

Synthesis, characterisation of polymer-supported palladium-2-methylimidazole complex catalyst for the hydrogenation of aromatic nitro compounds

Udayakumar Velua, Alexander Stanislaus^a, Gayathri Virupaiah^{a*}, Shivakumaraiah^b, Kashinath Rangu Patil^c and Viswanathan Balasubramanian^d

^aDepartment of Chemistry, Central College Campus, Bangalore University, Ambedkar Veedi, Bangalore, 560 001, India

^bSiddaganga Institute of Technology, Tumkur, Karnataka, 572 103, India

^cNational Chemical Laboratories, Pune, 411 008, India

^dNational Centre for Catalysis Research, I.I.T. Madras, Chennai, 600 036, India

A polymer-supported palladium-2-methylimidazole complex was synthesised and characterised by various physico-chemical methods. The complex was successfully used as a catalyst for the hydrogenation of nitrobenzene and a few of its derivatives under ambient conditions. Results reveal that the electronic as well as the steric effects of the substituent control the rate of hydrogenation of the nitro group in the studied nitro compounds. The kinetics of hydrogenation and the reusability of the catalyst were also studied.

Keywords: transition metal complexes, polymer-supported complex catalyst, hydrogenation, aromatic nitro compounds

Aromatic amines which are important intermediates for the synthesis of various chemicals are generally prepared by the hydrogenation of aromatic nitro compounds. Transition-metal complexes have been found to catalyse the hydrogenation of various nitro compounds in a homogeneous medium.^{1–4} As transition-metal complexes are often expensive to prepare, recent interest in the development of environmentally benign synthesis has evoked interest in the development of polymer-supported metal complex catalysts. Anchored metal complexes on polymer supports have been successfully used as catalysts for hydrogenation, oxidation, dehalogenation, epoxidation and polymerisation.^{5–17} In this context, present work was focused on the synthesis and characterisation of a polymer-supported palladium 2-methylimidazole complex catalyst and its use as a catalyst for the hydrogenation of various aromatic nitro compounds under ambient conditions. The reactivity of various nitro compounds for the hydrogenation reaction has been examined. Kinetic studies were carried out and the catalyst was recycled six times without any loss of efficiency or leaching of metal from the support.

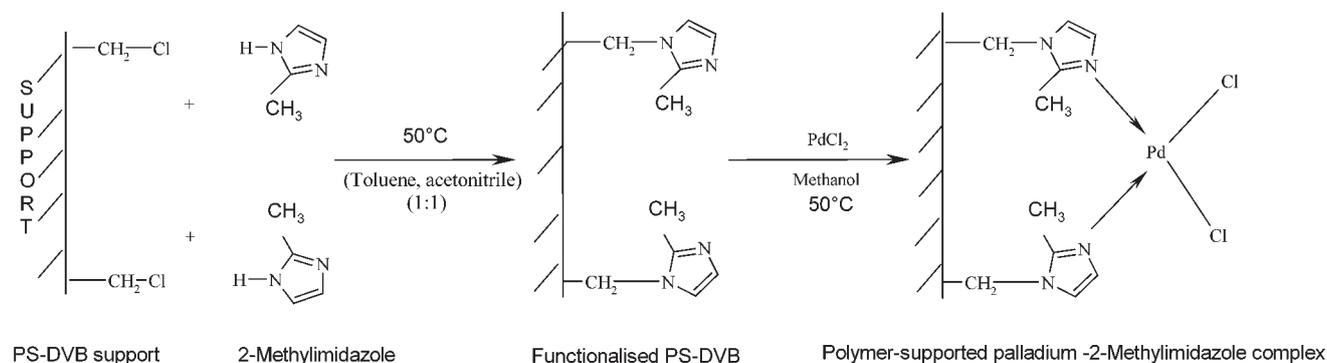
Experimental

Chloromethylated polystyrene beads cross-linked with 6.5% divinylbenzene (PS-DVB) was obtained as a gift from Thermax India Ltd, Pune, India. Palladium chloride was procured from Arora Matthey Ltd, India. All the substrates and solvents were purified before use. The IR spectra were recorded using a Shimadzu FTIR-8500S spectrometer and far-IR spectra by using a Perkin Elmer-Spectrum 1000

