation of the isomerisation sites rather than of rapid hydrogenation of the hydrocinnamaldehyde produced, since the hydrogenation of that hydrocinnamaldehyde continues only at a very slow rate. The high rate of formation of phenylpropanol from the hydrogenation of cinnamyl alcohol would rule out the possibility of the production and subsequent isomerisation of cinnamyl alcohol as an intermediate in the hydrogenation of cinnamaldehyde.

We note at this stage that catalysts formed from the calcination at 200°C of [Pd₂Cl₄(PET₃)₂] on silica followed by reduction performed in the same way for the hydrogenation of cinnamaldehyde as did the Pd/SiO₂ catalysts prepared from [Pd(NO₃)₂] on silica, indicating that under those rigorous conditions all the phosphine and chloride had been

essentially removed from the palladium. A catalyst made from PdCl₂/SiO₂ also behaved in the same way.

The preferential hydrogenation of the C=C bonds by the palladium catalysts is not surprising. Palladium catalysts are known to selectively adsorb and reduce alkenes (39). There is also a precedent for the coordination of cinnamaldehyde by its C=C bond only to platinum(0) in the molecular complex [Pt(PhCH=CHCHO)(PPh₃)₂] (41). There are also precedents for the reaction and activation of H₂ at Pt⁰ (42), and it is almost certain that palladium(0) complexes would behave in the same way, as would the palladium catalysts in the present study.

The second category of catalysts are those produced by the H₂ reduction of [Pd₂Br₄(PR₃)₂]. These can be unsupported, supported on silica by impregnation, or simply ground together with silica. The latter method produces the most active catalysts, but the activity of all of them is remarkable in view of the well known property of halides and phosphines to poison catalysts (43). All of the catalysts in this category selectively hydrogenate cinnamaldehyde to hydrocinnamaldehyde in the liquid phase. They require an induction period before reactions begin and are slowly deactivated with prolonged or repeated use. Exposure to air between the catalytic runs does not affect the rate of the deactivation process. Although these catalysts do not reduce hydrocinnamaldehyde, they readily convert cinnamyl alcohol to phenylpropanol, so the formation of cinnamyl alcohol followed by isomerisation cannot contribute to the mechanism.

Microanalyses of some of the silica-supported catalysts show that a substantial proportion of the bromine and phosphorus available in the precursors is retained by the catalysts, but it is not yet known what form this is in. The halide is presumably in intimate contact with the active sites, however, since catalysts prepared from the analogous iodo-complexes show the same selectivity but are much less active. There is also some evidence that the organic substituents are retained on phosphorus, since the reaction rates varied in the sequence $R = \text{Pr}^i > \text{Bu} > \text{Et} > \text{Me}$. This would have to be a size effect, since the electronic parameters of the four tertiary phosphines differ only slightly (37). However, some caution must be exercised in reaching this conclusion, as it is evident that the physical nature of the catalyst precursors also affects the rate. We cannot therefore entirely rule out the possibility that these, relatively small, activity differences might be assignable to coincidental particle size effects instead. This caveat appears the more relevant when it is realised that the large steric effects exerted by the halide ions operate in the opposite direction, the larger ions slowing the reactions.

It thus seems likely that these catalysts produce a single type of active site, capable of converting cinnamaldehyde to hydrocinnamaldehyde or cinnamyl alcohol to phenylpropanol. Whilst this again demonstrates the preference

of palladium for C=C coordination and reduction, these sites are clearly different from those of the Pd/SiO₂ catalysts above, which were also able to convert hydrocinnamaldehyde to phenylpropanol. While the major difference in this family of catalysts is the nature of the halide present, it must also be kept in mind that the presence of phosphine is necessary, since catalysts formed from the reduction of PdBr₂ on silica, though not identical with those produced from Pd(NO₃)₂ or PdCl₂, do produce some phenylpropanol as well as hydrocinnamaldehyde. Likewise, a standard Pd/SiO₂ catalyst modified before use by treatment with (Bu₄N)Br also produced both phenylpropanol and hydrocinnamaldehyde.

