J Mater Sci (2010) 45:2484–2493
DOI 10.1007/s10853-010-4220-2

Catalytic hydrogenation of various organic substrates using a reusable polymer-anchored palladium(II) complex

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Received: 6 October 2009 / Accepted: 9 January 2010 / Published online: 27 January 2010

Abstract A stable, reusable, and highly active catalyst for liquid phase hydrogenation reaction has been developed by reacting poly(3,6-diamino *N*-vinylcarbazole) with benzaldehyde to get polymer-anchored Schiff base which was then reacted with bis(benzonitrile)palladium(II)chloride [$Pd(PhCN)_2Cl_2$] to get the polymer-anchored complex. The complex was characterized by using scanning electron microscope (SEM), thermogravimetric analysis (TGA), elemental analysis, atomic absorption spectroscopy (AAS), and spectrometric methods like diffuse reflectance spectra of solid (DRS) and Fourier transform infrared spectroscopy (FTIR). The catalytic performance of this catalyst was investigated in hydrogenation of various organic substrates under high-pressure condition. The results showed that the catalyst were highly efficient for hydrogenation reaction and gave excellent yields of products. At the same time, the catalyst was very stable and could be reused for more than five times without noticeable loss of its catalytic activity.

Introduction

Hydrogenation is one of the most utilized catalytic reactions in the pharmaceutical, flavoring, fragrance, vitamin, and agrochemical industries [1]. Various transition metal catalysts are widely used for hydrogenation of many organic compounds [2]. Among supported noble metal catalysts, palladium is one of the most frequently used metal for hydrogenation reactions at laboratory as well as industrial scale. Palladium catalysts are often used in organic synthesis and versatile transformations using palladium catalysts have been developed. While homogeneous palladium catalysts are used in many cases but they have some disadvantages [3–5] such as they may easily be destroyed during the course of the reaction and they cannot be easily recovered after the reaction for reuse. These disadvantages can be overcome by anchoring metal on suitable supports. Heterogeneous catalysts are usually more robast, easy to handle, can be completely removed from a reaction mixture and reused in a subsequent transformation [6–12]. There are several organic and inorganic supports for immobilized Pd-catalytic systems including hydrotalcites [13], alumina [14], zeolite and zeolitic materials [15–17], carbon [18] organic polymer [19–22], and organic complexes bound to inorganic solids [23]. The organic polymer support can induce specific control over the catalytic and complexing ability of the ligand. Palladium coordinating with polymer ligands is increasingly attracting attention in recent time because of their fascinating molecular topologies and their application potential in developing new catalytic materials [24–28]. Poly (*N*-vinylcarbazole) is one of the most widely employed macromolecular supports. These supported materials offer advantageous features of heterogeneous catalysis such as thermal stability, selectivity, and recyclability to homogeneous systems and ease of their separation from the reaction products also leading to operational flexibility.

Herein we report the preparation and characterization of a new polymer-anchored Pd(II) Schiff base catalyst and illustrate its application in hydrogenation reaction of aliphatic nitro compounds, nitriles, and ketones under high-pressure condition. We have also studied the effect of

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solvent and temperature to obtain the optimized reaction condition. This polymer-anchored Pd(II) Schiff base catalyst has gained attention because of its high activity, stability and selectivity, and recyclables properties. The experimental results reveal that polymer-anchored Pd(II) Schiff base catalyst can be recycled more than five times without much loss in the catalytic activity.

Experimental

Materials

Analytical grade reagents, freshly distilled solvents, pure and dry hydrogen gas were used throughout the investigation. The liquid substrates were predistilled and dried by appropriate molecular sieve and the solid substrates were recrystallized before use. The chemical analysis was done by the usual procedure [29]. Poly(*N*-vinylcarbazole) (Art. No. 368350-5) was supplied by Aldrich Chemical company, U.S.A. bis(Benzonitrile)palladium(II)chloride [Pd(PhCN)$_2$ Cl$_2$] was purchased from Arora Matthey and was used as such without further purification.

Morphology and particle size of different functionalized polystyrene samples were analyzed using a scanning electron microscope (SEM) (ZEISS EVO40, England) equipped with EDX facility. The thermal stability of the immobilized catalyst was determined using a Mettler Toledo TGA/DTA 851. The FTIR spectra of the immobilized catalyst were recorded on a Perkin-Elmer FTIR 783 spectrophotometer using KBr pellets. Diffuse reflectance UV–Vis spectra were taken using a Shimadzu UV-2401PC doubled beam spectrophotometer having an integrating sphere attachment for solid samples. A Perkin-Elmer 2400C elemental analyzer was used to collect microanalytical data (C, H, and N). The metal loading in the polymer was analyzed using a Varian AA240 atomic absorption spectrophotometer (AAS). The reaction products were analyzed by Varian 3400 gas chromatograph equipped with a 30-m CP-SIL8CB capillary column and a flame ionization detector.

