Reduction of olefins, nitroarenes and Schiff base compounds by a polymer-supported [2-(2′-pyridyl)benzimidazole]palladium complex

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Abstract 2-(2′-Pyridyl)benzimidazole (PBIMH) was functionalized onto chloromethylated polystyrene beads crosslinked with 6.5 % divinylbenzene, and this solid support was then reacted with Na_2PdCl_4 in methanol. The functionalized beads were then activated using sodium borohydride. The resultant polymer-supported [2-(2′-pyridyl)benzimidazole]palladium complex (PSDVB–PBIM–$PdCl_2$) and its activated form were characterized by various physicochemical techniques. XPS studies confirmed the +2 oxidation state of palladium in the supported complex. The activated complex was found to catalyse the hydrogenation of various organic substrates including olefins, nitro and Schiff base compounds. Kinetic measurements for the hydrogenation of cyclopentene, cyclohexene and cyclooctene were carried out by varying temperature, catalyst and substrate concentration. The energy and entropy of activation were evaluated from the kinetic data. The catalyst showed an excellent recycling efficiency over six cycles without leaching of metal from the polymer support, whereas the unsupported complex was unstable as metal leached out into the solution during the first run.

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Introduction

Catalytic hydrogenation of carbon–carbon double bonds has been widely used in production scale synthesis. The development of versatile catalysts for the selective conversion of individual compounds or groups of compounds is an important problem concerning catalytic processes in organic synthesis [1]. The use of supported catalysts has proved to be a useful approach, and the product is often much cleaner than other reduction techniques.

For many years, the selective hydrogenation of unsaturated hydrocarbons has been of major interest to the fine chemical industry. Many catalytic systems have been investigated and palladium supported on conventional inorganic matrices appears to be one of the most selective [2]. Polymer supports have also found significant applications in catalysis [3, 4]. Novel porous polymers such as polystyrene divinyl benzene (PSDVB), which has good stability with simple functionalization of organic groups, have been reported [5–9]. Polymer supports associated with nitrogen-containing ligands have been studied because of their stability to oxidation [10]. Such systems have been applied with various ligands for the hydrogenation of a range of substrates. Catalytic hydrogenation generally gives purer products at lower cost and has thus been investigated in detail [11].

Many metal complexes supported either on inorganic oxides or on polymer supports show better catalytic activity than the equivalent unsupported complexes [12]. The catalytic hydrogenation of nitroaromatic compounds has gained importance as this reaction is used in the production of pharmaceuticals, dye stuffs, plastics and perfumes [13]. The polymer supports are used in solid state synthesis as they are cheap, stable, readily available, chemically inert and can undergo facile functionalization

by simple organic transformations [14, 15]. Some polymer-supported palladium catalysts show good catalytic activity towards oxidation of ethanol and CO, as well as hydrogenation of nitroarenes and coupling reactions [16–19].

We herein describe the coordination of palladium chloride to 2(2′-pyridyl)benzimidazole ligand functionalized PSDVB and its catalytic activity towards hydrogenation of various organic compounds. As a supported heterogeneous catalyst, it exhibits high activity, selectivity and excellent recyclability. On the basis of a kinetic study, the rate equation and a plausible reaction mechanism are presented.

Experimental

Materials and equipment

Chloromethylated polystyrene divinyl benzene copolymer with 6.5 % crosslinking (PSDVB) was obtained from Thermax Ltd., Pune, India. Sodium tetrachloropalladate [Na_2PdCl_4] was purchased from Arora Matthey Ltd.; 2(2′-pyridyl)benzimidazole was prepared according to the literature method [20]. Olefins, nitro compounds and other laboratory grade solvents were purified according to the literature methods before use [21]. Benzylideneaniline and its derivatives were prepared according to the literature method [22]. Elemental analyses were obtained with an Elementar Vario MICRO cube CHNS analyser. Surface area measurements using the Brunauer, Emmett and Teller (BET) method were carried out with a Micromeritics surface area analyser model ASAP 2020. Palladium was determined by AAS using a double-beam atomic absorption spectrometer ECIL make, after digestion of the polymer-supported catalyst with concentrated sulphuric acid and subsequent decomposition with H_2O_2. Chloride content was determined by Volhard's method and palladium content by using atomic absorption spectrophotometer. XPS was recorded at the MRC department, IISc,