Hydridopalladium complexes are not very robust, and any palladium hydrides formed on treatment of any of the [Pd₂X₄(PR₃)₂]/SiO₂ precursors with H₂ would be unlikely to survive under the conditions of our experiments. Likely elimination products would be HX and/or [PR₃H]⁺, resulting in formal reduction of palladium. The diminished levels of halogen and phosphorus in the catalysts are compatible with the formation of Pd⁰- and/or Pd^I-containing materials by these routes. Some phosphine loss was apparent from all of these catalysts, and minor peaks observed in the GC trace of the products correspond to the retention times of free R₃P. Some of the retained phosphorus could be in the form of [PR₃H]⁺, shown to be inactive by itself. These catalysts required a lengthy induction period before hydrogenation of cinnamaldehyde commenced. Since this differs from the behaviour of the Pd/SiO₂-based material, it is possible that surface activation or restructuring of a type different from that caused by contact of Pd with cinnamaldehyde is taking place.

The third category of catalysts, those prepared from the chloride complexes [Pd₂Cl₄(PR₃)₂], is the most intriguing. Supported or unsupported, the catalysts require an induction period and produce both hydrocinnamaldehyde and phenylpropanol. However, the phenylpropanol does not appear to come from the hydrocinnamaldehyde. Although a substantial amount of hydrocinnamaldehyde forms before any phenylpropanol is observed, the formation of the latter stops before hydrogenation of cinnamaldehyde to hydrocinnamaldehyde is complete. Fresh catalysts do not reduce hydrocinnamaldehyde to phenylpropanol, though this is possibly the result of a different surface modification in the absence of cinnamaldehyde. Some of the phosphorus and chloride from the precursor are retained by the catalysts, but the amount of chloride retained is less than the amount of bromide or iodide from the previous category discussed. This might be expected, as chloride is a poorer nucleophile towards palladium than towards bromide or iodide (44) and will thus be more easily removed. Cinnamyl alcohol is partially hydrogenated to phenylpropanol, but most is isomerised to hydrocinnamaldehyde which, unlike the case of the Pd/SiO₂ catalysts, is not re-

duced. Like the bromide catalysts, those derived from the PEt₃ derivative appear to be more active than those from PMe₃.

We conclude that at least two types of active sites operate in these chloro catalysts in the presence of cinnamaldehyde. One type is probably quite analogous to that which operates selectively in the bromide and iodide catalysts and is responsible for producing most (but not necessarily all) of the hydrocinnamaldehyde. A second type produces phenylpropanol. These appear to require a longer induction period than the first type before becoming active and are deactivated more quickly. This second site type could operate in one of three ways. It may produce phenylpropanol directly from cinnamaldehyde via a single visit to the catalyst. The diminished amount of halide in the catalyst might permit simultaneous coordination of both C=C and C=O to adjacent Pd atoms, both of which could be hydrogenated before desorption. Second, the second site types may produce cinnamyl alcohol, some of which is further (and rapidly) hydrogenated and some of which is isomerised to hydrocinnamaldehyde. It is known that chloride ions can promote isomerisation reactions at metal surfaces (45). Third, these sites could be the same as those produced by the adsorption of cinnamaldehyde on Pd/SiO₂.

In conclusion, we believe the hydrogen reductions of our [Pd₂X₄(PR₃)₂] compounds form Pd⁰- and/or Pd^I-containing materials which retain some of their X and P. The liquid-phase hydrogenation activities of these solid materials are dependent on the presence or absence of a support and on the physical nature of the precursors. It is likely that the hydrogenation of cinnamaldehyde takes place in the presence of a carbonaceous overlayer formed from adsorbed cinnamaldehyde in the case of all the catalysts studied. Cinnamyl alcohol may adsorb similarly to form an overlayer in the case of catalysts formed from [Pd₂Cl₄(PR₃)₂]/SiO₂ and Pd/SiO₂ but hydrocinnamaldehyde does not contribute to the activation process since only Pd/SiO₂ showed any activity in the hydrogenation of hydrocinnamaldehyde and even then the reaction was very slow. The failure to detect an induction period for the hydrogenation of cinnamaldehyde over Pd/SiO₂ reflects the fact that the carbonaceous overlayer is formed more rapidly on this catalyst than on the catalysts formed from [Pd₂X₄(PR₃)₂]/SiO₂. Partial loss of halide and/or phosphine, or surface restructuring, could occur during the induction periods for the catalysts formed from the supported binuclear palladium complexes. Furthermore, it is likely that the catalysts so formed, unlike the standard Pd/SiO₂ catalysts, are continuously changing during the course of the reactions, since they are slowly deactivated during use. The retained halides and phosphines, which control the activities and selectivities of the catalysts, may become labile under reaction conditions and block active sites or promote further (and detrimental) surface restructuring.

Work is underway to characterise the materials at each stage of their catalytic lifetime in order to understand the origins of the remarkable specificity displayed by some and to enable us rationally to modify the catalysts in a suitable way to extend their working lifetime.

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