FTIR spectrometer. Surface area was measured using a Nova 1000 instrument in a nitrogen atmosphere. TGA studies were carried out using a Perkin Elmer-Diamond instrument under an inert atmosphere. Scanning electron micrographs were recorded on a Leica S440i instrument. HPLC data were obtained using a Shimadzu-Prominence 2A with C18 column and UV detector. GC-MS was recorded using a Shimadzu GC-MS QP5050A instrument with a BP5 column. C, H and N analyses were carried out using a Thermo Finnegan Eager 300 and an Elementar Vario EL III, Carlo Erba 1108 analyser. Chloride content was estimated by Volhard's method. Palladium content was determined using a GBC Avanta-PM atomic absorption spectrophotometer. Photoelectron spectra were recorded on a ESCA-3000 electron spectrometer equipped with a hemispherical electron analyser using the Al-K α radiation (1486.6 eV) X-ray source.

[Pd(MeImz)₂Cl₂] (MeImz = 2-methylimidazole): The complex [Pd(MeImz)₂Cl₂] was prepared according to the literature method.¹⁸ PdCl₂ (177 mg, 1 mmol) was treated with a solution of 2-methylimidazole (164 mg, 2 mmol) dissolved in acetone (20 mL) and refluxed on a water bath for 4 h during which a yellow crystalline complex [Pd(MeImz)₂Cl₂] separated. The product was filtered off, washed with acetone and dried under reduced pressure.

Polymer-supported palladium-2-methylimidazole catalyst: Functionalisation of PS-DVB with 2-methylimidazole was carried out by treating PS-DVB (5 g, 5 mmol Cl g⁻¹ PS-DVB) with 2-methylimidazole (2.5 g, 3 mmol g⁻¹ PS-DVB) in a mixture of 1:1 toluene and acetonitrile on a hot water bath maintained at 50 °C for 60 hours. 5 g of the functionalised beads were treated with ethanolic solution containing palladium chloride (0.90 g, 1.2 mmol Pd g⁻¹ PS-DVB) at 50 °C for 10 h. The beads were filtered off and finally washed by Soxhlet extraction using ethanol (Scheme 1).^{19,20} The polymer-supported



Scheme 1 Preparation of the polymer-supported palladium-2-methylimidazole complex.

* Correspondent. E-mail: gayathritvr@yahoo.co.in

complex beads were treated with an ethanolic solution of sodium borohydride, washed several times with methanol, vacuum-dried and then used as catalyst for the hydrogenation reactions.²¹

Hydrogenation procedure: All the reactions were carried out using methanol as a solvent at 596 mm Hg hydrogen pressure in a glass reactor. In a typical experiment, the catalyst was added along with the solvent to the reactor which was flushed with hydrogen and then evacuated. A known quantity of the substrate was injected and the system was opened to hydrogen gas burette. The reaction was monitored by a hydrogen uptake at different intervals of time.²² The products obtained were identified using HPLC, IR spectra and GC-MS.²³ A blank reaction was also carried out for all the substrates without using the catalyst.

Abbreviations: PS-DVB: Chloromethylated polystyrene beads cross-linked with 6.5% divinylbenzene; PSMeimz: PS-DVB functionalised with 2-methylimidazole; PSPdMeimz: PSMeimz treated with palladium chloride; PSPdMeimz-actv : PSPdMeimz treated with methanolic solution of sodium borohydride; PSPdMeimz-rec : Recycled catalyst, MeImz = 2-methylimidazole; NB: nitrobenzene; PNA: *p*-nitroaniline; PNP: *p*-nitrophenol; PNT: *p*-nitrotoluene; PNBA: *p*-nitrobenzoic acid; PDNB: *p*-dinitrobenzene; PCNB: *p*-chloronitrobenzene, SEM = Scanning electron micrograph.