Bangalore, using a MultiLab 2000 Thermo Scientific instrument, UK. Far-IR spectra were recorded using a Thermo Nicolet 6700 instrument, SID, IISc, Bangalore. Thermogravimetric analyses of the polymer support and the anchored complex were carried out using a TA Instrument, SDT analyser model Q 600, under nitrogen atmosphere with heating rate of 10 °C min^{-1}. GC was recorded on a Shimadzu 14 B using BP5 capillary column. HPLC were recorded with Shimadzu using a C18 column with UV detector. The unsupported complex $PdCl_2$ (PBIMH) was prepared according to the literature method [23].
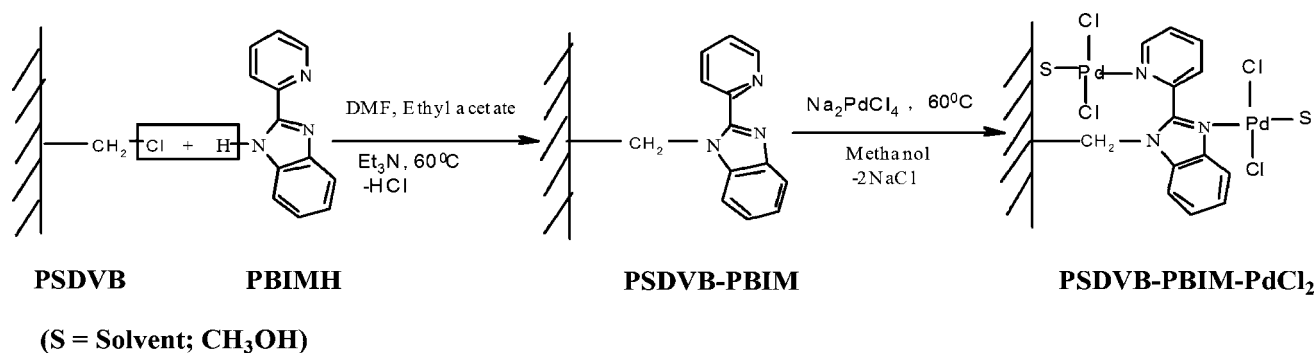
Preparation of the catalyst

PSDVB (1.0 g) was allowed to swell in DMF (10 mL) for 2 h. A DMF solution (20 mL) of PBIMH (1.310 g, 6.72 mmol) was added to the suspension, followed by a solution of triethylamine (3 mL) in ethyl acetate (35 mL). The reaction mixture was heated for 35 h at 60 °C. After cooling to room temperature, the cream-coloured beads were filtered off, washed with hot DMF, Soxhlet extracted with ethanol to remove unreacted ligand and dried in air at 120 °C.

Functionalized beads (3 g) were soaked in 50 mL of toluene and acetonitrile mixture (1:1 ratio) for 1 h and then filtered off. A solution of Na_2PdCl_4 (1.42 g) in methanol (50 mL) was then added and heated at 60 °C for 32 h. The resulting reddish-brown beads were filtered off, Soxhlet extracted with ethanol and dried under vacuum. The anchored beads (3 g) were treated with $NaBH_4$ (0.5 g, 13.3 mmol) in methanol (100 mL) for 15 min, then filtered out, washed with methanol, Soxhlet extracted with ethanol and dried (Scheme 1).

Catalytic hydrogenation procedure

The polymer-supported palladium complex (0.30 g) was added to superdry methanol (30 mL). The mixture was

PSDVB　　**PBIMH**　　　　　　　　**PSDVB-PBIM**　　　　　　**PSDVB-PBIM-PdCl$_2$**

(S = Solvent; CH$_3$OH)

Scheme 1 Preparation of the polymer-supported palladium complex

saturated in an atmosphere of hydrogen for ca. 1 h. The system was evacuated several times and again saturated with hydrogen gas for 30 min. A known quantity of organic substrate was injected into the reaction mixture, followed by releasing the system to a gas burette filled with hydrogen gas. The reaction was monitored by the change in the volume of the hydrogen absorbed at equal periods of time. The obtained products were identified by IR spectroscopy, melting point, TLC and gas chromatography/HPLC.

Blank reactions carried out in the absence of catalyst showed that reduction of organic substrates did not take place under these conditions. When the reaction was performed with PdCl$_2$(PBIMH) in methanol, the complex was found to be unstable, decomposing to the metal.

Results and discussion

Characterization of the polymer-bound catalyst

Functionalized, anchored and the activated polymer beads were characterized by microanalysis, spectroscopic studies and TGA measurements. The elemental analyses at various stages of preparation of the polymer-supported complex are given in Table 1. The presence of nitrogen and decrease in chloride content upon treatment of the beads with PBIMH indicated their successful functionalization. Increase in chloride content after reaction with PdCl$_2$ indicated that the metal salt was anchored onto the functionalized polymer. The metal contents on activation and recycling of the polymer-supported complex indicated that leaching of the metal did not occur. Decrease in surface area and pore volume on treatment with NaBH$_4$ was observed, which may be attributed to blockage of the pores of the polymer support after activation [24].

To study the effect of metal loading upon the polymer, different amounts of metal salt (2, 5, 10 and 12.78 %) were loaded and 12.78 % of Pd proved to be the maximum loading possible. The initial rate for the reduction of olefin was calculated for each of these samples. A plot of initial
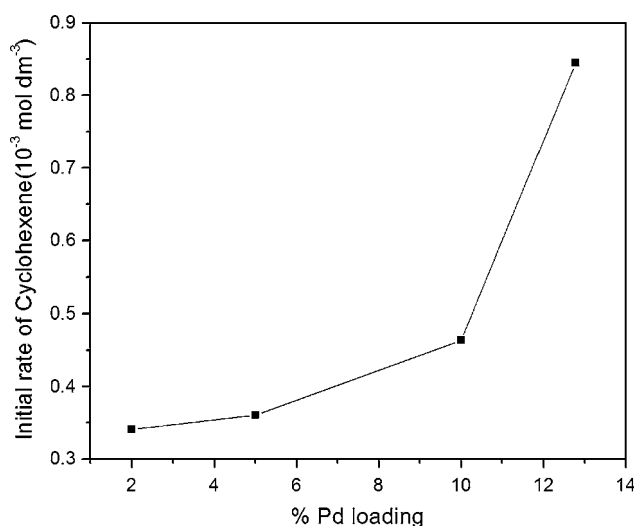

Fig. 1 Studies on metal loading on the polymer-supported complex

rate versus % metal loading as depicted in Fig. 1 showed that the polymer-supported complex worked well at higher metal concentrations such that the initial rate was highest for 12.78 % Pd loading.