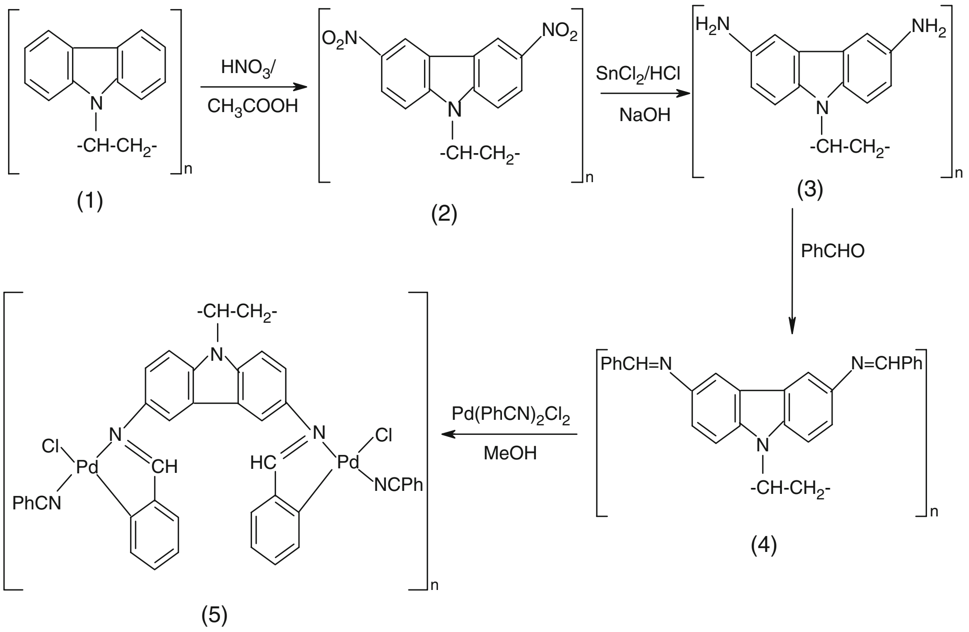
Hydrogenation procedure

The high-pressure hydrogenations of substrates were carried out at a temperature range of 50–90 °C in a 100-mL stainless steel autoclave. A predetermined quantity of substrate (0.5 mol L^{-1}), DMF (10 mL), and catalyst (1.20 mmol L^{-1}) were taken. The autoclave was purged with pure hydrogen gas three times to replace air and then subjected to the desired pressure of hydrogen. The autoclave was heated, stirring, started and the reaction time accounted. At the end of the reaction, the autoclave was cooled by flowing water to quench the reaction. The reaction products were analyzed by GC and GC–MS.

Preparation of Pd(II) poly(3,6-dibenzaldimino *N*-vinylcarbazole) complex catalyst

The outline for the preparation of poly(*N*-vinylcarbazole)-anchored Pd(II) complex [Pd(C$_6$H$_4$CH=N–P)(PhCN)Cl] (P = poly *N*-vinylcarbazole) is shown in Scheme 1.

The *p*-nitro functionalized poly(*N*-vinylcarbazole) was prepared by following the method of King and Sweet [30].



Scheme 1 Synthesis of polymer anchored Pd(II) complex

Poly(*N*-vinylcarbazole) (**1**) (5 g) was taken in 100 mL of 1,2-dichloroethane. A mixture containing 25 mL of concentrated HNO_3 and 50 mL of glacial acetic acid was added dropwise at room temperature to the above suspension with constant stirring and refluxed for 8 h. The resulting yellowish brown polymer was filtered, washed thoroughly with acetic acid, water, tetrahydrofuran, acetone in order and then dried under vacuum. Then a mixture containing stannous chloride (10 g) in concentrated hydrochloric acid (HCl) (12 mL) was added to the suspension of yellowish brown poly(3,6-dinitro *N*-vinylcarbazole) (**2**) (5 g) in 20 mL of acetic acid [30]. The mixture was stirred at room temperature for 48 h to reduce the nitro compound to the corresponding amine hydrochloride. The resulting yellow polymer was filtered, washed successively with water, tetrahydrofuran (THF), methanol, and acetone. The yellow polymer obtained as amine hydrochloride was dried under vacuum. The resulted poly(*N*-vinylcarbazole-3,6-diamine hydrochloride) after repeated treatment with 5% alcoholic NaOH solution for 6 h yielded corresponding amine (**3**). Then a suspension of poly(3,6-diamino *N*-vinylcarbazole) (3 g) in dry toluene (30 mL) medium containing 10-mL benzaldehyde was refluxed under nitrogen for 72 h using Dean–Stark apparatus. Then the material was washed thoroughly with toluene, tetrahydrofuran, and methanol and dried to yield the Schiff base ligand anchored to poly(*N*-vinylcarbazole) (**4**). The orthometallated complex of Pd(II) with poly(3,6-dibenzaldimino *N*-vinylcarbazole) ligand was prepared following the method of Kharasch et al. [31]. A suspension of the respective dried Schiff base ligand (**4**) in a slightly warm methanolic solution (25 mL) of $Pd(PhCN)_2Cl_2$ (0.7 g) was first stirred for 48 h at room temperature and then refluxed in a water bath for 3 h when the yellow polymer material slowly changes to brown and no further color change occurred on further refluxed. The resulting poly(*N*-vinylcarbazole)-anchored Pd(II) complex (**5**) was filtered and washed successively with tetrahydrofuran, methanol, and finally dried under vacuum.

Characterization

Due to insolubilities of the functionalized polymers and anchored Pd(II) complex in all common solvents, their structural investigations were limited to their physicochemical properties, chemical analysis, SEM, TGA-DTA, IR, and UV–Vis spectral data. Elemental analysis of the ligand and metal complex (Table 1) supports the formulation of the complex as proposed. From the data it is clear that the obtained values of the catalyst are quite comparable with the calculated values. The metal content of poly(3,6-dibenzaldimino *N*-vinylcarbazole)-anchored Pd(II) complex determined by atomic absorption spectroscopy suggested 9.48-wt% Pd, in the immobilized metal complex.

In Fig. 1, the SEM image of the poly(3,6-dibenzaldimino *N*-vinylcarbazole) ligand (Fig. 1a) and its metal complex (Fig. 1b) is shown. The morphological change in the polymer-anchored ligand and immobilized Pd(II) complex is quite evident from these images and suggesting the loading of palladium metal on the surface of the polymer matrix. EDX analysis shows the metal content along with C, N, and Cl, suggesting the formation of metal complex with the anchored ligand at various sites. The attachment of palladium metal on the polymer matrix was confirmed from this SEM image and EDX data.