Results and discussion

Elemental analysis: Elemental analysis at different stages of preparation of the catalyst was carried out and the data are given in Table 1. The presence of nitrogen in PSMeimz determines the extent of functionalisation of PS-DVB. The palladium content was determined by stripping the bound palladium complex from the support.²⁴ For stripping, the polymer-supported complex (25 mg) was digested with conc. sulfuric acid (about 3 mL) by heating followed by addition of hydrogen peroxide (about 2 mL). The clear solution was heated to decompose the excess of hydrogen peroxide and then cooled. The metal content in the solution was determined using an atomic absorption spectrophotometer.

Surface area, porosity, thermo-gravimetric, SEM analysis: Solid catalysts are generally porous in nature and the pores play a very important role in their adsorption behaviour and catalytic activity.²⁵ Surface area and porosity was determined by the BET (Bruanauer, Emmette, Teller) method in a nitrogen atmosphere.^{26,27} PSPdMeimz-actv had surface area 22 (m² g⁻¹), pore diameter 54.2 Å and pore volume 0.030 (cm³ g⁻¹). No significant changes in surface area and pore diameter were observed after recycling; the surface area remained the same 22 (m² g⁻¹) whereas pore diameter and pore volume were found to be 49.4 Å and 0.035 (cm³ g⁻¹) respectively. Thermo-gravimetric analyses of PSPdMeimz-actv in an inert atmosphere with a heating rate of 10 °C min⁻¹ up to 500 °C revealed that the catalyst was stable without significant weight loss up to 225 °C. Scanning electron micrographs revealed that PSPdMeimz-actv has a relatively rough surface when compared PS-DVB. This change in surface could be due to reconstruction of the surface during catalyst preparation.

Infrared spectroscopic studies: The IR spectra of PS-DVB, PSMeimz, PSPdMeimz, PSPdMeimz-actv, PSPdMeimz-rec and [Pd(MeImz)₂Cl₂] were recorded in nujol and a comparative study was made (Fig. 1). The peak at 1265 cm⁻¹ for PS-DVB due to -CH₂Cl (Spectrum A) decreased in intensity on functionalisation (Spectrum B).²⁸ The peak at 3170 cm⁻¹ corresponding to ν_{N-H} of 2-methylimidazole disappeared on functionalisation indicating the bonding of 2-methylimidazole to the support through -CH₂-. The decrease in intensity of the band at 833 cm⁻¹ corresponding to ν_{C-Cl} of PS-DVB after functionalisation further confirms the bonding of 2-methylimidazole with PS-DVB (Spectrum B).²⁹ [Pd(MeImz)₂Cl₂] exhibited ν_{N-H}

Table 1 Elemental analysis of polymer-support and polymer-supported catalyst

	% C	% H	% N	% Pd
PS-DVB ^a	69.50	5.78	–	–
PSMeimz ^b	57.86	5.37	8.02	–
PSPdMeimz	54.59	5.64	6.01	12.29
PSPdMeimz-actv ^c	55.54	5.22	7.01	12.27
PSPdMeimz-rec	55.28	6.43	7.11	12.00

^a 4.7 mmol Cl/g PS-DVB, ^b 2.8 mmol MeImz/g PS-DVB, ^c 1.14 mmol pd/g PS-DVB.