Swelling studies of both the polymer and the polymer-anchored complex were carried out in different solvents, namely methanol, ethanol, acetonitrile, DMSO, DMF, THF, benzene, acetone, toluene, ethyl acetate and water. It was observed that swelling of the beads was greater in DMF, DMSO and methanol. Maximum swelling was in DMF, followed by DMSO. Nevertheless, hydrogenation reactions were carried out in methanol, since the solubility of hydrogen is higher in this solvent compared to the others (0.068 mL hydrogen/mL of methanol; 0.037 mL of hydrogen/mL of DMF) [25–27].

Thermogravimetric analysis

Thermogravimetric analyses of the catalyst were carried out at various stages of the preparation. The TGA experiments showed that the polymer beads were stable up to 290 °C, whereas the catalyst PSDVB–PBIM–PdCl$_2$ was

Table 1 Elemental analysis of the polymer support and polymer-supported complex

Parameters	% Metal (Pd)	% C	% H	% N	% Cl	N/Pd	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})
Polymer beads PSDVB	–	73.9	6.2	–	18.2	–	20.8	0.24
Functionalized beads with PBIM	–	66.9	8.8	4.3	8.2	–	17.8	0.18
Functionalized beads with PBIM anchored with Na$_2$PdCl$_4$	15.2	55.6	6.8	3.7	13.8	0.24	15.7	0.14
Activated beads								
PSDVB–PBIM–PdCl$_2$	12.8	57.3	7.1	3.7	9.1	0.29	13.2	0.12
Activated beads recycled over six cycles	12.6	57.7	7.2	3.5	9.0	0.28	12.7	0.11

stable up to 238 °C, suggesting that the supported complex was less thermally stable than the polymer support (Supplementary data).

Spectroscopic studies

The IR spectra of chloromethylated beads (Fig. 2, spectrum A), PSDVB functionalized with PBIMH (Fig. 2, spectrum B), polymer-bound PBIMH anchored with palladium (Fig. 2, spectrum C) and activated polymer-bound complex (Fig. 2, spectrum D) were recorded in Nujol. PSDVB exhibited a peak at 1263 cm^{-1} attributed to $-CH_2Cl$ (spectrum A), whilst free PBIMH showed υ_{N-H} around 3400 cm^{-1}. The intensity of the former peak decreased and the latter peak was absent after functionalization of the polymer support, indicating that the N–H hydrogen of PBIMH was deprotonated and the heterocycle bonds to the polymer support through nitrogen. Decrease in intensity of the peak at 826 cm^{-1} attributed to υ_{C-Cl},
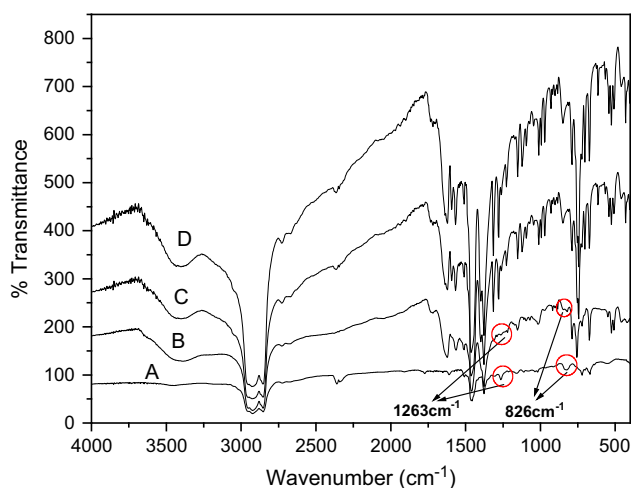

Fig. 2 Overlay of the IR spectra of: (A) PSDVB, (B) PSDVB–PBIMH, (C) PSDVB–PBIM,–PdCl$_2$ and (D) activated PSDVB–PBIM–PdCl$_2$

further confirmed successful derivatization of the polymer support. The far-IR spectrum of the polymer-bound palladium chloride complex exhibited a peak around 330 cm^{-1} which was assigned to terminal υ_{Pd-Cl} [10], whilst υ_{Pd-N} was observed at 286 and 257 cm^{-1} (Supplementary data).

The diffuse reflectance spectra of the anchored complex and the activated catalyst PS(PBIM)PdCl$_2$ exhibited absorption bands around 495 and 493 nm, respectively, typical of d^8 configuration due to $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions of square planar Pd(II) complexes (Supplementary data).

The XPS spectra were recorded for the catalyst before and after activation, in order to characterize the oxidation state of palladium by fixing the binding energy values of C1s at 285 eV [28] (Supplementary data). The XPS spectrum of the catalyst prior to activation showed peaks at 337.7 and 342.9 eV assigned to $3d_{5/2}$ and $3d_{3/2}$, respectively (Fig. 3a), revealing the presence of palladium(II). The activated beads (Fig. 3b) showed peaks at 337.5 eV ($3d_{5/2}$) and 343.0 eV ($3d_{3/2}$). After recycling the activated complex (Fig. 3c) for six times, the catalyst was subjected to XPS analysis. It gave peaks at 337.9 ($3d_{5/2}$) and 343.1 ($3d_{3/2}$), indicating that there was no change in the oxidation state of palladium (Fig. 3).

