

Catalytic hydrogenation of alkadienes and alkynes by palladium catalysts supported on heterocyclic polyamides

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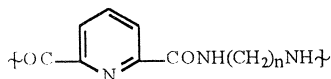
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Abstract

The catalytic behavior of palladium supported on polyamides having a pyridine moiety has been studied in the liquid phase hydrogenation of alkadienes and alkynes at 25°C and 1 atm pressure. The palladium centre was introduced into the polyamides of formula



with $n = 2$ and 6, by ligand exchange using $\text{PdCl}_2(\text{PhCN})_2$. The resulting precursor catalysts, which were activated in an hydrogen atmosphere, selectively reduced alkadienes and alkynes to monoenes and alkenes, respectively. The reaction stopped after 1 molar equivalent of hydrogen had been consumed. The effects of solvent polarity and of support structure has also been investigated. Several techniques have been used to characterize these palladium catalytic systems. The type of interaction between palladium and pyridine modified polyamides was studied by using low molecular weight model compound and IR spectroscopy. X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD) were used to characterize the palladium catalysts before and after use. It can be concluded from these results that both matrix functional groups i.e. N_{py} and $\text{O}_{\text{C=O}}$ act as coordination sites for the palladium centre and mixed valence state species are formed, giving a selective palladium catalyst. Evaluation of the stability of the supported palladium catalyst was tested in eleven successive runs involving 4300 catalytic cycles: neither loss of activity nor selectivity was found. © 1998 Elsevier Science B.V.

Keywords: Pyridine modified polyamides; Supported catalyst; Selective hydrogenation; Palladium; Mixed valence states

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1. Introduction

For many years the selective hydrogenation of unsaturated hydrocarbons has been of major interest to the fine chemicals industry. Many catalytic systems have been investigated and palladium supported on conventional inorganic matrices appears to be one of the most selective. In the search for more selective hydrogenation catalysts extensive studies have been carried out on the use of polymer immobilized palladium complex catalysts (Refs. [1,2] and references cited therein). Little information is available on palladium on natural and synthetic polyamides [3–11]. It has been found that palladium/polyamide systems exhibited a different catalytic reactivity to metal catalysts supported on inorganic oxides and palladium/polyamide catalysts showed high selectivity in partial hydrogenation of unsaturated compounds, though the nature of the active sites was not clear. This particular catalytic behavior has been ascribed to the presence of stable bivalent polyamide/Pd(II) species [5–7,10] and to the presence of palladium in both zero-valent and higher oxidation states [8,9].

Recently, "elegant research has been presented by Cum and coworkers [11–13]. They have synthesized and characterized oligomeric aramides and used them as catalyst supports. By reacting PdCl₂ with the terminal groups of oligomeric matrices they obtained systems which selectively reduced phenylacetylene to styrene at 70°C and after all the substrate had been consumed catalyzed hydrogenation of the styrene to ethylbenzene. The activity–selectivity behavior of this catalyst was dependent on the reduction temperature and metal loading and also on the 'unusual' strong metal–support interaction [11].

We have already reported the synthesis and characterization of thermostable polyamides having a pyridine moiety in their repeat unit [14]. These semicrystalline materials are insoluble in most solvents and have been successfully used by us for the immobilization of a series of

transition metal complex catalysts. These supported species have been found to be effective and selective catalysts for the hydrosilylation of unsaturated bonds [14–16].

Here Pd(II) catalyst precursors are attached to pyridine modified polyamides. When appropriately activated, these are potent catalysts for the liquid phase hydrogenation of carbon–carbon multiple bonds.

2. Experimental

2.1. Materials

All solvents and reagents were of analytical or chemical grades. Benzene, toluene, methanol and butanol were purified by standard methods. All dienes and alkynes were commercial samples. PdCl₂(PhCN)₂ was synthesized using a reported procedure [17]. The hydrogen used was electrolytically generated in the apparatus similar to that described by Pruchnik [18].

2.2. Synthesis of polymer supports and model compound A

The pyridine modified polyamides were synthesized by low temperature interfacial polycondensation between 2,6-pyridinedicarboxylic acid chlorides and aliphatic diamines, H₂N(CH₂)_nNH₂, where *n* = 2 and 6. This synthesis has previously been described [14]. Table 1 shows some characteristic properties of the samples used.

The low-molecular weight model compound, diethyl-2,6-pyridine dicarboxamide (compound A), was prepared from diethylamine and 2,6-pyridinedicarboxyldichloride by a similar procedure to that described earlier [14]. The melting point of the resulted crystalline material was 184°C.

