

# Hydrogenation reactions catalysed by a supported palladium complex

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Received 6 September 1999; accepted 15 December 1999

## Abstract

The catalytic activity of the cross-linked polymer obtained by reaction of  $\text{Pd}(\text{AAEMA})_2$  [HAAEMA = 2-(acetoacetoxy)ethyl methacrylate] and suitable acrylates as comonomers and cross-linkers was investigated in the hydrogenation reactions of substrates such as olefins, aromatic and unsaturated aldehydes, unsaturated ketones and nitrocompounds. The polymer-supported palladium was found to be active and recyclable without loss of metal. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Palladium; Heterogeneous hydrogenation; Cross-linked polymers

## 1. Introduction

The efforts made to bind palladium onto polymeric matrices have always explored several aspects of its chemistry [1]. Recent reports number the oxidation reactions promoted by polyphenylene-bound Pd(II) complexes [2], the synthesis and characterisation of supported palladium complexes such as:  $\text{PdCl}_2(\text{IPA})_2$  (IPA = 3-isocyanopropylacrylate) copolymerized with *N,N*-dimethylacrylamide (DMAA) and *N,N'*-methylenebisacrylamide (MBAA) [3] and a Pd(II) complex of *L*-2-amino butanol anchored on poly-styrene-divinylbenzene copolymer [4]. The

catalytic activity of palladium supported on heterocyclic polyamides [5], pumice [6], or amphiphilic microporous synthetic organic matrices [7,8] has also been described.

Pursuing our studies on  $\beta$ -ketoesterato polymerizable complexes [9–12] we have recently reported the synthesis and characterization of  $\text{Pd}(\text{AAEMA})_2$  [AAEMA<sup>−</sup> = deprotonated form of 2-(acetoacetoxy)ethyl methacrylate] and its heterogeneous analogous, obtained by copolymerization of  $\text{Pd}(\text{AAEMA})_2$  with ethyl methacrylate (EMA) and ethylene glycol dimethacrylate (EGDMA) [13, 14].

We report here on the catalytic activity of this polymer-supported complex towards the hydrogenation of several unsaturated compounds, such as olefins, alkynes,  $\alpha,\beta$ -unsaturated aldehydes,  $\alpha,\beta$ -unsaturated ketones, and nitrocompounds.

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## 2. Results and discussion

Table 1 collects the results obtained in the hydrogenation reaction of unsaturated organic substrates. If not otherwise specified, the reactions were carried out in methanol at ambient conditions (1 atm H<sub>2</sub> and 21°C).

The hydrogenation of 1-heptene in the presence of 0.63% supported palladium yielded

quantitatively *n*-heptane in 2 h (entry 1). The time course of the reaction is reported in Fig. 1 and shows the intermediate isomerization to 2-heptenes.

The resin was recovered by filtration and used for 11 recycles without loss of activity (Fig. 2). The metal content in the resin recovered after the last cycle was equal to that of the fresh catalyst.

Table 1

Hydrogenation of unsaturated compounds under 1 atm of H<sub>2</sub> at room temperature, in the presence of supported palladium (molar ratio Pd/substrate = 1/160)

Entry	Substrate	<i>t</i> (h)	Conversion (%)	Products	Selectivity (%)
1 <sup>a</sup>	1-heptene	2	100	<i>n</i> -heptane	100
2 <sup>a</sup>	cyclohexene	2	100	cyclohexane	100
3 <sup>a</sup>	1-octyne	2.5	78	1-octene	94
				<i>n</i> -octane	6
4		5	100	<i>n</i> -octane	99
5 <sup>a</sup>	phenylacetylene	2.5	78	styrene	95
				ethylbenzene	5
6		7	100	ethylbenzene	99
				oligomers	1
7 <sup>b</sup>	diphenylacetylene	2.5	69	<i>cis</i> -styrene	97
				<i>trans</i> -styrene	3
8		5.5	100	1,2-diphenylethane	100
9 <sup>a</sup>	2-cyclohexen-1-one	2	100	cyclohexanone	91
				phenol	9
10 <sup>c</sup>	2-cyclopenten-1-one	3	100	cyclopentanone	100
11 <sup>a</sup>	cinnamaldehyde	9	100	3-phenylpropanal	60
				3-phenylpropanol	40
12 <sup>d</sup>	cinnamaldehyde	33	100	3-phenylpropanal	83
				3-phenylpropanol	17
13 <sup>a</sup>	citral	10.5	100	citronellal	70
				dihydrocitronellal	30
14		36.5	100	citronellal	30
				dihydrocitronellal	70
15 <sup>a</sup>	(-)-carvone	7	100	carvomenthone	70
				2-methyl-5-isopropylphenol	30
16 <sup>a,e</sup>	benzaldehyde	1	100	benzyl alcohol	95
				toluene	5
17 <sup>d,e</sup>	benzaldehyde	4	100	toluene	100
18 <sup>a</sup>	nitrobenzene	7	100	aniline	100
19 <sup>a</sup>	2-nitrotoluene	7	100	<i>o</i> -toluidine	100
20 <sup>f</sup>	2,4-dinitrotoluene	23	100	2-nitro- <i>p</i> -toluidine	77
				4-nitro- <i>o</i> -toluidine	15
				2,4-diaminotoluene	8
21		49	100	2,4-diaminotoluene	100

