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### Characterization of a Polymer-Bound Palladium Acetate Catalyst and Studies on the Selective Hydrogenation of Dienes and Alkynes

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## **CHARACTERIZATION OF A POLYMER-BOUND PALLADIUM ACETATE CATALYST AND STUDIES ON THE SELECTIVE HYDROGENATION OF DIENES AND ALKYNES**

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### **ABSTRACT**

Palladium(II) acetate has been anchored onto a copolymer support containing pyridyl and carboxyl groups. XPS studies showed the Pd 3d binding energies for the recovered catalyst to be less by 1 eV after being used in hydrogenation studies. However, x-ray studies and a chemical test based on KCN treatment failed to reveal any palladium oxide or palladium metal formation in the recovered catalyst. It is presumed that an acetate ligand is lost during hydrogenation, which could be the reason for the lowering of the palladium 3d binding energies in the recovered catalyst. Results of investigations of the hydrogenation of olefins and selectivity of the catalyst toward the hydrogenation of dienes and alkynes are presented. The loss of palladium due to leaching under the reaction conditions employed was found to be very low (< 1%/cycle).

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## INTRODUCTION

Polymer-supported catalysts are a class of hybrid catalysts which were developed as a consequence of Merrifield's pioneering work on solid-phase synthesis [1]. There are reports in the literature of a number of polymer supports used to anchor palladium catalysts and their subsequent application in hydrogenation reactions (for example, Refs. 2–10). However, most of the reports deal with preparation and catalytic reactivity, and data on catalyst characterization are relatively scarce. The reason may be the limited number of techniques that can be applied to these studies. Nonetheless, such data as the nature of the catalyst are vital for understanding the catalysis of hydrogenation reactions. We have recently reported the hydrogenation of olefins using bis-benzonitriledichloropalladium(II) supported on the same copolymer reported in this paper [11]. Unlike the polymer-bound palladium chloride catalyst, polymer-bound palladium acetate catalyst showed differences in the XPS data between the fresh and recovered states. The palladium acetate supported catalyst was found to show excellent selectivity toward the hydrogenation of nitro and azo compounds [12]. In this paper we report a detailed characterization of the polymer-bound palladium acetate catalyst by XPS and other techniques. Preliminary data on the hydrogenation of olefins and the selectivity of the catalyst toward the hydrogenation of dienes and alkynes are also reported here.

## EXPERIMENTAL

MgK $\alpha$  x-ray photoelectron spectra were recorded using a VG-Scientific ESCA-3 Mark-III instrument. X-ray powder diffractograms were obtained on a Phillips PW1140 instrument using Ni-filtered CuK $\alpha$  radiation. IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer. Pd(OAc) $_2$  was purchased from Johnson Matthey. Methanol (Merck, India), used as the solvent for hydrogenation reactions, was purified by a standard method. All hydrogenation experiments were carried out at a constant pressure (1 atm) in a hydrogenation apparatus. Details of the experimental set-up and the procedure were described earlier [12]. The recycling procedure was also described earlier [11].

The 2% crosslinked copolymer support was prepared by copolymerizing styrene, divinylbenzene, methyl methacrylate, and 4-vinylpyridine by the suspension technique followed by hydrolysis [11, 12]. The copolymer analyzed for 2.8 meq/g polymer of nitrogen and 4.9 meq/g polymer of carboxyl groups.

### Preparation of Polymer-Bound Palladium Complex

The polymer support (5.0 g) was stirred with palladium acetate (1.25 g, 5.63 mmol) in a benzene-ethanol (3:1) mixture (100 mL) for 24 hours at room temperature. The dark-green catalyst obtained was filtered off and washed with benzene, methanol, and acetone. It was finally Soxhlet-extracted with acetone for 6 hours and dried under vacuum. The palladium content was found to be 7.0% [11].

### Chemical Analysis

A weighed amount (1–2 g) of the polymer-bound palladium complex was added to 25 mL saturated ethanolic KCN solution, and the reaction mixture was stirred for 12 hours at room temperature. The white polymer ligand obtained was washed several times with ethanol and acetone and dried in vacuum. A control experiment (*vide infra*) was carried out for the recovered catalyst using degassed ethanol under a hydrogen atmosphere. This was necessary in order to determine the influence of oxygen on the analytical procedure.