2.3. Catalyst preparation

The polymer bound palladium complex was prepared from a known amount of polymer

matrix (1 g) to which a solution of 0.038 g (0.1 mmol) of the $\text{PdCl}_2(\text{PhCN})_2$ in 6 ml of benzene was added. The mixture was stirred at room temperature for 2–3 days when all the Pd complex had reacted with the polymer. The yellow product was filtered off, washed thoroughly with benzene and dried under vacuum. The dry catalyst could be stored in air for many months without change. The Pd content was determined by AAS spectroscopy.

2.4. General hydrogenation procedure

Reactions were carried out at 25°C in a 30 ml flat bottom glass vessel attached to a 1 atm hydrogenation apparatus and having a side-arm sealed by a glass stopcock and septum cap. The vessel was fitted with a magnetic stirrer and

charged with 0.12 g of polymer-supported palladium complex (1.2×10^{-2} mmol Pd) and solvent (about 4.5 ml). The air was removed from the system by electrolytically generated hydrogen, purified by the BASF RO-21 catalyst in a repeated freeze–thaw cycles. Hydrogen was then passed for 1 h over the catalyst suspended in the solvent at 25°C with stirring. The stirring was then stopped and an appropriate amount of substrate (about 0.5 ml) injected through the side-arm. The total volume of the solvent and substrate was 5.0 ml. The reaction was then immediately initiated by turning on the stirring again. The rate of H_2 consumption was monitored by measuring the current in the electrolysis apparatus. Samples for analysis were withdrawn via the side-arm at regular time intervals. The reaction products were identified by IR, GC-MS and

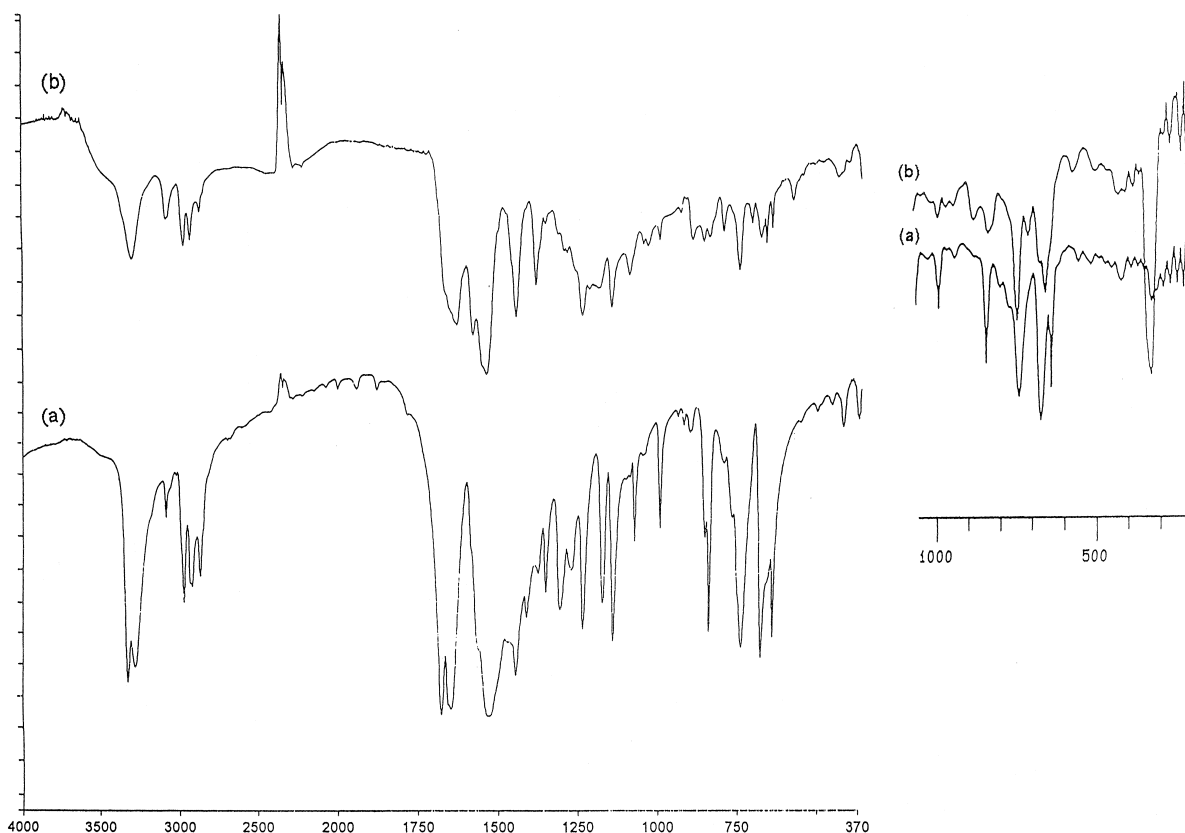


Fig. 1. IR spectra of (a) the model low-molecular-weight compound A and (b) when complexed with the precursor complex $\text{PdCl}_2(\text{PhCN})_2$.