Structure of the supported complex

If the ligand acts as a chelating bidentate ligand, the expected N/Pd ratio is 0.40. However, the obtained experimental N-to-Pd ratio is 0.24. These values suggest that the ligand acts in a bridging bidentate mode and that some of the ligands present on the polymer beads may not be available for coordination to the metal. The polymer-supported complex exhibited two υ_{Pd-N} peaks at 257 and 286 cm^{-1}. One may be due to coordination of Pd to the pyridine N and the other may be due to coordination of metal to the nitrogen of the benzimidazole ring. Although there are three nitrogen atoms in the ligand, only two are available for bonding to the metal. Hence, the ligand does
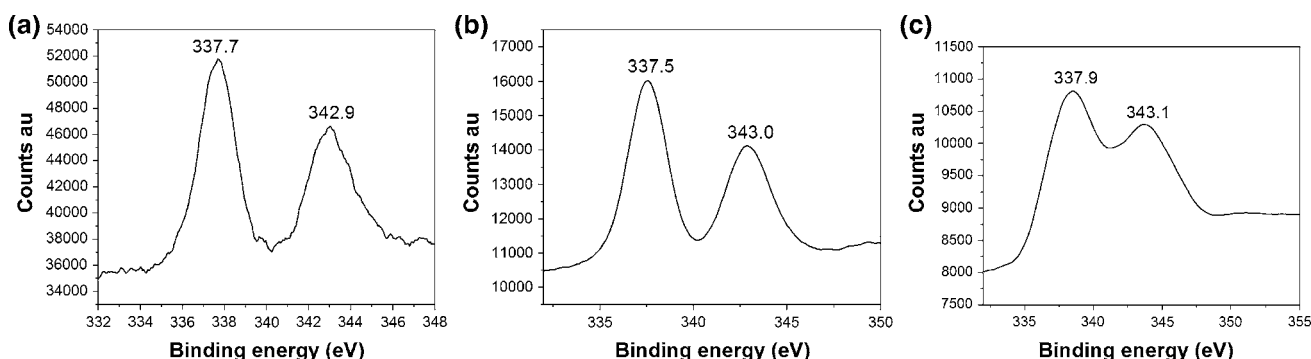

Fig. 3 XPS spectra of anchored PSDVB–PBIM–PdCl$_2$, activated PSDVB–PBIM–PdCl$_2$ and recycled PSDVB–PBIM–PdCl$_2$. **a** Anchored PSDVB–PBIM–PdCl$_2$, **b** activated PSDVB–PBIM–PdCl$_2$ and **c** recycled PSDVB–PBIM–PdCl$_2$

Table 2 Initial rate of hydrogenation of various [substrates] $= 4.930 \times 10^{-3}$ mol dm^{-3} by [PSDVB–PBIM–PdCl$_2$ complex] $= 1.2 \times 10^{-4}$ mol of Pd at 30 °C with 596 mm Hg hydrogen pressure in 30 mL methanol

No.	Substrates	Initial rate (10^{-3} mol dm^{-3} min^{-1})	Products	Time (min)	% Conversion[a]	TON[b]
1	1-Hexene	1.143	n-Hexane	40	96	571
2	1-Heptene	0.684	n-Heptane	45	78	342
3	1-Octene	0.373	n-Octane	35	92	93
4	Cyclopentene	0.897	Cyclopentane	50	72	449
5	Cyclohexene	0.845	Cyclohexane	58	88	422
6	Cyclooctene	0.768	Cyclooctane	85	91	384
7	Diethylmaleate	1.011	Diethylsuccinate	60	68	506
8	Diethylfumarate	0.495	Diethylsuccinate	60	95	248
9	Styrene	0.962	Ethylbenzene	54	84	481
10	1,5-Cyclooctadiene	0.452	Cyclooctene, cyclooctane	130	82	226
11	2,5-Norbornadiene	0.837	Norbornene, norbornane	105	95	419
12	Cinnamaldehyde	0.682	Phenylpropanal	140	94	341
13	Cinnamonitrile	0.955	Phenylpropionitrile	130	96	478
14	Ethyloleate	0.421	Ethyloctadecanoate	130	84	210
15	Crotonaldehyde	0.813	n-Butanal	70	79	407
16	Benzylideneaniline	1.026	N-Benzylaniline	50	68	513
17	p-Chlorobenzylideneaniline	0.553	N-(4-Chlorobenzyl)aniline	90	75	276
18	p-Hydroxybenzylideneaniline	0.858	4-(Anilinomethyl)phenol	80	92	429
19	p-Methoxybenzylideneaniline	0.825	N-(4-Methoxybenzyl)aniline	77	86	412
20	p-Nitrobenzylideneaniline	0.956	4-Nitrobenzylaniline	97	72	478
21	Nitrobenzene	1.299	Aniline	80	82	650
22	p-Nitroaniline	1.963	p-phenylenediamine	65	76	981
23	p-Nitrophenol	1.365	p-Aminophenol	80	86	683
24	p-Nitrotoluene	1.325	p-Toluidine	92	70	663
25	p-Nitrobenzoic acid	1.265	p-Aminobenzoic acid	100	72	633