### Reduction of the Polymer-Bound Palladium Catalyst Using NaBH<sub>4</sub>

The catalyst (1 g) was suspended in methanol (50 mL) in an ice bath. NaBH<sub>4</sub> (1 g) was slowly added to the suspension and stirred for 1 hour while slowly bringing the reaction temperature to room temperature. The black catalyst obtained was isolated by filtration, washed thoroughly with methanol and acetone, and dried under reduced pressure. No change in the palladium content was observed.

### Hydrogenation of Dienes and Alkynes

A typical hydrogenation procedure is described as follows. Ethyl sorbate (1 mL, 6.8 mmol) in methanol (9 mL) was hydrogenated using 100 mg (3.2 mmol Pd) of the catalyst at room temperature and 1 atm total hydrogen pressure. The reaction was stopped after consumption of 1 equivalent of hydrogen (~150 mL), the catalyst was separated by filtration, and the solvent was removed under reduced pressure.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 5.5 (d, 1H, C<sub>2</sub> olefinic proton, *J* = 15 Hz) and δ 6.6 (m, 1H, C<sub>3</sub> olefinic proton); δ 4.0 (q, COOCH<sub>2</sub>CH<sub>3</sub>) and δ 1.2 (t, COOCH<sub>2</sub>CH<sub>3</sub>) confirms the formation of ethyl 2-hexenoate. Relatively weak signals at δ 5.3 (m, 2H, C<sub>3</sub>, C<sub>4</sub> olefinic protons) and δ 2.9 (d, 2H, C<sub>2</sub> protons) indicate the formation of a small amount of ethyl 3-hexenoate. The product distribution was found to be ethyl 2-hexenoate (80%), ethyl 3-hexenoate (15%), and ethyl hexenoate (5%).

### Dicyclopentadiene

The product was isolated as a white solid (mp 46–47°C).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 5.35 (m, 10, 2H, C<sub>4</sub>, C<sub>5</sub> protons); δ 3.0–1.0 (m, 70, aliphatic protons). The data are consistent with the formation of tricyclo [5,2,1,0<sup>2,6</sup>] dec-4-ene(II) in greater than 95% yield.

### 2-Butyne-1,4-diol

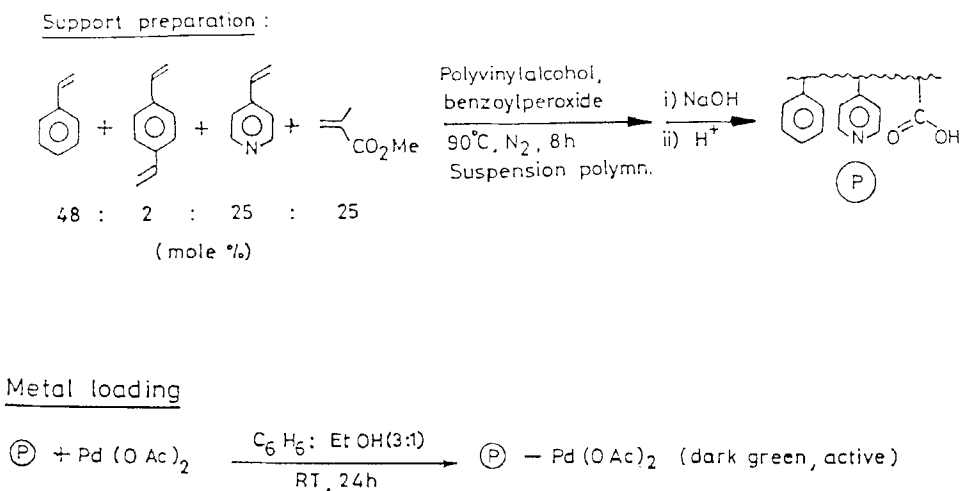
<sup>1</sup>H-NMR (DMSO-d<sub>6</sub>) δ 5.45 (t, 2H, *J* = 3 Hz); δ 3.95 (d, 4H, —CH<sub>2</sub>OH); δ 1.55 (q, 4H, —CH<sub>2</sub>—CH<sub>2</sub>—); and δ 3.3 (s, 4H, HOCH<sub>2</sub> of the unreacted alkyne). The data confirmed a product distribution of *cis*-1,4-butanediol (80%), 1,4-butanediol (14%), and 1,4-butyndiol (6%).