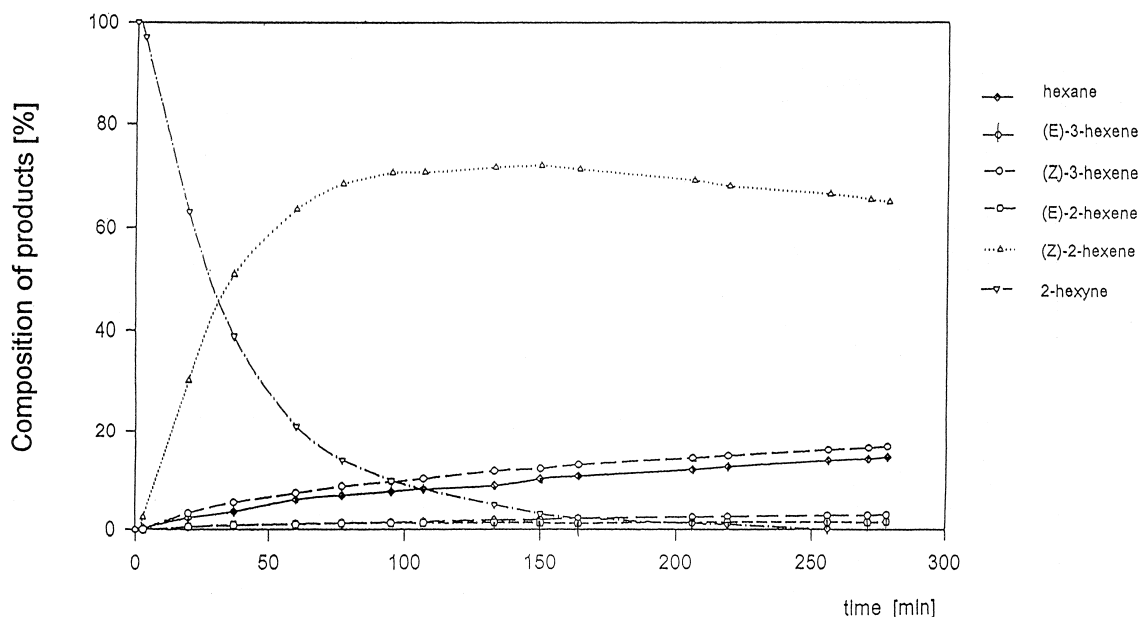


Fig. 2. Hydrogenation of 2-hexyne on the polyamide 2,6-py H/Pd catalyst: composition of products versus time.

NMR and were consistent with those of authentic samples.

2.5. Catalyst lifetime

Recycling tests were performed for a 2,6-py H/Pd catalyst in the hydrogenation of 2-methyl-1,3-pentadiene according to the above procedure. After each run, when the diene was completely consumed a new portion of substrate was added to the reaction vessel. The rate of H₂ uptake and product distribution were monitored.

2.6. General methods

Gas chromatographic analyses were carried out on a Hewlett-Packard model 5890 II gas chromatograph equipped with a thermal conductivity detector and 3396 series II integrator, using a column of 6 ft of 10% OV-101 and 6 ft of 10% OV-225 on 100–120 mesh Chromosorb W HP.

Infrared spectra of compound A and its complex with palladium were recorded on a FTIR Perkin-Elmer 2000 spectrometer using KBr pel-

lets over the range 4000–370 cm⁻¹ (Fig. 1). An FTIR Philips Analytical PU 9800 spectrometer and CsI pellets were used to obtain the spectra in the range 1000–200 cm⁻¹.

XPS measurements were made on a VG ESCALAB 210 spectrometer with Mg K α ($h\nu = 1253.6$ eV) excitation from an X-ray tube (reduced power 10 kV, 10 mA). The pressure in the spectrometer chamber was about 5×10^{-9} mbar. Samples were pressed to pellets under a pressure of 100 kbar for 10 min before these measurements. The C 1s, N 1s, O 1s, Cl 2p and Pd 3d core level spectra were recorded. The analyser pass energy was set at 20 eV. A take-off angle of 90° was used in all XPS studies. Curve fitting was performed using the ECLIPSE data system software. This software describes each of the components of a complex envelope as a Gaussian–Lorentzian sum function. The background was fitted using a non-linear model function proportional to the integral of the elastically scattered electrons (Shirley background).