[a] Conversions are as per GC/HPLC analysis

[b] TON = Initial rate/[catalyst] $\times$ 60 mol (g atom Pd)$^{-1}$ h^{-1}

Table 3 Initial rate of hydrogenation of cyclohexene with various solvents (30 mL) using [activated catalyst] $= 1.2 \times 10^{-4}$ mol dm^{-3} and [substrate] $= 5 \times 10^{-3}$ mol dm^{-3} at 30 °C with 596 mm Hg hydrogen pressure using 30 mL of the solvents

Solvent	Initial rate (10^{-3} mol dm^{-3} min^{-1})
Methanol	0.545
Ethanol	0.412
Acetonitrile	0.126
Toluene	0.048
Benzene	0.105
Dimethyl sulphoxide	0.009
Dimethyl formamide	0.053
Acetone	0.299
Ethylacetate	0.585
Tetrahydrofuran	0.351
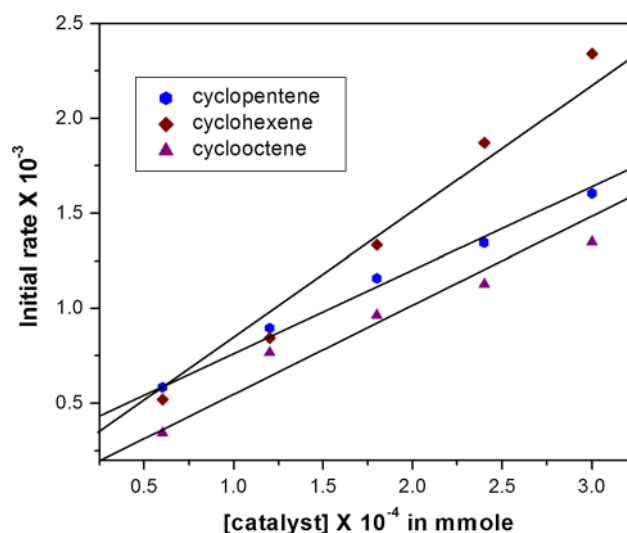
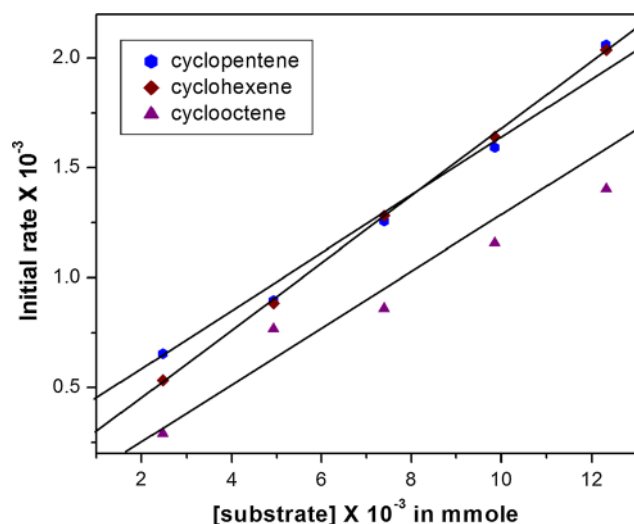**Fig. 4** Dependency of initial rate of hydrogenation on [catalyst]

Fig. 5 Dependency of initial rate of hydrogenation on [substrate]
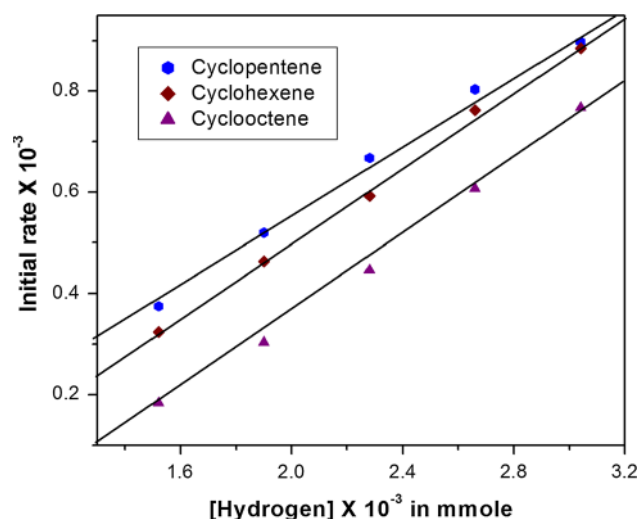

Fig. 6 Effect of partial pressure of hydrogen

not act in a chelating bidentate mode but rather a bridging bidentate mode, such that the suggested structure of the polymer-supported complex is as given in Scheme 1.

Catalytic hydrogenation reactions

Hydrogenation reactions were carried out for olefins, nitro and Schiff base compounds using PSDVB–PBIM–PdCl$_2$ as catalyst. Although the polymer complex was found to be active for hydrogenation reactions, the initial rate of the reaction was very slow. Hence, it was activated using sodium borohydride, resulting in enhanced catalytic activity. This activated form of the catalyst was used in all subsequent hydrogenations. The initial reaction rates for various substrates are presented in Table 2. The percentage conversion is as per GC/HPLC analysis.