## Diphenylacetylene

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  2.8 (s, 4H, aliphatic);  $\delta$  6.35 (s, 2H, *cis*-olefinic protons);  $\delta$  6.9–7.3 (m, aromatic and *trans*-olefinic protons). The product distribution was found to be *cis*-stilbene (71%), *trans*-stilbene (5%), and 12% each of diphenylacetylene and dibenzyl.

## RESULTS AND DISCUSSION

The copolymer support and loading of the metal complex onto the polymer are shown in Scheme 1. IR results indicated that both carboxyl and pyridyl groups are involved in the coordination reaction [12]. The Pd 3d lines in the XPS spectra of the fresh and recovered catalyst are shown in Fig. 1. The binding energies (B.E.) and the full width at half maximum values (fwhm) are given in Table 1. The Pd 3d B.E. values for the fresh catalyst are within the region observed for several palladium(II) complexes by Jones and coworkers [13]. These values correspond to those reported by Holy [7] and Andersson et al. [14] for polymer-palladium(II) catalysts. Compared to the fresh catalyst, the Pd 3d lines are shifted by 1 eV toward lower B.E. side but the values are still greater than those reported for Pd metal (Pd 3d<sub>5/2</sub> = 335.7 eV). A shift toward the lower B.E. side by 1 eV is generally considered as lowering the oxidation state of the metal by one. Accordingly, the metal in the recovered catalyst should be expected to be present in the +1 oxidation state. However, the highly unstable nature of the Pd(I) species [15] or the absence of any ESR signal for the recovered catalyst excludes this possibility. Treatment with a saturated ethanolic solution of KCN [16] resulted in total stripping of the metal with both the fresh and recovered catalysts, leaving behind the white polymer ligand. The polymer ligand showed neither any activity for hydrogenation nor any Pd 3d lines



SCHEME 1.

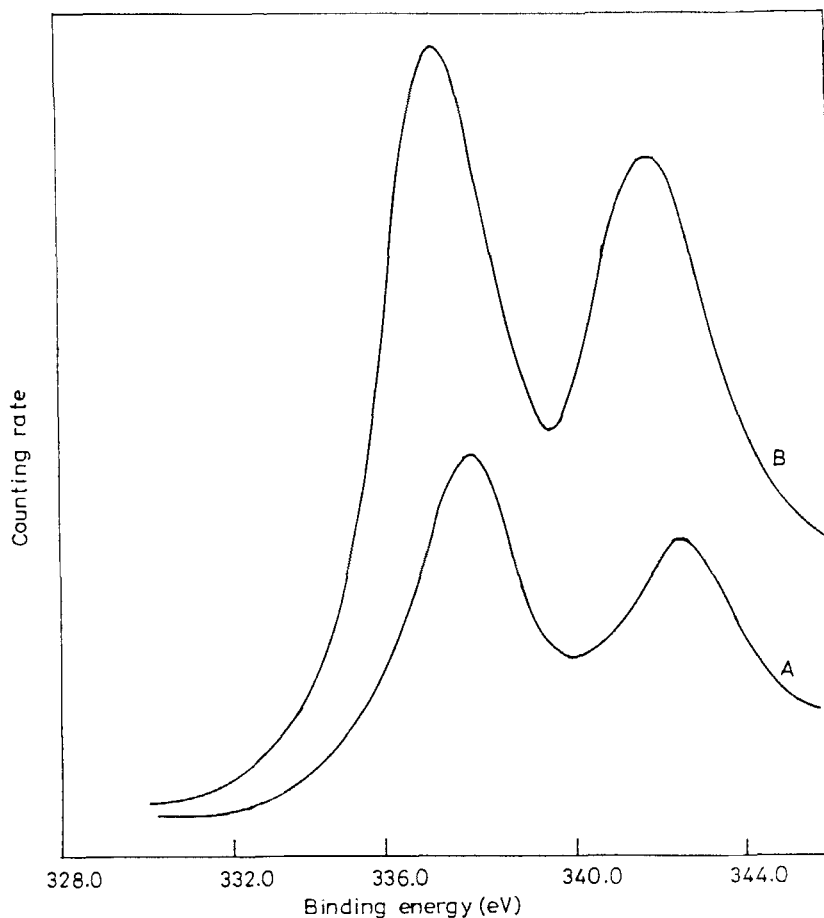


FIG. 1. Pd 3d XPS spectra of polymer-bound palladium acetate (A) fresh catalyst and (B) recovered catalyst.