The structure of the model compound A and knowledge of chemical shifts from the literature were used to decide the number, position and

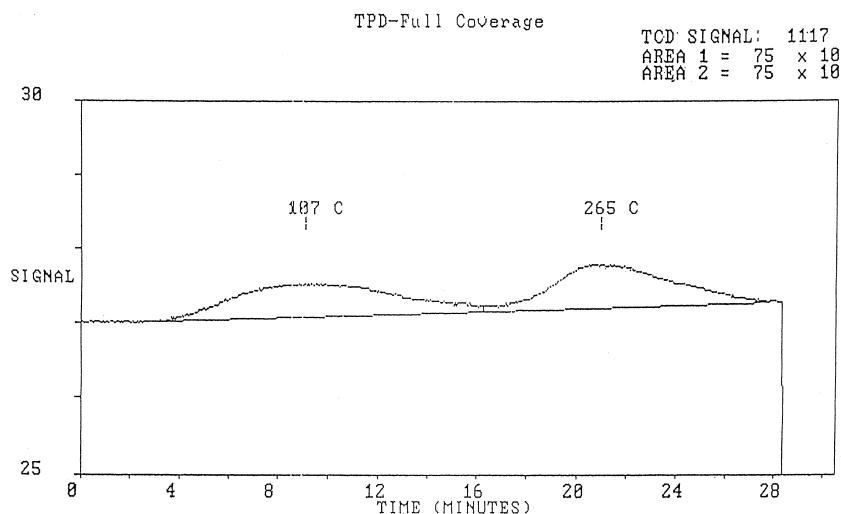


Fig. 3. TPD profile of the polyamide 2,6-py H/Pd catalyst.

area ratio of component peaks in the core-line envelope.

Two difficulties were encountered during the XPS measurements. Firstly, the surface metal content was low, hence, in order to observe the palladium peaks, numerous scans had to be accumulated. After a long period of exposure of the X-rays we observed changes in the Pd 3d

peaks shape and position of the maximum. Hence the number of scans was a compromise between high signal to noise ratio and a minimum period of samples exposure to irradiation. Secondly, as the polymer is an insulator, the contribution of the charge effect may be important. The spectrum of the C 1s was very broad and asymmetric, according to different environ-

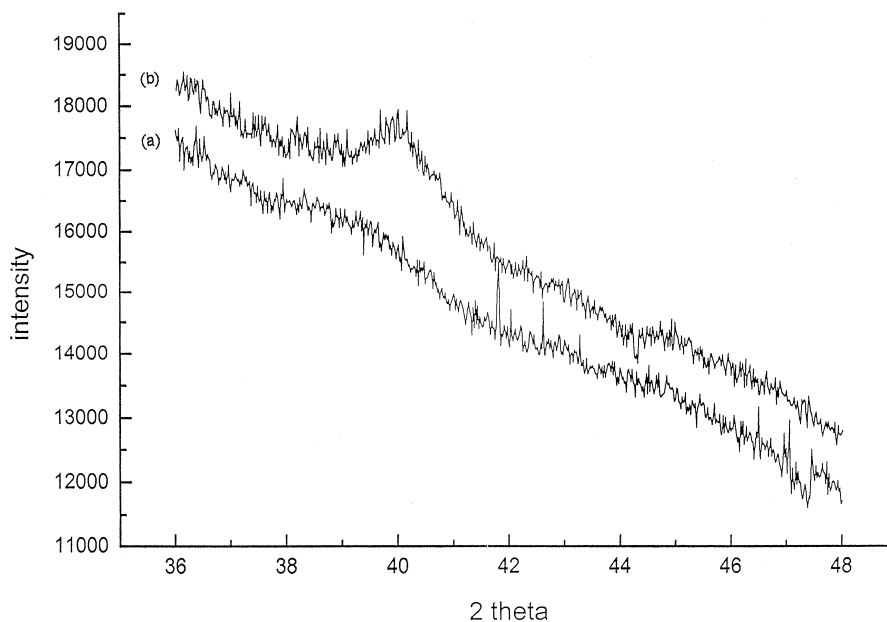


Fig. 4. X-ray diffraction pattern of (a) the polyamide 2,6-py H support and (b) Pd supported catalyst.

ments of the C atoms in a polymer chain [19]. The lowest C1s peak which was assigned to carbon in the pyridine ring, at BE = 284.7 eV, was used as the reference peak. The nitrogen N1s peaks were fitted into two major peaks: 399.3 eV and 399.8 eV assigned to amide and pyridine nitrogens, respectively, having an area ratio of 2:1 according to the 'Beamson' and polymer stoichiometry data.