<sup>a</sup>In 3 ml CH<sub>3</sub>OH.

<sup>b</sup>In 4 ml CH<sub>2</sub>Cl<sub>2</sub>.

<sup>c</sup>In 2 ml CH<sub>3</sub>OH.

<sup>d</sup>In 2 ml CH<sub>2</sub>Cl<sub>2</sub>.

<sup>e</sup>At 10 atm H<sub>2</sub>.

<sup>f</sup>In 2 ml CH<sub>2</sub>Cl<sub>2</sub> + 2 ml CH<sub>3</sub>OH.

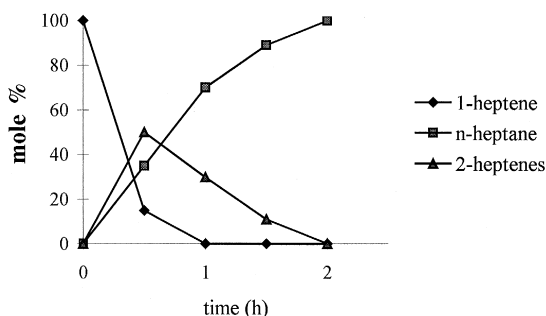


Fig. 1. Hydrogenation of 1-heptene under 1 atm  $H_2$  at room temperature in  $CH_3OH$ , in the presence of Pd catalyst (Pd/substrate = 1/160 mol/mol).

Cyclohexene was quantitatively converted into cyclohexane in 2 h reaction (entry 2).

When 1-octyne was submitted to hydrogenation, the reaction mixture analysed after 2.5 h showed a conversion as high as 78% and a selectivity into 1-octene as high as 96%, (entry 3). *n*-octane was quantitatively obtained after 5 h reaction (entry 4). The time course of the reaction is shown in Fig. 3.

Analogously phenylacetylene hydrogenation gave 74% yield of styrene after 2.5 h (at 78% conversion, entry 5) and 99% yield of ethyl benzene after 7 h reaction (entry 6), whereas

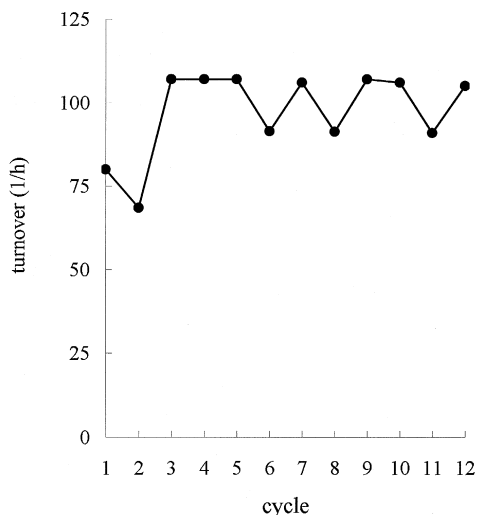


Fig. 2. Recyclability of the Pd resin in the quantitative hydrogenation of 1-heptene (1 atm  $H_2$ , R.T.,  $CH_3OH$ , Pd/substrate = 1/160 mol/mol).

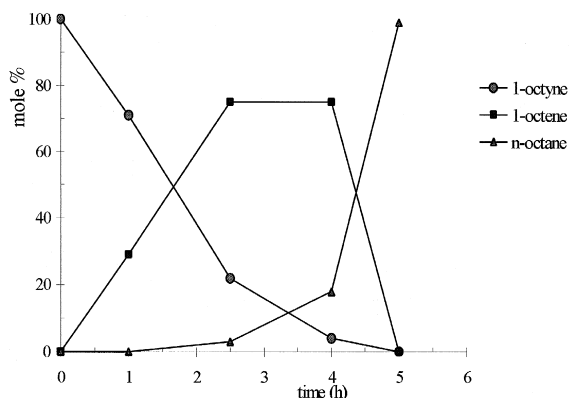


Fig. 3. Hydrogenation of 1-octyne under 1 atm  $H_2$  at room temperature in  $CH_3OH$ , in the presence of Pd catalyst (Pd/substrate = 1/160 mol/mol).

diphenylacetylene hydrogenation, carried out in dichloromethane gave 67% yield of *cis*-stylybene after 2.5 h (at 69% conversion, entry 7) and 100% yield of 1,2-diphenylethane after 5.5 h (Fig. 4; Scheme 1).