TABLE 1. XPS Data for the Polymer-Bound Palladium Acetate Catalyst

Sample	Pd 3d binding energies <sup>a</sup> (eV)		Full width at half maximum (eV)
	3d <sub>5/2</sub>	3d <sub>3/2</sub>	
Fresh catalyst	337.5	342.4	2.1
Recovered catalyst	336.5	341.5	2.2
NaBH <sub>4</sub> reduced catalyst	335.8	340.6	2.1
Catalyst used for nitro group reduction	335.8	340.8	1.9

<sup>a</sup>The B.E. values are referred to carbon 1s (285.0 eV) measured with an accuracy of  $\pm 0.2$  eV.

when analyzed by XPS. The chemical test for Pd(II) devised by Bruner et al. [16] thus suggests that the metal in both the fresh and recovered catalysts is present in the +2 oxidation state.

The polymer-bound palladium acetate catalyst, however, when reduced with sodium borohydride ( $\text{NaBH}_4$ ) or when used for nitro group reduction, was found to show Pd 3d B.E.s corresponding to palladium in the zero oxidation state (Table 1). The reduction of Pd(II) to Pd(0) in the presence of nitro compounds is known from the literature [17, 18].

XPS data on polymer-bound palladium acetate are scarce. Holy [7] observed a shift of 0.5 eV of the Pd 3d lines toward the lower B.E. side for the recovered catalyst after using it for hydrogenation. Although the metal in the recovered catalyst was assigned the +2 oxidation state based on the KCN test, no further explanation was given by the author for the observed difference in the XPS data. Modelli et al. [19], in their studies on polystyryl-bipyridyl-Pd(OAc)<sub>2</sub>, demonstrated the presence of a mixture of Pd(II) and Pd(0) species. In the present study, the absence of any line broadening or shoulders corresponding to a mixture of Pd(II) and Pd(0) species in the XPS spectrum of the recovered catalyst suggests that only one type of species is present, presumably Pd(II). Further, the absence of any IR signals in the region around  $2000\text{ cm}^{-1}$  [15], corresponding to  $\gamma_{\text{Pd-H}}$  in the recovered catalyst, suggests that the metal species is not the divalent palladium hydride.

The possibility of the metal being present as palladium oxide (bulk or surface adsorbed) as a result of air oxidation of the Pd metal formed during hydrogenation was considered. This was due to the fact that the Pd 3d B.E. values for the recovered catalyst (336.5 eV) closely match those reported for palladium oxide (bulk) [20]. Andersson et al. [14] reported the formation of  $\text{PdO}_{\text{ads}}$  due to air oxidation of Pd metal in phosphinated polystyrene-PdCl<sub>2</sub> catalyst. The authors observed time-dependent changes in the Pd 3d lines by XPS. The band at 336.7 eV in the equilibrium spectrum was assigned to  $\text{PdO}_{\text{ads}}$ . However, the following experimental facts clearly exclude the possibility of formation of either palladium oxide (bulk or adsorbed) in the recovered catalyst in the present study.

1. The conversion of Pd metal to PdO is known to proceed only at elevated temperatures [20, 21]. In the present study, the catalyst was not subjected to temperatures greater than 30°C.

2. The x-ray diffractogram of the recovered catalyst did not show any peaks corresponding to PdO, as reported by Lam and Boudart [20]. If the PdO were a small portion of the oxide of the bulk palladium metal that is formed on the surface, as reported by Andersson et al. [14], this could not have been observed by x-ray, which is a bulk technique. Since XPS is a surface technique, it should be able to detect surface PdO, and thus the results from these two methods may not necessarily agree. However, if this were the case, x-ray studies should have revealed the presence of bulk Pd metal, similar to that reported by Andersson et al. in their studies. X-ray studies of the recovered catalyst did not reveal any Pd metal in the present study.

3. Lastly, it is known from the literature [15, 20] that PdO can easily be reduced to Pd metal by reaction with hydrogen at room temperature. The recovered catalyst in the present study was treated with hydrogen for 30 minutes, and the KCN test was carried out immediately under hydrogen atmosphere using degassed ethanol. The metal could be completely stripped of the polymer support. This

should not have resulted if the chemical test devised by Bruner was as sensitive to PdO as suggested by Andersson et al. [14].