Temperature-programmed desorption (TPD) was performed in an AMI-7 (Altamira Instruments). The sample of the catalyst was prereduced in a stream of hydrogen at a temperature of 250°C for 2 h and cooled in a stream of argon to ambient temperature. Then pulses of hydrogen were introduced onto the catalyst followed by TPD of the adsorbate in the temperature range 25–300°C. The heating rate was 20°/min and the argon flow rate was 30 cm³/min (Fig. 3).

X-ray diffraction spectra were recorded on a Rigaku-Denki diffractometer using Cu-K_α radiation (Fig. 4).

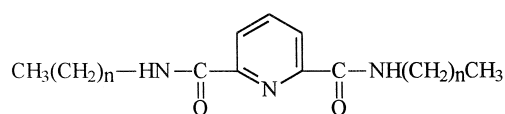
3. Results and discussion

3.1. Catalyst preparation and characterization

Two polyamide samples derived from 2,6-pyridine dicarboxylic acid dichloride and

aliphatic diamines H₂N(CH₂)_nNH₂, *n* = 2 and 6, were prepared. These materials differ in the degree of crystallinity and in their porosity (see Table 1).

The metal centre was introduced into the polymer matrix by routine ligand exchange using soluble bis(benzonitrile)dichloropalladium(II). The site of the palladium coordination was established by infrared and X-ray photoelectron spectroscopy and by the use of the low-molecular weight model compound A which was synthesized to mimic the polymer repeat unit [14].



A

(n = 1 and 3)

The Pd(II) complex of compound A had a different IR spectrum to that of A (Fig. 1), with major differences appearing in the amide (I, II and III) bands between 1700 and 1200 cm⁻¹.

Band shifts from 1678 to 1632 cm⁻¹ for νC=O and from 1531 to 1582 cm⁻¹ for (νCN + δNH) were observed. These changes were very similar to those previously reported for the rhodium and platinum complexes bonded to

Table 1
Characteristics of polyamide supports^a

Repeat unit	Polymer abbreviation	Crystallinity (%)	S (m ² g ⁻¹)	Porosity in swollen state	T _m (°C)
	2,6-py E	10	6.7	0.15	356
	2,6-py H	15	1.4	0.09	298

^aThese polymeric matrices have been described previously [15]. These are soluble in 96% H₂SO₄, *m*-cresol and HMPA/*N*-methyl-2-pyrrolidone (1/1) system only; reduced viscosity η_i/c = 0.79 (0.5 g/100 cm³ in conc. H₂SO₄ at 25°C). We retain the original symbols for immediate comparison. S: specific surface area; T_m: melting temperature.

Table 2
The binding energy values (eV)

	N 1s		O 1s	Pd 3d _{5/2}			Cl 2p _{3/2}
	N _{py}	N _{amide}	O _{C=O}	Pd ⁺²	Pd ⁰ _{clusters}	Pd ⁰ _{metal}	
Model compound A	400.3	400.9	533.0				
Compound A/Pd(II)	400.6	399.8	534.0	399.0 (97.1)	337.1 (2.9)		199.0
Polymer matrix 2,6-py H	401.2	400.8	533.0				
Catalyst precursor 2,6-py H/Pd(II) before activation	401.7	400.7	534.0	338.0 (90)	336.5 (10)		198.6
Catalyst after H ₂ activation	400.2	400.7	533.0	339.0 (9)	336.5 (91)		198.1 (82) 200.0 (18)
Recycled catalyst	399.9	400.5	533.0		337.1 (41) 335.0 (59)		199.2 (35) 220.2 (52)

Binding energies referenced to C 1s = 284.7 eV.

polyamides with aliphatic and aromatic fragments in their repeat units [20].

In the N–H stretching region, the spectrum of the complexed compound A shows only the broad band around 3330 cm⁻¹ of H-bonded amide groups; no new bands suggesting the formation of a Pd–NH bond were observed. Marked changes were seen in the range 1000–400 cm⁻¹ where the intensity of the pyridine bands of model compound A sharply decreased after palladium complexation. New bands appeared at 581.9 and 441.2 cm⁻¹ which can be

assigned to Pd–N_{py} stretching vibrations [21]. Spectra in the far-infrared region also revealed the presence of a new band at 337.5 cm⁻¹ for Pd complex of compound A; this is the characteristic terminal *trans* Pd–Cl stretching frequency. The weak bands observed at 302 and 279 cm⁻¹ could be assigned to a bridged Pd–Cl_b stretching vibration.