The hydrogenation of open-chain olefins was generally faster compared to closed-chain olefins. The nature of the double bond structure and the substituent present on the olefins all influence the rate of hydrogenation, by virtue of their tendency to form a complex with the catalyst. 2,5-Norbornadiene reduces at a faster rate compared to the non-conjugated diene (1,5-cyclooctadiene) due to its highly strained nature. Under identical experimental conditions, the rate of hydrogenation of terminal olefins decreased with increasing length of the carbon chain.

Hydrogenations of a few nitro and Schiff base compounds were carried out using [catalyst] $= 1.2 \times 10^{-4}$ mol of Pd, [substrate] $= 4.930 \times 10^{-3}$ mol dm^{-3} at 30 °C, 596 mm of hydrogen in 30 mL of methanol. Hydrogenation of the Schiff base, *p*-nitrobenzylideneaniline gave 4-nitrobenzylaniline, indicating selective hydrogenation of C=N in the presence of a NO$_2$ group. This is in contrast to our earlier studies, in which a polymer-supported imidazole complex used for the catalytic hydrogenation of *p*-nitrobenzylideneaniline gave *p*-aminobenzylaniline and selectivity was not observed [29]. For the nitro compounds, the initial rate was found to be higher for the compounds having electron donating groups but lower in the presence of electron withdrawing groups, as compared to nitrobenzene.

Kinetics of the hydrogenation of olefins

The kinetics of hydrogenation of cyclopentene, cyclohexene and cyclooctene were studied, varying the temperature, concentration of catalyst, substrate and hydrogen, in order to obtain the experimental rate law. In order to study the solvent effect on the rate of the reaction, the rate of hydrogenation of cyclohexene in various solvents was also studied (Table 3). The initial rate of hydrogenation was calculated from the plot of the volume of hydrogen consumed as a function of time. The hydrogenation of cyclohexene was carried out at constant [cyclohexene] $= 5 \times 10^{-3}$ mol dm^{-3}, [catalyst] $= 1.2 \times 10^{-4}$ mol dm^{-3}, temperature $= 30$ °C, at 596 mm of Hg hydrogen pressure using 30 mL of solvent. Initial rate of hydrogenation was the highest in methanol. Dimethylformamide and dimethyl sulphoxide, although polar, may coordinate strongly with the catalyst and so hinder coordination of hydrogen and/or olefin with the catalyst, resulting in low reaction rate. The higher solubility of hydrogen in methanol as compared to DMF and DMSO would also enhance the rate [30, 31]. Hence, methanol was used as solvent for the hydrogenation of olefins and also for nitro compounds and Schiff bases (Table 3).

The influence of catalyst concentration upon the rate was studied in the concentration range 0.5981×10^{-4} to 2.990×10^{-4} mol dm^{-3} Pd (Fig. 4). The order of reaction was calculated from the slope of the plot of log [initial rate]

Scheme 2 Plausible reaction mechanism
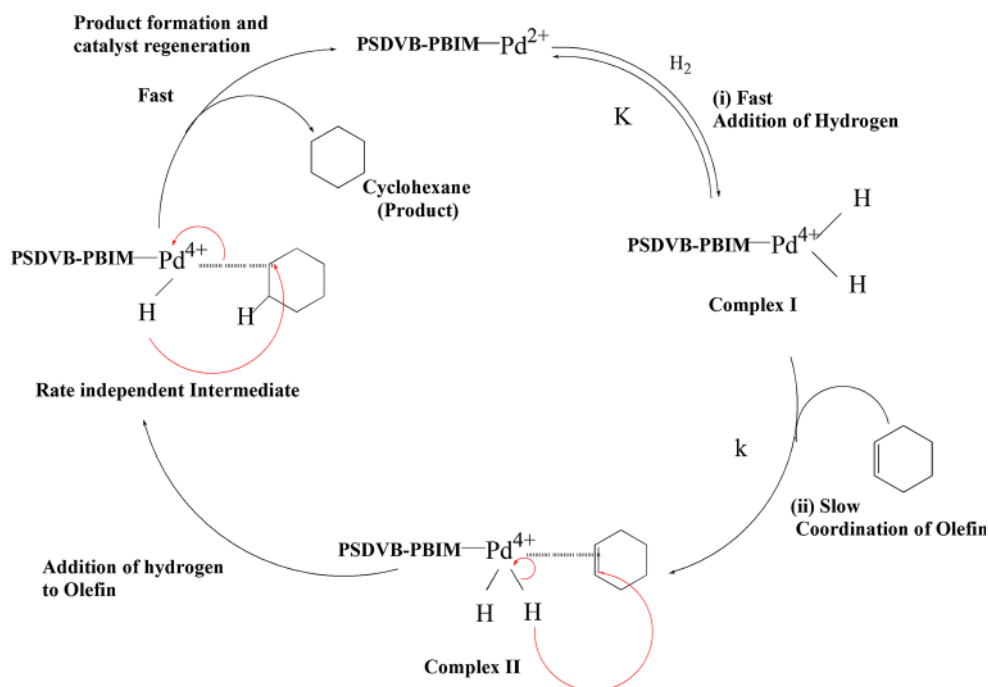
versus log[catalyst] at fixed $(4.930 \times 10^{-3}$ mol dm$^{-3})$ substrate concentration, 596 mm of Hg pressure of hydrogen at 30 °C, and was found to be first order.