IR data of polymer-anchored metal complex and its precursors are presented in Table 2. Poly(3,6-dinitro *N*-vinylcarbazole) was yellowish brown in color and showed characteristic IR peaks at 1600, 1585, 1490, 1520, and 1340 cm^{-1}. The strong absorption peaks at 1520 and 1340 cm^{-1} (v NO_2 vibration, aromatic) were new and absent in the original polymer. The polymer P-NO_2 is reduced to the corresponding P-NH_3Cl by the ($SnCl_2$ + HCl) procedure [30]. The estimation of chloride and nitrogen in P-NH_3Cl suggests approximately 90% reduction of P-NO_2 which is also supported by the reduced intensity of v NO_2 peaks and appearance of a new peak at 2550 cm^{-1} due to v NH_3Cl moiety [30]. The amine hydrochloride can be completely converted to the

Table 1 Analytical data of the functionalized polymers and the Pd(II) complex

Compound	Color	Cl (%)	C (%)	H (%)	N (%)	Pd (%)
poly(N-MeCz)	Faint yellow		87.05	5.70	7.25	
poly(N-MeCz)-NO_2	Yellowish brown		76.04 (75.70)	4.51 (4.67)	10.19 (10.35)	
poly(N-MeCz)-NH_3Cl	Yellow	7.92 (8.01)	73.97 (74.48)	5.21 (5.36)	10.01 (10.18)	
poly(N-MeCz)-NH_2	Yellow		81.85 (82.14)	5.60 (5.63)	11.12 (11.23)	
[(C_6H_4CH=N–P)(PhCN)Cl]	Yellow		84.71 (84.79)	5.34 (5.41)	8.91 (8.99)	
[Pd(C_6H_4CH=N–P)(PhCN)Cl]	Yellowish brown	3.09 (3.14)	73.90 (73.92)	4.45 (4.69)	8.20 (8.29)	9.48 (9.44)[a]

poly(N-MeCz) = poly(*N*-vinylcarbazole)

Figure in parenthesis indicate the calculated value

[a] Pd content after fifth recycle of the catalyst

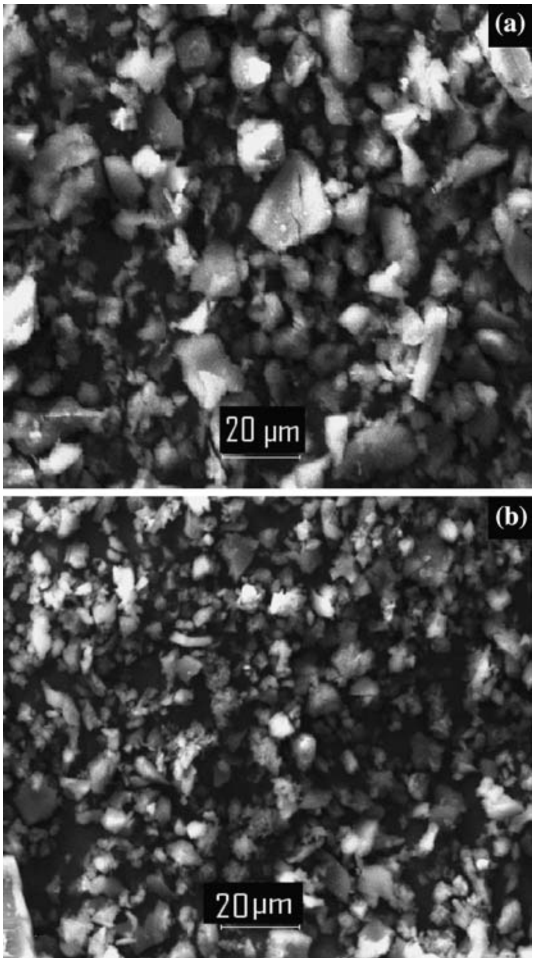


Fig. 1 FE SEM image of poly(3,6-dibenzaldimino *N*-vinylcarbazole) ligand (**a**) and poly(3,6-dibenzaldimino *N*-vinylcarbazole) Pd(II) complex (**b**)

corresponding free amine by treatment with 5% alcoholic NaOH solution. The resulting poly(3,6-diamino *N*-vinylcarbazole) showed bands at 3350 and 3400 cm^{-1} corresponding to N–H stretching vibration. The peak at 2550 cm^{-1} due to ν NH_3Cl disappeared completely.

Reaction of the free amine with benzaldehyde produced the corresponding Schiff base ligand. The broad bands due to NH_2 groups (N–H stretching vibration) in the region 3350–3400 cm^{-1} almost disappeared with the appearance of characteristic peaks at 1630 cm^{-1} for poly(3,6-dibenzaldimino *N*-vinylcarbazole) ligand corresponding to –C=N– stretching vibration. This indicated the reaction of $-NH_2$ groups with benzaldehyde to form the corresponding Schiff base. The complex derived from poly(3,6-dibenzaldimino *N*-vinylcarbazole) ligand exhibited important IR peaks at 1620 cm^{-1} (ν –C=N– stretching), 1590 cm^{-1} (ν –C=C– stretching, aromatic), 720 cm^{-1} (orthometallation) [32], 2290 cm^{-1} (ν –C≡N of benzonitrile), 455 cm^{-1} (ν Pd–N) [33], and 355 cm^{-1} (ν Pd–Cl) [4]. The room-temperature magnetic moment of the polymeric Pd(II) complex has been found to be diamagnetic due to spin paired d^8 system [34]. This diamagnetic nature supports the formation of a low-spin square-planar geometry around Pd(II).