The IR spectra are consistent with the results from XPS measurements (Table 2). The N 1s signal consists of two peaks: one for the amide group and one for pyridine nitrogen. The peak

Table 3
Hydrogenation of alkenes

Diene	Polymer support	Time ^a (min)	Products ^a	%	Selectivity ^b to C=C (%)
2-Methyl-1,3-pentadiene	2,6-py H	15	2-methyl-2-pentene	35	88
			<i>cis</i> -4-methyl-2-pentene	33	
	2,6-py E	35	2-methyl-1-pentene	20	
			higher boiling products	12	
1,4-Cyclohexadiene	2,6-py E	10	cyclohexene	80	80
			cyclohexane	20	
4-Vinyl-cyclohexene	2,6-py H	55	ethylcyclohexenes	83	83
			ethylcyclohexane	17	
1,7-Octadiene ^{c,d}	2,6-py H	8	octene-1	65	65
			octane	35	
	2,6-py E	8	octene-1	70	70
			octane	30	

Reaction conditions: 1 atm H₂ pressure; temp. = 25°C; solvent: MeOH; [catalyst] = 2 × 10⁻³ mol Pd/l; [diene] = 1 mol/l. Product distribution was determined by GLC.

^aDetermined at 100% of diene conversion.

^bSelectivity = % alkene(s)/% all products during the first mole of H₂ uptake.

^cInitial H₂ uptake was 19 ml/min and 4 ml of H₂/min at 100% diene conversion.

^dAfter 80 min only octane was found as reaction product.

Table 4
Hydrogenation of alkynes

Alkyne	Polymer support	Time at 100% conversion (min)	Products at 100% of alkyne conversion (%)	100	Selectivity to C=C (%)
Phenylacetylene	2,6-py H	50	styrene	100	100
1-Phenyl-1-propyne	2,6-py H	40	<i>cis</i> -1-phenyl-1-propene propylbenzene	77 23	77
1-Phenyl-1-butyne	2,6-py H	15	<i>cis</i> -1-phenyl-1-butene <i>trans</i> -1-phenyl-1-butene butylbenzene	80 10 7	90
	2,6-py E	60	higher boiling products <i>cis</i> -1-phenyl-1-butene <i>trans</i> -1-phenyl-1-butene butylbenzene higher boiling products	3 73 21 3 3	94
2-Hexyne	2,6-py H	160	<i>cis</i> -2-hexene <i>trans</i> -2-hexene <i>cis</i> -3-hexene <i>trans</i> -3-hexene hexane	61 2 16 2 19	81
	2,6-py E	17	<i>cis</i> -2-hexene <i>trans</i> -2-hexene <i>cis</i> -3-hexene <i>trans</i> -3-hexene hexane	70 1 14 2 13	87
1-Octyne	2,6-py H	25	1-octene <i>n</i> -octane	82 18	82

The reaction conditions are the same as described in Table 3, but the [alkyne] was 0.77 mol/l.

of the amide nitrogen remains almost constant in the range of 400.7–400.9 eV for all samples with the exception of that of compound A complexed with Pd(II). The reverse change to that expected in the binding energy of N_{amide} 1s is difficult to explain. The peaks of the pyridine nitrogen N_{py} 1s and carbonyl oxygen $O_{\text{C=O}}$ 1s are shifted to higher values after the Pd complex formation for both compound A and polymer matrix. These results indicate that the sites of

the metal coordination to the polymer matrix are the N_{py} and $O_{\text{C=O}}$.

3.2. Catalytic hydrogenation

The precursor catalyst was activated by passing hydrogen through the reactor for 1 h at 25°C, when the colour of the catalyst changed from yellow to black. The activated system was used in the hydrogenation of conjugated and

Table 5
Hydrogenation with 0.1% Pd/C catalyst

Alkyne/diene	Products	Time at 100% formation of saturated products (min)
Phenylacetylene	ethylbenzene	35
2-Hexyne	hexane	30
1-Octyne	octane	35
2-Methyl-1,3-pentadiene	2-methylpentane	180 ^a

^aAfter 50 min no trace of the initial substrate was found by GLC. Reaction conditions are the same as described in Tables 3 and 4.

nonconjugated dienes and alkynes by H₂ gas at 1 atm pressure and 25°C.

Results in Table 3 show that the hydrogenation of conjugated dienes proceeded with a constant rate of H₂ uptake until 1 molar equivalent of hydrogen had been consumed. At this point the hydrogenation virtually stopped; the product was monoenes with yields between 80–90%. The hydrogenation of 4-vinyl-1-cyclohexene gave 83% reduction of exocyclic bond and 17% ethylcyclohexane when the diene had fully reacted. However, when nonconjugated diene with two equivalent double bonds was used hydrogenation was rapid to the equivalence point and then slowed markedly. Hydrogen uptake continued and the final product consisted only saturated compound (see footnote under Table 3).