The hydrogenation of  $\alpha,\beta$ -unsaturated carbonyl compounds was also investigated. 2-cyclohexen-1-one was quantitatively converted after 2 h reaction obtaining a 91% yield into cyclohexanone and 9% in phenol, an isomerization product of the starting compound (entry 9). 2-cyclopenten-1-one was quantitatively converted in cyclopentanone after 3 h (entry 10; Scheme 2).

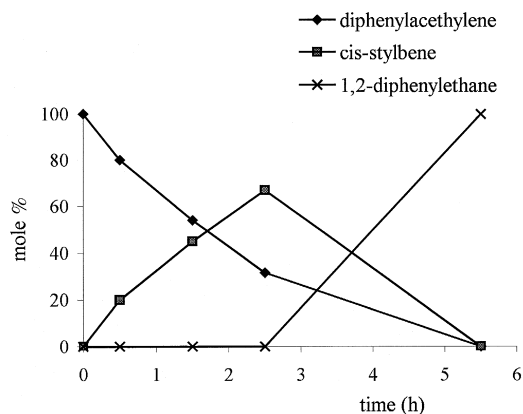
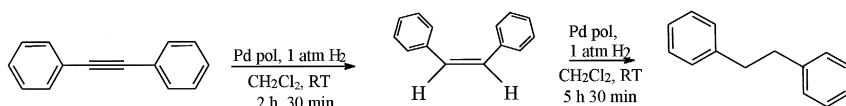


Fig. 4. Hydrogenation of diphenylacetylene under 1 atm  $H_2$  at room temperature in  $CH_2Cl_2$ , in the presence of Pd catalyst (Pd/substrate = 1/160).



Scheme 1.

The hydrogenation of cinnamaldehyde was achieved after 9 h reaction yielding 60% 3-phenylpropanal and 40% 3-phenylpropanol (entry 11). The same reaction carried out in  $\text{CH}_2\text{Cl}_2$  was much slower but more selective towards 3-phenylpropanal (83% yield after 33 h, entry 12; Scheme 3).

The hydrogenation of citral yielded citronellal (70%) and dihydrocitronellal (30%) after 10 h reaction (entry 13). The yield in dihydrocitronellal increased up to 70% after 36 h (entry 14 and Fig. 5; Scheme 4).

The hydrogenation of *R*-(-)-carvone was complete after 7 h and yielded 2-methyl-5-isopropylcyclohexanone (70%) and 2-methyl-5-isopropylphenol (30%), the latter being a carvone isomerization product (entry 15).

The selectivity towards the hydrogenation of the isolated double bond was as high as 53% at 94% conversion of the substrate (Scheme 5).

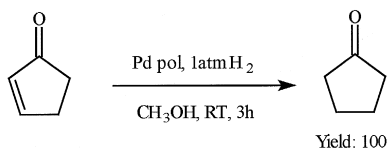
Benzaldehyde reacted sluggishly at ambient conditions taking 78 h to be converted into benzyl alcohol (95%) and toluene (5%). When the reaction was carried out under 10 atm of  $\text{H}_2$  at room temperature, the reaction reached completion within 1 h without loss in selectivity (entry 16). Performing the reaction in

dichloromethane under 10 atm  $\text{H}_2$  a quantitative transformation into toluene was achieved (entry 17).

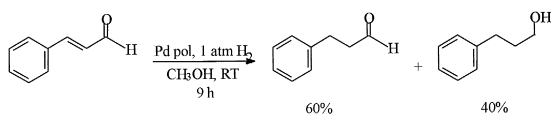
Nitrobenzene and 2-nitrotoluene were quantitatively hydrogenated in 7 h to aniline and *o*-toluidine respectively (entries 18–19).

2,4-dinitro toluene hydrogenation carried out in dichloromethane/methanol 1:1 gave 77% yield of 2-nitro-*p*-toluidine after 23 h (at 100% conversion, entry 20). 2,4-diaminotoluene was quantitatively obtained after 49 h reaction (entry 21). No reduction occurred when the hydrogenation was carried out at ambient conditions in  $\text{CH}_2\text{Cl}_2$  (Scheme 6).