Based on the foregoing discussion, it is very likely that palladium in the fresh and recovered catalysts is present in the divalent state and that the divalent metal species in the recovered catalyst is neither Pd hydride nor Pd oxide. The lowering of Pd 3d B.E. for the recovered catalyst could be the result of the loss of an acetate ligand during hydrogenation. The presence of carboxyl groups (in a large proportion relative to Pd) on the polymer may still allow for the retention of the ligand environment around the metal. If a ligand exchange of the aforementioned nature had taken place during hydrogenation, the electron density on Pd in the recovered catalyst would not be expected to be the same as that of the fresh catalyst which should be detected in the XPS results. This may be the reason for the observed differences in the Pd 3d B.E.s for the fresh and recovered catalysts in the present study. However, the loss of an acetate ligand could not be determined by IR studies [12], as reported by Neckers et al. [4], because of the presence of carboxyl groups in the polymer.

It has been clearly demonstrated by Andersson et al. [14] that the polymer ligand/Pd ratio plays an important role in the stabilization of Pd(II) on the polymer. At a low ligand/Pd ratio, the metal is more susceptible to reduction. The authors have demonstrated that the lower the metal content of the polymer (mmol Pd/g polymer), or, in other words, the larger the ligand/Pd ratio, the lower the amount of Pd(0) that is formed. The large polymer ligand/Pd ratio ( $\sim 12$ ) in the present study may be the reason for the enhanced stability of Pd(II) on the polymer support.

TABLE 2. Rate of Hydrogenation of Olefins Using Polymer-Bound Palladium Acetate Catalyst in Methanol at 30°C ([catalyst] = 0.32 mmol·L<sup>-1</sup>; [substrate] = 0.04 mol·L<sup>-1</sup>; 1 atm hydrogen total pressure; total reaction volume = 20 mL)

Substrate	Rate $\times 10^5$ , mol·L <sup>-1</sup> ·s <sup>-1</sup>	TON <sup>a</sup>
Acrylonitrile	10.06	1132
Methacrylate	9.39	1056
Methylvinylketone	8.38	943
Styrene	8.21	923
Norbornene	6.03	678
1-Octene	3.69	415
Cyclohexene <sup>b</sup>	4.69	106
Diethylmaleate <sup>c</sup>	10.73	241
Diethylfumarate <sup>c</sup>	3.58	80

<sup>a</sup>TON: The turnover number is the number of moles of the substrate reduced per gram atom palladium in 1 hour.

<sup>b</sup>[catalyst] = 1.598 mmol·L<sup>-1</sup>.

<sup>c</sup>[catalyst] = 1.598 mmol·L<sup>-1</sup>; [substrate] = 0.10 mol·L<sup>-1</sup>.



Preliminary data on the rate of hydrogenation of a few olefins are presented in Table 2. The results indicate that linear olefins are reduced faster than cyclic olefins. A *cis*-olefin is reduced three times as fast as a *trans*-olefin, and olefins containing a double bond in conjugation with a cyano or phenyl group are reduced at a faster rate than isolated terminal olefins like 1-octene. However, the catalyst does not affect the hydrogenation of a cyano or carbonyl group under the present reaction conditions. The results for the hydrogenation reactions indicate that the catalyst displays an activity comparable to that of 10% Pd/C. Moreover, the Pd(OAc)<sub>2</sub>-supported catalyst, unlike the PdCl<sub>2</sub>-supported catalyst [11], need not be activated before being used for hydrogenation reactions. The reason may be the more labile nature of the Pd—O bond in Pd(OAc)<sub>2</sub> [15], which can be presumed to readily facilitate the displacement of an acetate ligand upon the approach by a hydrogen or a substrate rendering it more active and also obviating the need for any external activation. In addition, the higher surface area of this catalyst (96.8 m<sup>2</sup>/g) when compared to that of the PdCl<sub>2</sub>-supported catalyst (52.04 m<sup>2</sup>/g) could also contribute to its greater reactivity. A comparison of the catalytic activity (estimated by the turnover number) for the hydrogenation of cyclohexene with earlier reported polymer-bound palladium catalysts is shown in Table 3. The catalyst in the present study required milder conditions than some of the other reported catalysts [6, 7]. Under similar reaction conditions, the reactivity was comparable or better than for other reported catalysts.