The electronic spectrum of the poly(3,6-dibenzaldimino *N*-vinylcarbazole) Pd(II) catalyst has been recorded in diffuse reflectance spectrum mode as $BaSO_4$ disk due to its solubility limitation in common organic solvents. The low-spin Pd(II) complex may exhibit three spin-allowed d–d transitions from lower lying d orbital to higher empty d_{x-y}^{22} orbital, which may be designated as $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1A_{1g} \rightarrow {}^1B_{1g}$, and $^1A_{1g} \rightarrow {}^1E_g$ transitions [35]. In case of carbazole ligand the absorption maxima around 280–320 nm may be attributed to $\pi \rightarrow \pi^*$ transition in carbazole and phenyl moiety and the absorption at higher range (370–440 nm) is due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of imine system in conjugation with the aromatic nuclei. The above bands do not shift much in the corresponding Pd(II) complex as the ligand remains in almost same geometry within the complex except slight blue shift indicates

Table 2 IR data of the complexes

Compound	ν NO_2 (cm^{-1})	ν NH_3Cl	ν C=N– (cm^{-1})	ν N–H stretching	ν –C≡N– (cm^{-1})	Ortho metallation	ν Pd–Cl
poly(N-MeCz)-NO_2	1520(s) 1340(s)						
poly(N-MeCz)-NH_3Cl	1520(w) 1340(w)	2550					
poly(N-MeCz)-NH_2	1520(w) 1340(w)			3350, 3400			
[(C_6H_4CH=N–P)(PhCN)Cl]	1520(w) 1340(w)		1630				
[Pd(C_6H_4CH=N–P)(PhCN)Cl]	1520(w) 1340(w)		1620		2290	720	355

poly(N-MeCz) = poly(*N*-vinylcarbazole)

(*s*) Strong, (*w*) weak

coordination of Pd(II) through imine nitrogen. In the Pd(II) carbazole complex, the bands around 460 and 350 nm may be assigned as $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions, respectively [36].

Thermogravimetric analysis of supported catalyst and its precursor poly(*N*-vinylcarbazole) anchored Schiff base ligand were carried out in an air atmosphere over a temperature range of 30–600 °C with a heating rate of 10 °C min^{-1} TGA–DTA curves of poly(3,6-dibenzaldimino *N*-vinylcarbazole) ligand and supported Pd(II) complex are shown in Fig. 2. The catalyst decomposes in the temperature range 330–500 °C. DTA study reveals that all the decomposition stages are exothermic in nature. The TG profiles as shown in Fig. 2 suggest that polymer-anchored Pd(II) complex degrades at considerably high temperature.

From the different microanalytical and spectral data, probable structure of poly(3,6-dibenzaldimino *N*-vinylcarbazole) Pd(II) complex may be described according to the Scheme 1.

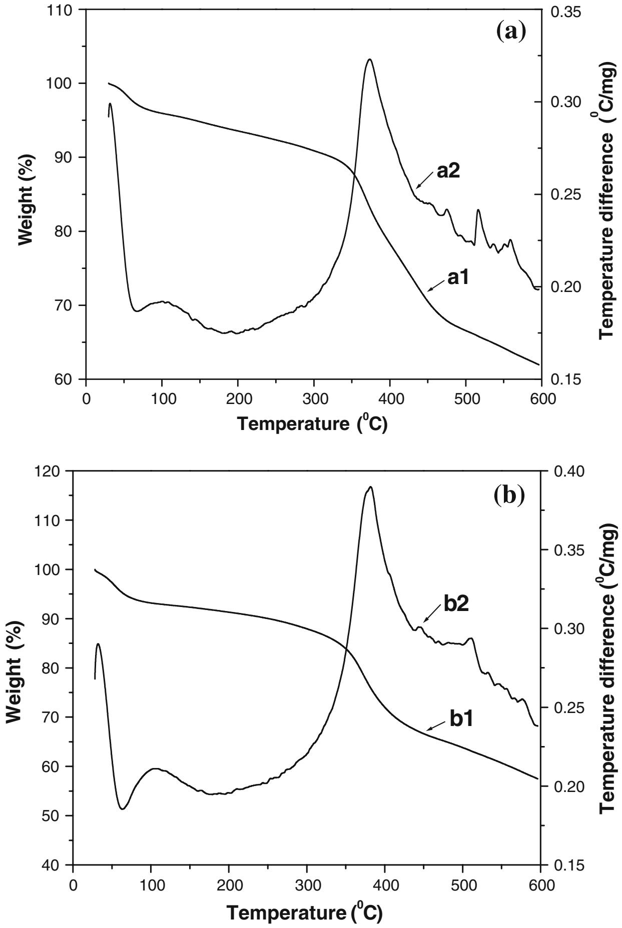


Fig. 2 Thermogravimetric weight loss (*a1* and *b1*) and differential thermal analysis (*a2* and *b2*) of poly(3,6-dibenzaldimino *N*-vinylcarbazole) ligand and poly(3,6-dibenzaldimino *N*-vinylcarbazole) Pd(II) complex, respectively

Results and discussion

The polymer-bound orthometallated complex [Pd(C_6H_4CH=N–P)(PhCN)Cl] (P = poly *N*-vinylcarbazole) was very effective and efficient heterogeneous catalyst for hydrogenation reaction. Reductions of various organic substrates were carried out under high-pressure condition using this catalyst. Nitroalkanes, nitriles, and ketones were reduced under high-pressure of H_2 and at ambient temperature.

The nature and yields of different products, the initial rate of hydrogenation, and the optimum conditions for the reduction of various substrates using [Pd(C_6H_4CH=N–P) (PhCN)Cl] (P = poly *N*-vinylcarbazole) under high-pressure conditions are presented in Table 3.

Effect of solvent

Among different organic solvents, DMF was found to be the best solvent for these catalytic hydrogenation processes under high-pressure condition. The rate of hydrogenation was found to be slow in stronger coordinating solvent like THF, dioxin, and was immeasurably slow in non-coordinating solvents like toluene, chloroform, petroleum ether, benzene, etc. The reductions were however possible only in polar solvents having mild coordinating power likes DMF. It appeared that some type of interaction between the solvent and complex is required for activating the metal complex. In completely non-coordinating media, the intermediate decomposes so fast that the substrate do not get chance to coordinate with the metal atom center. The stronger coordinating solvent binds the metal atom too strongly that the substrate is probably unable to replace these solvents from the metal atom center and thus prevents substrate coordination to the metal. Probably a moderately strong coordinating solvent capable of stabilizing the catalytic intermediate is necessary for the progress of the reaction.