Next, the effect of substrate concentration on the rate was studied in the range 2.465×10^{-3} to 12.320×10^{-3} mol dm^{-3} at fixed catalyst concentration $(1.196 \times 10^{-4}$ mol dm^{-3} of Pd), 596 mm of Hg pressure of hydrogen at 30 °C. The reaction again followed first-order kinetics (Fig. 5).

The hydrogenation of cyclopentene, cyclohexene and cyclooctene was carried out at different partial pressures of hydrogen with [catalyst] = 1.2×10^{-4} mol of Pd, [substrate] = 4.930×10^{-3} mol dm^{-3}. The concentration of dissolved hydrogen was calculated using Henry's law [32]. Hydrogenation was carried out at different concentrations of hydrogen at 30 °C in 30 mL of methanol. The order of the reaction was found to be fractional under these conditions (Fig. 6).

Reaction mechanism and rate law

The hydrogenation of olefins followed first-order kinetics with respect to catalyst and substrate concentration and fractional-order kinetics with respect to hydrogen concentrations between 3.04×10^{-3} and 1.52×10^{-3} mol. Based on these results, a plausible mechanism is proposed as shown in Scheme 2, from which a rate Eq. (1) was derived (Supplementary data).

$$\text{Rate} = \frac{Kk[\text{Catalyst}]_t[\text{Cyclohexene}][\text{Hydrogen}]}{1 + K[\text{Hydrogen}]} \quad (1)$$

The effect of temperature on the rate of hydrogenation was studied in the range of 25–45 °C at fixed substrate and catalyst concentrations with hydrogen pressure 596 mm of Hg. The values of the activation energy and entropy were calculated from the Arrhenius plot (Fig. 7) and are given in Table 4.
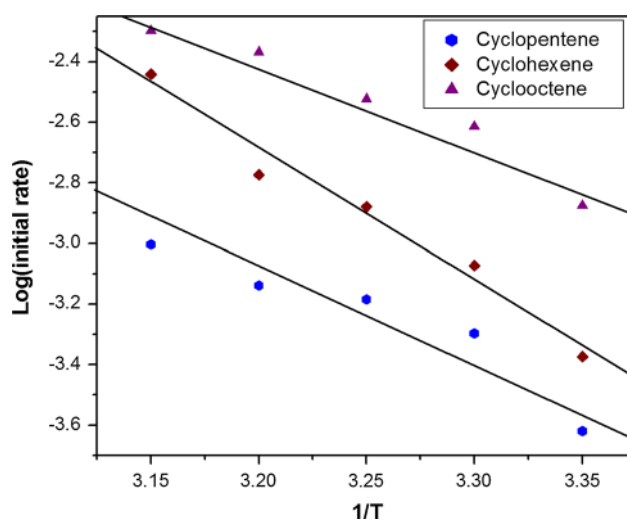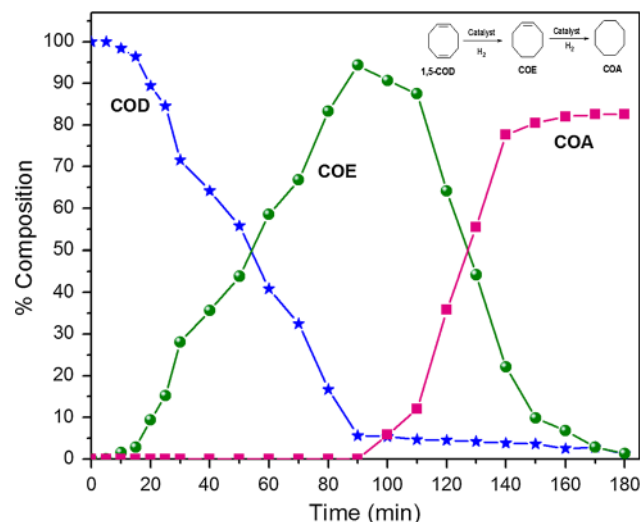

Fig. 7 Arrhenius plot

Table 4 Activation energy and activation entropy for the hydrogenation reaction

Substrate	Activation energy (kJ mol^{-1})	Activation entropy (J K^{-1}mol^{-1})
Cyclopentene	21	−275
Cyclohexene	33	−237
Cyclooctene	42	−192

Fig. 8 Sequential hydrogenation of 1,5-cyclooctadiene

Sequential hydrogenation of 1,5-cyclooctadiene

1,5-Cyclooctadiene (COD) was found to undergo sequential hydrogenation, as shown by GC analysis. COD was first converted into cyclooctene (COE) then to cyclooctane (COA). The overall reaction took place in 180 min. Formation of COA commenced after 90 min of the reaction. The COE concentration was found to be highest at 100 min, with 90.7 % conversion at this point. When the reaction was continued, COA was obtained in 82 % yield. The preferential coordination of 1,5-COD onto the anchored catalyst as compared to COE may be the reason for the sequential hydrogenation (Fig. 8).