### SELECTIVITY STUDIES

The ability to selectively reduce one particular site of unsaturation in the presence of other potentially reducible sites is an important factor which makes a catalyst useful in synthetic organic chemistry. We demonstrated earlier [12] that polymer-bound palladium(II) acetate exhibits very high selectivity in the hydrogenation-

TABLE 3. A Comparison of the Reactivities of Various Palladium-Bound Palladium Catalysts for Cyclohexene Hydrogenation

Catalyst	Olefin Pd	Solvent/reaction conditions	TON <sup>a</sup>	Ref.
Ⓟ-PPh <sub>2</sub> -PdCl <sub>2</sub>	105	C <sub>6</sub> H <sub>6</sub> /EtOH, 25°C, 1 atm	53	3
Ⓟ-bpy-Pd(0)	145	THF, 25°C, 1 atm	95	4
Polyamide-Pd(0)	36	MeOH, 25°C, 1 atm	17	5
Ⓟ-Pd(0)	<sup>b</sup>	MeOH, 25°C, 2 atm	300	6
Ⓟ-PdCl <sub>2</sub>	7692	Nil, 80°C, 400 psig	290	7
Ⓟ-Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl	245	MeOH, 30°C, 1 atm	17	8
Ⓟ-Pd(OAc) <sub>2</sub>	315	MeOH, 30°C, 1 atm	88	Present study

<sup>a</sup>TON (turnover number): Number of moles of the substrate reduced per gram atom palladium in 1 hour.

<sup>b</sup>0.017–0.019 mmol Pd; 0.2–0.3 M olefin.

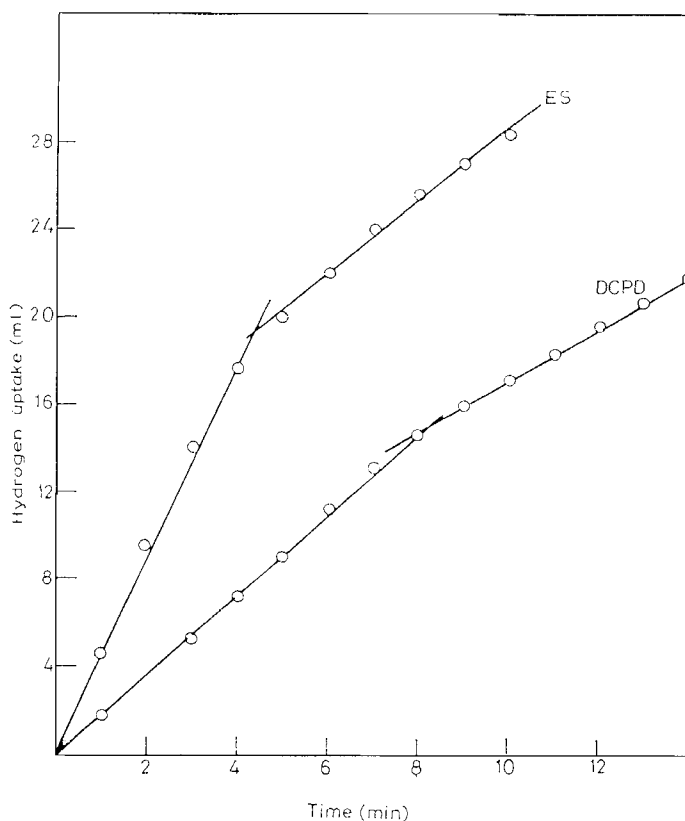
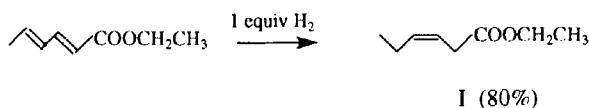


FIG. 2. Plots of hydrogen consumption with time in methanol at room temperature and 1 atm total hydrogen pressure: [catalyst] = 1.6 mmol/L; [ethylsorbate] = 0.04 mol/L; [dicyclopentadiene] = 0.03 mol/L.

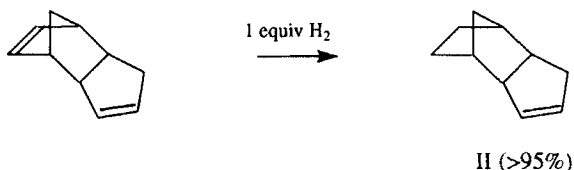
tion of azo and nitro compounds. We report here the selectivity of the catalyst toward the hydrogenation of dienes and alkynes.