Effect of temperature

The reaction temperatures have great influence on the high-pressure hydrogenation reactions. The reactions were carried out at different temperatures ranged from 40 to 90 °C to investigate the effect of reaction temperature on the hydrogenation reactions. Rate of reductions of nitroalkanes were found to be low below 40 °C at a H_2 pressure of 50 bar. Appreciable reduction rate was observed in the temperature range 70–80 °C and the rate remained almost constant above 90 °C. The catalyst did not decompose at all even at a temperature of 120 °C.

Table 3 Substrates and the corresponding product(s) with catalyst [Pd(C_6H_4CH=N–P)(PhCN)Cl] (P = poly *N*-vinylcarbazole) under high-pressure condition

S. no.	Substrates	Product(s)	Hydrogen pressure (bar)	Temp (°C)	Reaction time (h)	Yield (%)	Initial TON (min^{-1})
1	Nitromethane	Methylamine	30	70	3.5	95	7.75
2	Nitroethane	Ethylamine	30	70	3.5	93	7.48
3	1-Nitropropane	1-Aminopropane	35	70	4.5	92	7.03
4	2-Nitropropane	2-Aminopropane	35	70	5	90	6.00
5	Benzil	Dihydrobenzoin	50	80	5	86	5.67
6	Benzonitrile	Dibenzylamine	50	90	5.5	96	7.22
		Benzyl amine				3	
7	Acetonitrile	Diethylamine	50	90	5.5	92	4.45
		Ethylamine				4	
8	Benzoin	Dihydrobenzoin	50	80	6.0	88	4.97
9	Benzophenone	Diphenylmethanol	50	80	4.5	89	12.72
10	Acetophenone	Phenylmethylmethanol	50	80	4.5	88	9.76
11	Acetone	2-Propanol	50	80	5.0	87	5.97

Reaction condition: [Sub] = 0.5 M; [Cat] = 1.20 mmol L^{-1}; medium = DMF

Total volume = 10 mL

Yield refers to GC & GC–MS analysis

Let the percentage of Pd in the catalyst be X; let the no. of mole of Pd per gram of catalyst = $X/100 \times 107$. Let the number of moles of substrate reduced by 1 g of catalyst per minute = Y. The turnover number (TON) = $Y/(X/100 \times 107) = Y \times 100 \times 107/X$

High-pressure hydrogenation

The poly(3,6-dibenzaldimino *N*-vinyl carbazole) Pd(II) complex was found to be very much active toward the reduction of nitroalkanes, nitriles, and ketones under high-pressure and high-temperature condition. The nitroalkanes used in the present investigation were reduced to the corresponding amines at the final stage. They may be arranged in the following order on the basis of their reduction rate:

nitromethane > nitroethane > 1-nitropropane
> 2-nitropropane

Lower nitroalkanes generally reduced at faster rates than the higher ones under identical experimental condition. The reduction rate decreased with increasing branching at the α-carbon atom. Greater steric hindrance experienced by highly branched or higher nitroalkanes during their coordination to the metal atom center may be the cause of their lower rate of reduction. During the reduction of nitroalkanes, corresponding hydroxylamine produced as intermediate product at the initial stage of reaction. From Fig. 3, it is seen that with the progress of reduction the percentage of conversion of hydroxylamine decreases. Alkyl hydroxyl amines were completely reduced to the corresponding amines at the end of reaction.

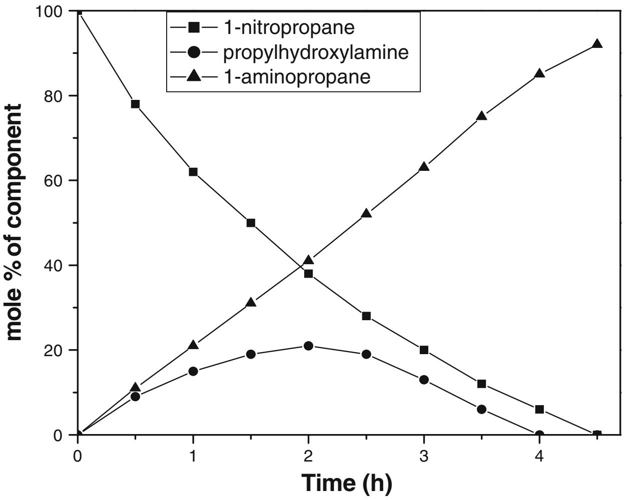
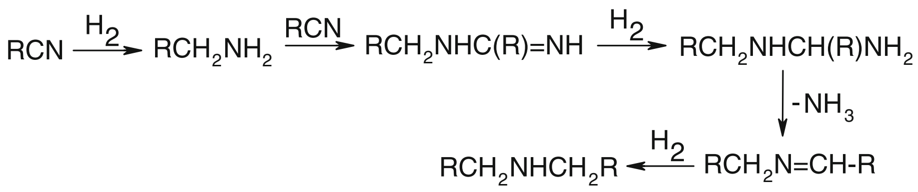


Fig. 3 Reduction of 1-nitropropane with the catalyst [Pd(C_6H_4CH=N–P)(PhCN)Cl] (P = poly *N*-vinylcarbazole). [Cat] = 1.20 mmol L^{-1}; P_{H_2} = 35 bar; medium = DMF; total volume = 10 mL; temp. = 70 °C; [1-nitropropane] = 0.5 M

The present catalyst was active toward the hydrogenation of nitriles, RCN (R = CH_3, Ph) under high-pressure and high-temperature condition. Both primary RCH_2NH_2 (minor) and secondary amines $(RCH_2)_2NH$ (major) were formed at intermediate stages and the final products in both cases were mainly the corresponding secondary amines (~95%). The low selectivity for the formation of RCH_2NH_2 is probably due to the catalytic

Scheme 2 Reduction of nitriles



reaction of the latter with RCN which was accompanied by the liberation of ammonia and the formation of $(RCH_2)_2NH$.