Selective catalytic hydrogenation

The catalyst was investigated for the selective hydrogenation of C=C bonds in the presence of other functional groups, namely CO and CN. Crotonaldehyde, cinnamaldehyde and cinnamonitrile were chosen as the substrates. Upon hydrogenation of crotonaldehyde, n-butanal was formed with 79 % conversion, whilst cinnamaldehyde gave phenylpropanal (94 %), indicating that the catalyst is selective towards reduction of C=C bonds in the presence of CO. The final product was confirmed by GC–MS analysis (Supplementary data). Hydrogenation of cinnamonitrile yielded

Table 5 Recycling efficiency of the catalyst PS(PBIM)PdCl$_2$ for hydrogenation of cyclohexene at 303 K in 30 mL methanol at 1 atm pressure of hydrogen

Number of cycles	Initial rate (10^{-3} mol dm^{-3} min^{-1})
1	0.85
2	0.83
3	0.79
4	0.74
5	0.76
6	0.71

phenylpropionitrile (96 %), again showing selectivity for C=C bonds.

Recycling efficiency of the catalyst

Recycling of the catalyst was studied by carrying out the reactions over six cycles at a constant catalyst concentration of 1.2×10^{-4} mol dm^{-3} Pd and cyclohexene concentration of 5.0×10^{-3} mol dm^{-3} at 303 K in 30 mL of methanol. The initial rate remained almost constant and physicochemical studies of the catalyst also indicated that there was no leaching of the metal even after six recycling experiments (Table 5).

Conclusion

A polymer-supported [2-(2′-pyridyl)benzimidazole]palladium complex was synthesized and successfully used for the hydrogenation of various olefins, nitro compounds and Schiff bases under ambient conditions. The catalyst can be recovered by simple filtration and can be recycled without much loss in activity. Based on kinetic studies, a plausible reaction mechanism has been proposed. The catalyst showed good selectivity towards C=C bonds in the presence of CO, CN and nitro groups.

References

1. Chepaikin EG, Khidekel ML (1978) J Mol Catal A Chem 4:103–112
2. Zofia MM, Ostaszewski B, Zientarska J, Sobczak JW (1998) J Mol Catal A Chem 129:207–218
3. Cornils B, Herrmann WA (1996) Applied homogeneous catalysis with organometallic compounds. Wiley-VCH, Weinheim
4. Hartley FR (1985) Supported metal complexes–a new generation of catalysts, I edn. Academic Press, Dordercht Holland
5. Alexander S, UdayKumar V, Nagaraju N, Gayathri V (2010) Trans Met Chem 35:247–251
6. Drelinkiewicz A, Knapik A, Waksmundzka GA, Bukowska A, Bukowski W, Noworol J (2008) React Funct Polym 68:1059–1071
7. Hsiao MC, Liu ST (2010) Catal Lett 139:61–66
8. McGrath MP, Erik DS, Samuel JT (1995) Chem Rev 95:381–398
9. Xi Xiangli, Liu Yingliang, Shi Jun, Cao Shaokui (2003) J Mol Catal A Chem 192:1–7
10. Selvaraj PC, Mahadevan V (1997) J Polym Sci A Polym Chem 35:105–122
11. Figueras Francois, Coq Bernard (2001) J Mol Catal A Chem 173:223–230
12. Dilip RP, Ram RN (1998) J Mol Catal A Chem 130:57–64
13. Wan BS, Liao SJ, Xu Y, Yu DR (1998) React Kinet Catal Lett 63:397–401
14. McNamara CA, Dixon MJ, Bradley M (2002) Chem Rev 102:3275–3300
15. Alexander S, Udayakumar V, Gayathri V (2009) J Mol Catal A Chem 314:21–27
16. Ghosh S, Teillout A-L, Floresyona D, de Oliveira P, Hagege A, Remita H (2015) Int J Hydrogen Energy 40:4951–4959
17. Zhou Y, Xiang Z, Cao D, Liu CJ (2013) Chem Commun 49:5633–5635
18. Anna MMD, Intini S, Romanazzi G, Rizzuti A, Leonelli C, Piccinni F, Mastrorilli P (2014) J Mol Catal A Chem 395:307–314
19. Sun Q, Zhu LF, Sun ZH, Meng XJ, Shou XF (2012) Sci China 55:2095–2103
20. Shilpa ML, Gayathri V (2013) Trans Met Chem 38:705–713
21. Perrin DD, Armanego WCF, Perrin DR (1966) Purification of laboratory chemicals, chap 3, I edn. Pergamon Press, New York
22. Roe A, Montgonery JA (1953) J Am Chem Soc 75:910–912
23. Jose SC, Castineiras A, Martinez EG, Parajo Y, Perez Paralle ML, Gonzalez AS, Sordo J (2005) Z Anorg Allg Chem 631:2258–2264
24. Shilpa ML, Gayathri V (2013) Trans Met Chem 38:53–62
25. Belyaev SV, Vainshtein EF, Klyuev MV (2002) Kinet Catal 43:245–248
26. Pomogailo AD (2004) Kinet Catal 45:61–103
27. Purwanto P, Deshpande RM, Chaudhari RV, Delmas H (1996) J Chem Eng Data 41:1414–1417
28. Alexander S, Udayakumar V, Nararaju N, Gayathri V (2010) Trans Met Chem 35:427–435
29. Udayakumar V, Alexander S, Gayathri V, Shivakumaraiah, Patil KR, Vishwanathan B (2010) J Mol Catal A Chem 317:111–117
30. Udayakumar V, Alexander S, Gayathri V, Shivakumaraiah, Vishwathan B (2011) Chin J Catal 32:280–285
31. Welton T (1999) Chem Rev 99:2071–2083
32. Jainamma M, Mahadevan V (1990) J Mol Catal 60:189–207