The polymer supported palladium catalyst demonstrated high activity for alkyne hydrogenation. The data summarized in Table 4 indicate that reduction of alkynes to alkenes was highly stereoselective giving ~80% *cis*-products at 100% alkynes conversion (see also Fig. 2). However, when the *cis*-alkenes were left in contact with the catalyst for several days isomerization to the more stable *trans*-alkenes was observed. Under the same reaction conditions, hydrogenation over 0.5% Pd/C (palladium on charcoal) gave fully reduced products (Table 5). Such a difference in selectivity can be ascribed to the strong metal–support interaction that exists between palladium and the polymer func-

tionalties. The presence of pyridine moieties, electron donor species, in polyamide supports should favor the desorption of the monoenes to give a high yield of partially hydrogenated molecules. An increase in selectivity by addition of electron donor compounds such as piperidine or ammonia to alumina supported Pd catalysts has been reported recently by Boitiaux [22] and Del Angel [23].

Another factor that can play a role in promoting selectivity of hydrogenation to the alkene is the low specific area of the polyamide support. Such an effect has often been observed [24,25].

3.3. Effect of polymer support

The data collected in Tables 3, 4 and 6 demonstrate that the chemical and physical structure of the polymer matrices affects the rate of hydrogenation.

In our earlier studies [14,15] we have shown that the activity of metal complex catalysts supported on pyridine modified polyamides decreased with increasing polymer crystallinity. These results are contrary to this; higher reduction rates are observed for the palladium catalyst supported on 2,6-py H which is the polymer of higher crystallinity.

We believe that the explanation for this lies in a local polarity around the catalytic sites. A polymer chain having a short ethylene spacer (2,6-py E) contains a greater number of polar

Table 6
Effect of solvent on 2-methyl-1,3-pentadiene hydrogenation

Solvent	Dielectric constant, ϵ	Solubility of H ₂ ^a (mol% of H ₂) × 10 ²	Polymer support			
			2,6-py E		2,6-py H	
			initial rate of H ₂ absorption (ml/min)	time at 100% diene conversion (min)	initial rate of H ₂ absorption (ml/min)	time at 100% diene conversion (min)
Methanol	32.63	1.33	6.2	35	8.2	15
<i>n</i> -Butanol	17.10	—	5.2	35	6.2	20
THF	7.50	2.89	4.0	40	2.2	70
Benzene	2.27	2.69	1.0	145	4.7	45

The reaction conditions are the same as described in Table 3.

^aAt 25°C, 1 atm; Ref. [26].

amide functions in comparison with that whose functional sites are separated by six methylene groups (2,6-py H). In methanol these sites are solvated by a polar solvent so migration of a nonpolar substrate to the active metal centers 'buried' in the polar microenvironment is more inhibited in 2,6-py E than in 2,6-py H type polymer. This accounts for the lower reaction rates for the Pd catalyst on the 2,6-py E support (see Table 6). This is certainly so for the experiments performed in benzene (Table 6). A much higher reaction rate was found for the Pd catalyst on 2,6-py H. These results indicated that in a non-polar solvent the non-polar substrate finds better access to the catalytic centres which are separated by the larger aliphatic fragments in the polymer chain; thus the reduction rate for the Pd/2,6-py H catalyst was more than four times higher than for the catalyst supported on 2,6-py E polymer. The lower reaction rate in polar THF for the 2,6-py/Pd catalyst may be due to the coordinating character of this solvent, which can compete with the substrate for the metal centre.

3.4. Effect of solvent

The rate of reduction over supported catalysts is also affected by the polarity and the molecular size of the solvent used for hydrogenation. The results shown in Table 6 indicate that the rate of hydrogenation is affected more by the solvent polarity than by the solubility of hydrogen in the solvent [26].

3.5. XPS studies

The hydrogenation activity and selectivity depends on both the electronic state of the metal and its dispersion on the support. It has been found already by Russian [27] and Chinese workers [28,29] that palladium of different valence states gives a more active hydrogenation catalyst than the precursor Pd(II) complex.

Using the XPS method we have studied the composition of the active Pd surface species. From the measurement of Pd 3d binding energy (Table 2) it is clear that in the precursor catalyst the palladium is present in the 2⁺ oxidation