Initial addition of excess RCH_2NH_2 along with RCN reduced the reaction time slightly but increase the proportion of $(RCH_2)_2NH$ in the final product mixture. The reduction probably occurs as per scheme proposed by Holy et al. [37] (Scheme 2).

The Pd(II) complex reduced the carbonyl compounds, RCOR ($R = CH_3$, Ph), at 80 °C under the hydrogen pressure of 50 bar to their corresponding alcohols. Even under high-pressure condition, carbonyl compounds could be reduced very slowly at low temperature. Under identical reduction condition the reduction rates and yields of product of three substrates vary in the order: benzophenone > acetophenone > acetone. Preferential reduction of benzophenone occurs to the extent of 100% in presence of acetone. The results are presented in Fig. 4. The higher reduction rate of benzophenone is due to its planar structure and the presence of extensive π-electron delocalization of carbonyl group which strongly coordinates with metal complex. Due to non-planar structure of acetone, it weakly coordinates with metal center and give lower yield of product. Hence former undergoes preferential reduction. The diketo compound, benzil undergoes stepwise reduction, first to benzoin and then to dihydrobenzoin.

Reaction kinetics and mechanisms

The kinetics of hydrogenation of 1-nitro propane under high-pressure condition was studied with the present catalyst (**5**) $[Pd(C_6H_4CH{=}N{-}P)(PhCN)Cl]$ (P = poly *N*-vinylcarbazole) in DMF medium. The influence of various parameters on the rate of reactions was studied. The rate was determined by GC analysis of the product composition at different time intervals and the initial rates were determined from graphical extrapolation of the rate curve to zero time.

Variation of catalyst concentration

The influence of catalyst concentration on the rate of hydrogenation of 1-nitropropane was studied over a range of 1.0×10^{-3} to 6.0×10^{-3} mol L^{-1} palladium at a fixed substrate concentration of 0.5 M and constant hydrogen pressure. The rate increased with an increase in catalyst concentration linearly. The results with the catalyst $[Pd(C_6H_4CH{=}N{-}P)(PhCN)Cl]$ are given in Fig. 5. From the

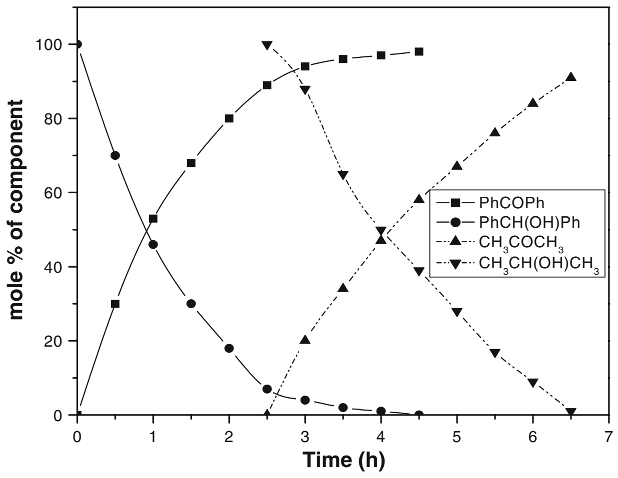


Fig. 4 Preferential hydrogenation of benzophenone in presence of acetone with the catalyst $[Pd(C_6H_4CH{=}N{-}P)(PhCN)Cl]$ (P = poly *N*-vinylcarbazole). [Cat] = 1.20 mmol L^{-1}; $P_{H_2} = 50.0$ bar; medium = DMF; total volume = 10 mL; temp. = 80 °C; [PhCOPh] = 0.5 M; $[CH_3COCH_3] = 0.5$ M

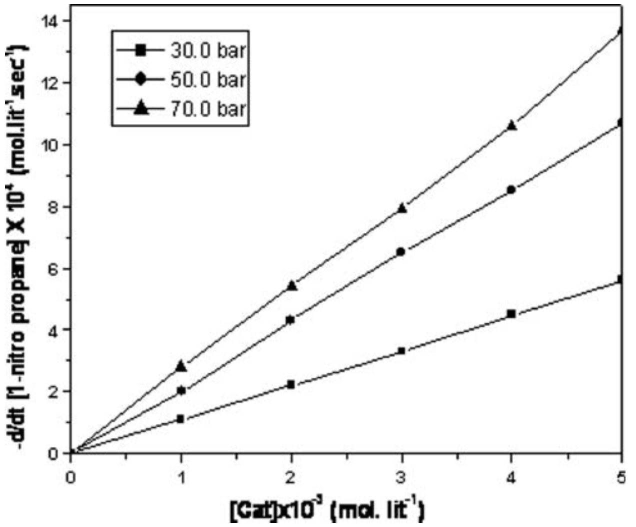


Fig. 5 Rate dependence on catalyst concentration for the reduction of 1-nitropropane with $[Pd(C_6H_4CH{=}N{-}P)(PhCN)Cl]$ (P = poly *N*-vinylcarbazole) as catalyst. [1-nitropropane] = 0.5 M; medium = DMF; total volume = 10 mL; temp. = 70 °C

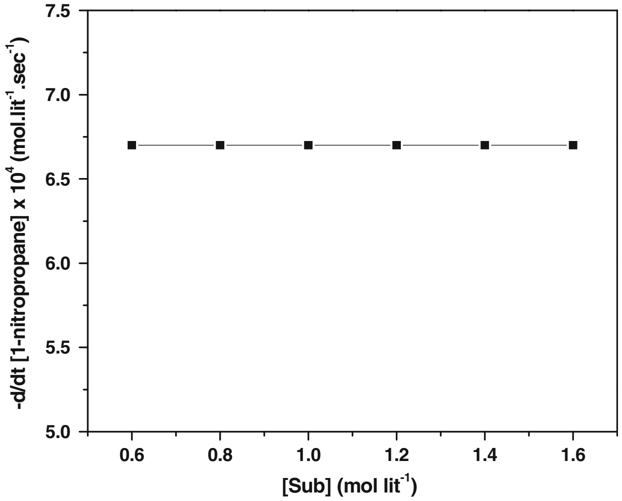


Fig. 6 Rate dependence on substrate concentration for the reduction of 1-nitropropane with [Pd($C_6H_4CH{=}N–P$)(PhCN)Cl] (P = poly *N*-vinylcarbazole) as catalyst medium = DMF; total volume = 10 mL; temp. = 70 °C

figure it is seen that the initial rate of hydrogenation of 1-nitropropane was first order dependent on catalyst concentration.