### Hydrogenation of Dienes

Plots of hydrogen consumption with time for ethyl sorbate (ES) (a conjugated diene) and dicyclopentadiene (DCPD) (a cyclic diene) are shown in Fig. 2. A distinct break in each plot is observed after consumption of approximately one equivalent of hydrogen ( $\sim 19.8$  mL for ES and 14.9 mL for DCPD), which indicates that one of the double bonds is being reduced preferentially. A comparison of the rate of hydrogenation at identical substrate (0.1 mol/L) and catalyst (0.32 mmol/L) concentrations indicated DCPD to be more reactive ( $8.3 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}$ ) than ES ( $4.36 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}$ ). The higher rate of hydrogenation for DCPD can be attributed to the high ring strain associated with this molecule. Analysis of the reaction products by GC and  $^1\text{H-NMR}$  indicated the preferential reduction of the terminal double bond in the case of ES (I):



In the case of DCPD, the norbornene ring double bond was preferentially reduced to give the product, tricyclo [5,2,1,0<sup>2,6</sup>] dec-4-ene (II), in greater than 95% yield (vide Experimental):



### Hydrogenation of Alkynes

A comparison of the relative rates of hydrogenation of the alkynes studied (Table 4) indicates phenylacetylene to be more reactive than diphenylacetylene, which can be attributed to steric factors. The lower reactivity with 2-butyne-1,4-diol can be related to the presence of an electron-withdrawing substituent which can be expected to lower the electron density on the triple bond (in other words, increase the  $\pi$ -acid character). It is well known [22] that the presence of a ligand with a  $\pi$ -acid character on the metal increases the promotional energy and makes the oxidative addition of hydrogen more difficult. Since the mechanism of hydrogenation [11] involves initial complexation of the substrate followed by oxidative addition of hydrogen, which is the rate-determining step, the relative rate of hydrogenation of 2-butyne-1,4-diol can be expected to be lower.

The product distribution (GC analysis) of the hydrogenation of phenylacetylene as a function of time (Fig. 3) indicates the preferential formation of styrene. The fully reduced product, ethylbenzene, is formed only after almost all the phenylacetylene is converted to styrene. The selectivity was found to be greater than 95%. Interestingly, the hydrogenation of diphenylacetylene and 2-butyne-1,4-diol gave *cis*-products predominantly.

TABLE 4. Relative Rates of Hydrogenation of Alkynes in Methanol at 30°C and  $\text{pH}_2 = 613.13$  mmHg ([catalyst] = 1.6 mmol/L, [alkyne] = 0.1 mol/L)

Alkyne	Rate $\times 10^5$ , $\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$
Phenylacetylene	14.41
2-Butyne-1,4-diol	6.2
Diphenylacetylene	6.03