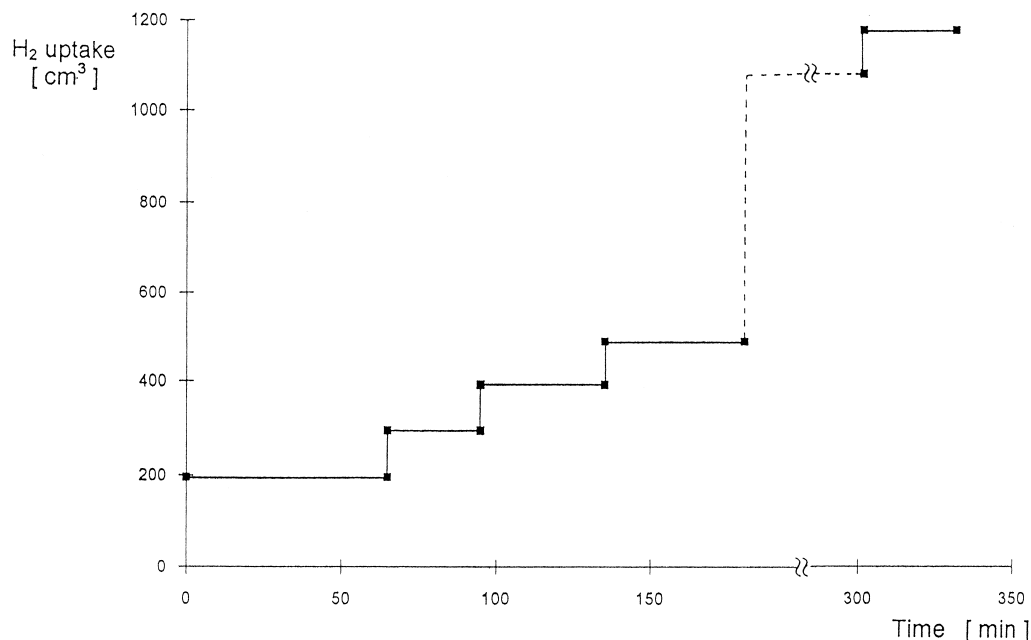


Fig. 5. Lifetime of the polyamide 2,6-py H/Pd catalyst in the hydrogenation of 2-methyl-1,3-pentadiene. Conditions were the same as described in Table 3. Initial hydrogenation rate for the 1st and 11th runs were 8.2 and 7.8 ml H₂/min, respectively.

state. After activation with hydrogen, this is reduced to the monovalent metastable species with the binding energy E_b larger than that of Pd metal. This valence state is often referred to Pd clusters, or electron deficient $\text{Pd}^{\delta+}$ [30], or Pd^+ species [28,29]. They are not stable under normal conditions, but their prolonged life is related to the protection afforded by the polymer matrix.

After several catalytic cycles the catalyst contains palladium in two valence states: monovalent palladium (or palladium clusters) and palladium metal in the ratio of about 1:1.

Additional evidence that palladium is present as two different active forms comes from the temperature-programmed desorption studies. The TPD profile of the Pd catalyst for several catalytic runs indicated the presence of weakly and strongly adsorbed hydrogen with two desorption peaks with maxima at 107 and 265°C, in the ratio of about 1:1 (Fig. 3).

Since the polyamide matrix possesses two kinds of coordination sites of different coordination ability, N_{py} and $\text{O}_{\text{C=O}}$, it seems very likely that the zero-valent palladium, Pd^0 , comes from the reduction of Pd^{2+} coordinated to the carbonyl oxygen, the weaker of the two coordination sites, whereas monovalent Pd^+ comes from the reduction of Pd^{2+} coordinated to the pyridine nitrogen N_{py} , the stronger coordination site [28].

Such a combination of sites enables us to achieve a fine dispersion of the metal in the polymer after reduction. Indeed, the X-ray diffraction analysis showed that the palladium is finely dispersed on the polymer matrix and the size of the palladium crystallites is about 30 Å (Fig. 4). There are reports in the literature indicating that such small particles favor alkene formation [31,32].

3.6. The lifetime of the catalyst

Evaluation of the lifetime of the catalyst was carried out for the hydrogenation of 2-methyl-1,3-pentadiene in methanol. 11 runs, which was

equivalent to 4300 catalytic cycles per palladium atom were carried out (Fig. 5) and no loss in activity or selectivity was found. The initial rate of hydrogen uptake was 8.2 ml H_2 /min for the first run and 7.8 ml H_2 /min for the eleventh run. The product distribution after 11 cycles was the same as given in Table 3 for 2-methyl-1,3-pentadiene. The catalyst is air stable and after one year is still active and as selective as a freshly prepared sample.

4. Conclusions

Heterocyclic polyamides are very useful and versatile polymeric supports for the preparation of palladium hydrogenation catalysts. The different coordination sites in the polymer promote the formation of active catalytic species as finely dispersed metal particles with mixed valence states. Strong metal–support interactions, as shown by TPD analysis, are also present. These features lead to catalysts selectivity in the hydrogenation of dienes and alkynes to monoenes and alkenes, respectively.

Moreover the stability and a very good recycling efficiency of these catalysts make them useful for prolonged use.

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