Variation of substrate concentration

The effect of variation of substrate concentrations on the rate of reduction was studied under high-pressure condition. The substrate concentration was varied from 0.50 to 2.0 mol L^{-1}. The variation of substrate concentration and the corresponding rate of hydrogenation at high pressure are given in Fig. 6. The initial rate of hydrogenation was found independent on substrate concentration in this range.

Variation of hydrogen pressure

The effects of hydrogen pressure on the rate of the reaction are shown in Fig. 7. To analyzed the dependence of hydrogen pressure on the reduction of 1-nitropropane, a series of experiments were carried out by varying the pressure over the range 30–70 bar at 70 °C keeping both the initial substrate concentration (0.5 M) and the catalyst concentration (1.20 mmol L^{-1}) constant. The initial rate of reduction of 1-nitropropane was found to be first order dependent on the hydrogen pressure.

The following tentative mechanism may thus be suggested for the reduction of 1-nitropropane.

According to the Scheme 3

$$\text{Rate} = k_1[7]\,[H_2] \qquad \text{(I)}$$

Let $[\text{Cat}]_T$ = total amount of catalyst (in mol of palladium/L)

$$\text{Then, } [\text{Cat }]_T = [6] + [7] + [8] + [9] + [10] \qquad \text{(II)}$$

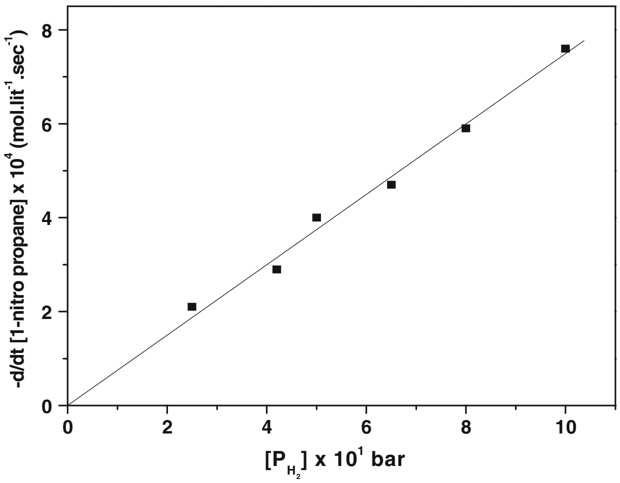


Fig. 7 Rate dependence on hydrogen pressure for the reduction of 1-nitropropane with [Pd($C_6H_4CH{=}N–P$)(PhCN)Cl] (P = poly *N*-vinylcarbazole) as catalyst. [1-nitropropane] = 0.5 M; medium = DMF; total volume = 10 mL; temp. = 70 °C

At equilibrium the rate of formation of (7) is equal to the rate of its decomposition. Now substituting the value of [6], [8], [9], and (10) in Eq. II, we get

$$\begin{aligned}[\text{Cat }]_T &= [6] + [7] + [8] + [9] + [10] \\ &= \frac{[7][\text{DMF}]}{K_1[\text{RNO}_2]} + [7] + k_4[7] + \frac{K_4[\text{RNHOH}][7]}{[\text{RNO}_2]} + \frac{K_5[\text{RNH}_2][7]}{[\text{RNO}_2]}\end{aligned}$$

where $\frac{k_1}{k_2} = k_4$, $\frac{1}{K_1K_2} = K_4$, $\frac{1}{K_1K_3} = K_5$

$$= \frac{[7]\{[\text{DMF}] + (1 + k_4)K_1[\text{RNO}_2] + K_1K_4[\text{RNHOH}] + K_1K_5[\text{RNH}_2]\}}{K_1[\text{RNO}_2]}$$

$$= \frac{[7]\{K_6 + K_7[\text{RNO}_2] + K_8[\text{RNHOH}] + K_9[\text{RNH}_2]\}}{K_1[\text{RNO}_2]}$$

where $[\text{DMF}] = K_6$, $(1 + k_4)\ K_1 = K_7$, $K_4K_1 = K_8$, $K_1K_5 = K_9$

$$[7] = \frac{K_1[\text{Cat}]_T[\text{RNO}_2]}{\{K_6 + K_7[\text{RNO}_2] + K_8[\text{RNHOH}] + K_9[\text{RNH}_2]\}}$$

$$\text{Rate} = \frac{k_1K_1[\text{Cat}]_T[\text{RNO}_2][H_2]}{\{K_6 + K_7[\text{RNO}_2] + K_8[\text{RNHOH}] + K_9[\text{RNH}_2]\}}$$