For all tested hydrogenation, the used catalyst was recycled at least once with results comparable with those obtained in the first cycle. In all



Scheme 2.



Scheme 3.

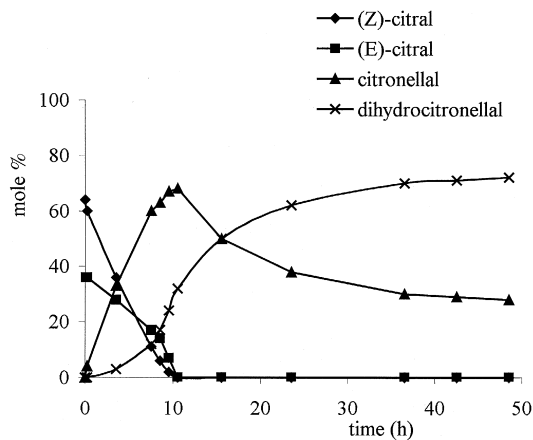
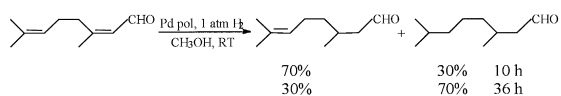
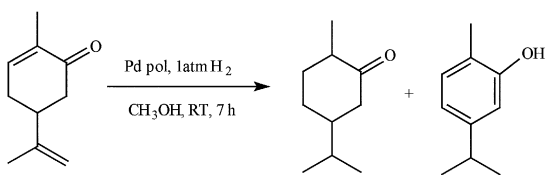


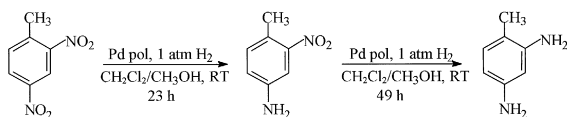
Fig. 5. Time course for the hydrogenation of citral under 1 atm  $\text{H}_2$  at room temperature in  $\text{CH}_3\text{OH}$ , in the presence of Pd catalyst (Pd/substrate = 1/160).



Scheme 4.



Scheme 5.



Scheme 6.

cases, no metal leaching was observed, even after several cycles. A higher activity (turnovers 20–40% higher than in the first cycle) was exhibited by the recycled polymer-supported palladium in cyclohexene, phenylacetylene, and 2-cyclopenten-1-one hydrogenations, probably due to catalyst activation during duty. In the case of 2-cyclohexen-1-one, a different selectivity was observed in the recycle that yielded 70% cyclohexanone and 30% phenol.

### 3. Experimental

The synthesis of the supported complex was obtained by copolymerization of Pd(AAEMA)<sub>2</sub> with EMA and EGDMA in acetone in the presence of a small quantity of AIBN at 70°C. The palladium content was assessed by atomic absorption and was 5.7% w/w.

Atomic absorption analyses were performed on a Perkin Elmer 3110 instrument using a hollow cathode lamp. Chromatographic analyses were carried out on Hewlett Packard 6890 instruments using a 19091Z-236 HP-1 methylsiloxane capillary column (60.0 m × 250 μm × 1.0 μm) or a HP 19091J-413 HP-5 phenylmethyl siloxane 30.0 m × 320 μm × 0.25 μm. GCMS data (EI, 70 eV) were acquired on a HP 6890 instrument using a HP 19091S-433 HP-5MS 5% phenyl-methyl siloxane 30.0 m × 250 μm × 0.25 μm coupled with a mass spectrom-

eter HP 5973 (EI, 70 eV). Conversions were calculated by GLC analysis as moles of hydrogenated product per mole of starting unsaturated compound by using the internal standard method. Turnovers were calculated as moles of converted substrate per moles of catalyst per time unit.

#### 3.1. Hydrogenation tests

A Schlenk tube charged with the unsaturated substrate (3.5 mmol) and the supported palladium (containing 0.022 mmol of metal) in methanol or CH<sub>2</sub>Cl<sub>2</sub> (2–3 ml as indicated in the caption of Table 1) was stirred under 1 atm hydrogen at room temperature following the reaction course by GLC and GCMS. After duty, the heterogeneous catalyst was recovered by centrifugation, washed with methanol and diethyl ether, dried under vacuum and opportunely recycled. After the last cycle of reaction the recovered catalyst was submitted to elemental analysis to determine the residual metal content. In the case of reactions carried out at pressures other than ambient, a 50 ml steel autoclave equipped with an on line spilling device was used.

#### Acknowledgements

Italian MURST and CNR are gratefully acknowledged for financial support.

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