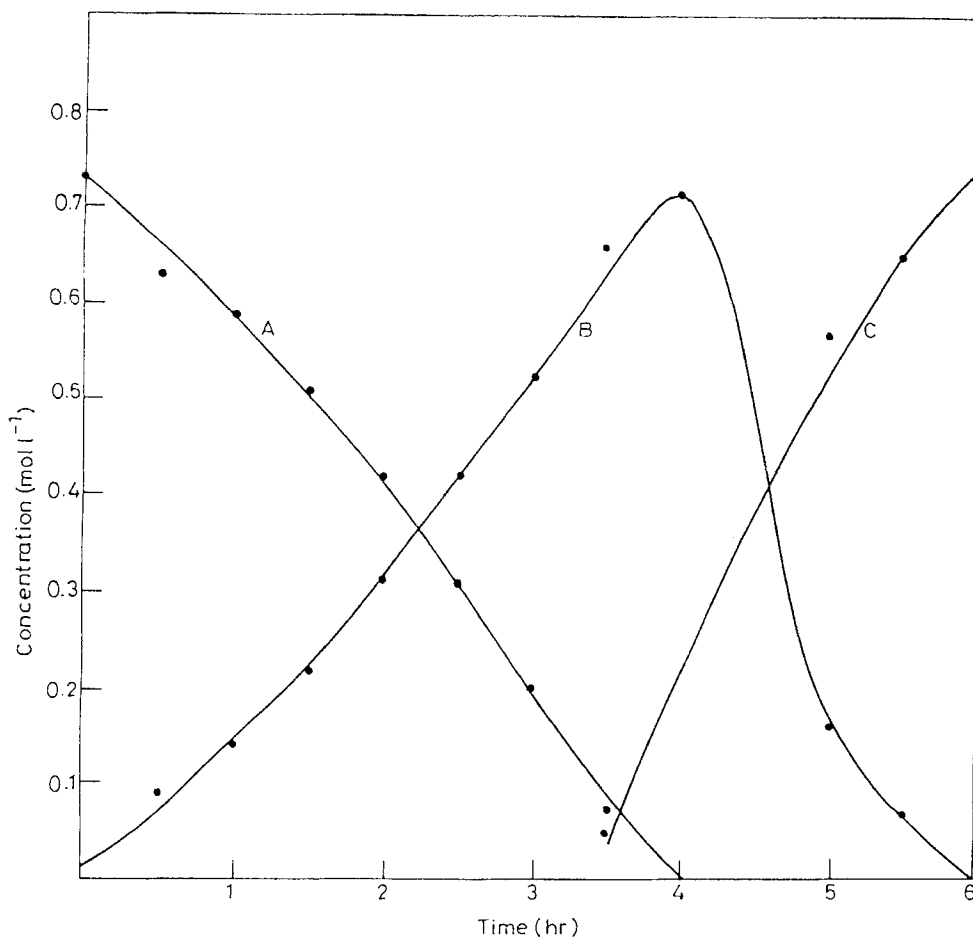


FIG. 3. Product distribution with time of the hydrogenation of phenylacetylene in methanol at room temperature: [catalyst] = 3.2 mmol/L; [phenylacetylene] = 0.73 mol/L. A = phenylacetylene, B = styrene, and C = ethylbenzene.

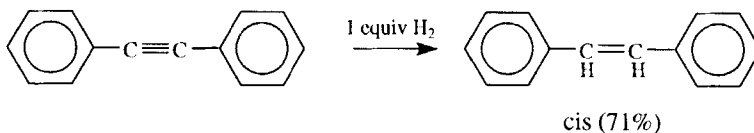
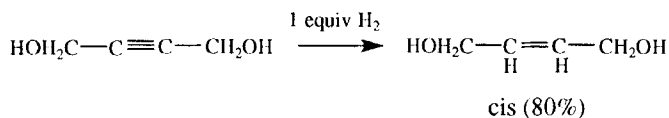


TABLE 5. Recycling Data of the Polymer-Bound Palladium Acetate Catalyst

Sample	Palladium content (mg per gram polymer) for a recycle number of				
	Fresh	II	IV	VII	X
Catalyst	70	69	68	67	66

The selectivities observed in the hydrogenation of alkynes to alkenes are comparable to some of the best catalytic systems reported in the literature; viz., cationic Rh complex [23] and Lindlar catalyst [24]. However, unlike the Lindlar catalyst, the polymer-bound palladium catalyst is stable and can be stored and handled in air. The polymer-bound Pd(II) catalyst was thus found to be highly selective for the hydrogenation of dienes and alkynes, and stereospecific in the hydrogenation of disubstituted alkynes.

The reproducibility of data after anchoring Pd(OAc)<sub>2</sub> to the copolymer support was checked for 3 batches and gave fairly consistent results (within  $\pm 3\%$  accuracy). Results on the recycling efficiency of the catalyst (Table 5) indicate the loss of the metal to be  $< 1\%$  per cycle, which is very low.

### CONCLUSIONS

Pd(OAc)<sub>2</sub> has been anchored onto a copolymer support containing carboxyl and pyridyl groups. The polymer-bound Pd(OAc)<sub>2</sub> catalyst has been characterized by various experimental techniques. The results indicate the formation of a stable Pd(II) species. The observed differences in the XPS results of fresh and recovered catalysts are attributed to the loss of an acetate ligand from palladium acetate. The large ligand/metal ratio accounts for the greater stability of the Pd(II) species in the present study. The catalyst was found to be highly selective for the hydrogenation of dienes and alkynes. In the case of disubstituted alkynes, *cis*-alkenes were formed predominantly. The loss of metal due to leaching was very small under the conditions employed.

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