$$= \frac{k_1K_1[\text{Cat}]_T[\text{RNO}_2][H_2]}{K_6 + K_7[\text{RNO}_2]}$$

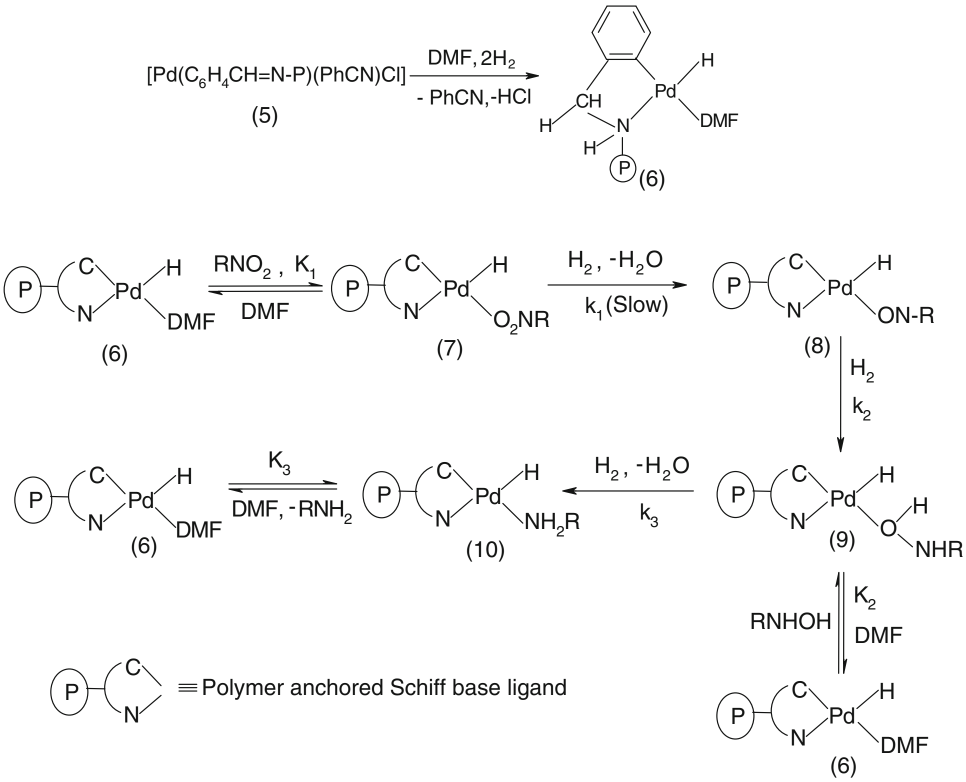
At $t = 0$, $[\text{RNHOH}] \rightarrow 0$, $[\text{RNH}_2] \rightarrow 0$

If $K_6 \ll K_7\ [\text{RNO}_2]$, then

$$\text{Rate} = \frac{k_1K_1[\text{Cat}]_T[\text{RNO}_2][H_2]}{K_7[\text{RNO}_2]} = \frac{k_1K_1[\text{Cat}]_T[H_2]}{K_7}$$

$$\text{Rate} = k'[\text{Cat}]_T[H_2]; \quad \text{Rate} = k\ [\text{Cat}]P_{H_2}$$

Scheme 3 Reduction of 1-nitro propane



Heterogeneity test

The heterogeneity test was performed in the hydrogenation reaction using the present catalyst system. During catalytic hydrogenation of 1-nitropropane, the solid catalyst was separated from the reaction mixture by filtration after 2.5 h and the determined conversion was 72%. The reaction was carried out for a further 2 h. The gas chromatographic analysis showed no increment in the conversion. Atomic absorption spectrometric analysis of the liquid phase of the reaction mixtures collected by filtration confirms that Pd is absent in the reaction mixture. These results suggest that the Pd is not being leached out from the catalyst during hydrogenation reactions.

Recycle of the catalyst

When using a supported metal catalyst, one important point is the deactivation and recyclability of the catalyst. To test the stability and recycling ability as well as leaching of palladium metal from polymer matrix under reaction conditions, recycling experiments were carried out using DMF as solvent. The typical recycling procedure was as follows: after the initial reaction, the catalyst was separated from the reaction mixture, washed, dried under vacuum and the catalytic run was repeated with further addition of substrates in appropriate amount under same reaction conditions. The recovered catalyst is found to exhibit almost the same catalytic activity for hydrogenation reaction. From Fig. 8, it is seen that there was almost no change in catalytic activity even after fifth recycle. Metal content of the recycled catalyst remained unaltered indicating no leaching of the metal from the polymer support (Table 1).

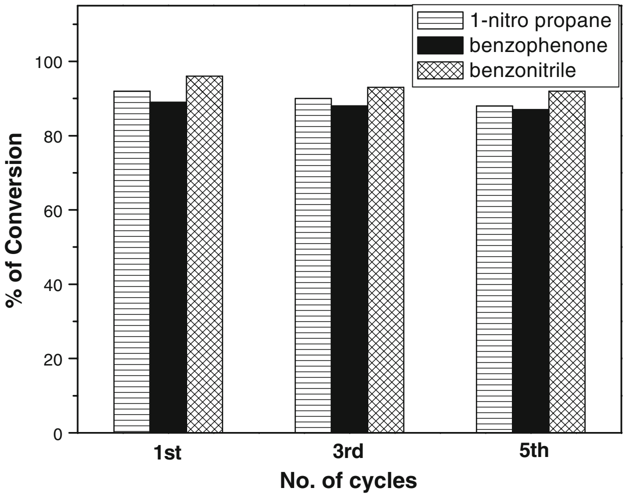


Fig. 8 Recycling activity of polymer-anchored Pd(II) complex catalyst toward the catalytic hydrogenation of organic substrates

Conclusions

In summary, poly(3,6-dibenzaldimino *N*-vinylcarbazole) palladium(II) complex was prepared, characterized, and explored the utility for the liquid phase hydrogenation reactions of various organic substrates under high-pressure condition. DMF was found to be best solvent for these catalytic systems. Easy preparation, handling, stability and moisture insensitivity, easy recoverable and reusable make the catalyst environmentally acceptable. Isolation of the used catalyst from the product mixture encounters no difficulty. The catalyst can be recovered and recycled at least five times with almost constant catalytic activity and product selectivity. Hence, the present catalytic system may find wide application in the synthesis of fine organic chemicals either in the laboratory or on an industrial scale.

Acknowledgements We thank the IACS, Kolkata for providing the instrumental support. One of the authors, K. Tuhina, is thankful to University Grants Commission (Eastern Region), India, for financial support. We acknowledge Department of Science and Technology (DST), Council of Scientific and Industrial Research (CSIR) and University Grant Commission (UGC), New Delhi, India for funding.

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