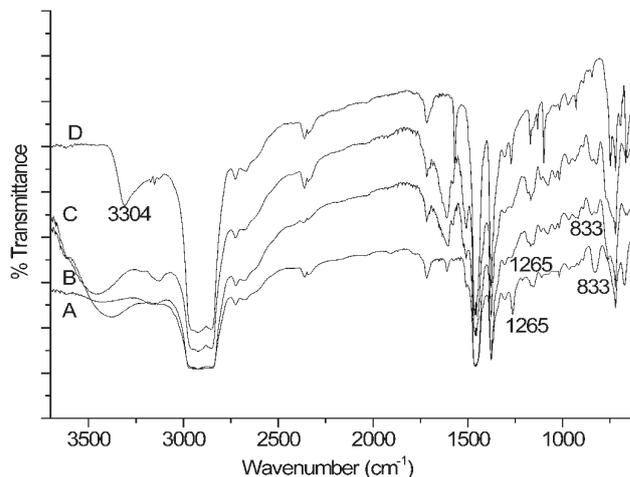


Fig. 1 Overlay of IR spectra of PS-DVB (spectrum A); PSMeimz (spectrum B); PSPdMeimz (spectrum C); [Pd(MeImz)₂Cl₂] (spectrum D).

at 3304 cm⁻¹ (Spectrum D), whereas this peak was not found in the polymer-supported complex catalyst, since the complex has bonded to the polymer support through nitrogen. No significant changes in the spectroscopic features were observed for PSPdMeimz (Spectrum C), PSPdMeimz-actv and PSPdMeimz-rec. An intense peak at 326 cm⁻¹ in the far-IR spectrum recorded for PSPdMeimz-actv was assigned to Pd-Cl stretching.

X-ray photoelectron spectroscopy studies: The oxidation state of the palladium in PSPdMeimz, PSPdMeimz-actv and the recycled catalyst was ascertained by X-ray photoelectron spectroscopy (XPS) studies (Fig. 2). PSPdMeimz exhibited two peaks with binding energies 337.7 eV (3d_{5/2}) and 342.9 eV (3d_{3/2}) indicating the +2 oxidation state of palladium (Spectrum A). PSPdMeimz-actv did not show

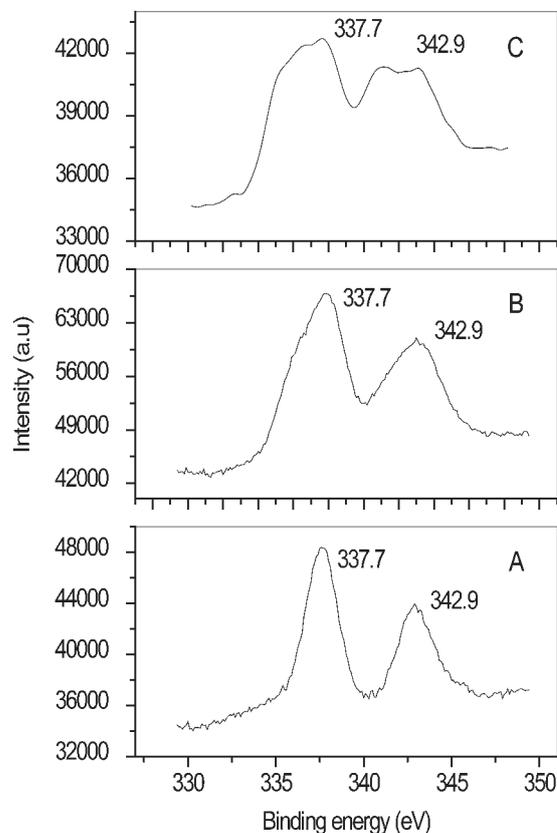


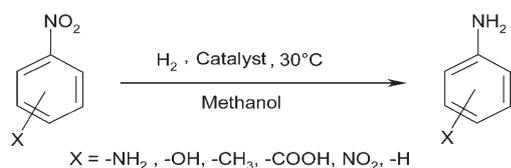
Fig. 2 XPS spectra of PSPdMeimz (spectrum A); PSPdMeimz-actv (spectrum B); recycled catalyst (spectrum C).

any significant changes in the XPS results (Spectrum B).^{21,30} Similar observations are reported by Mathew and Mahadevan²⁴ and Mani *et al.*³¹ The XPS spectrum of the recycled catalyst (Spectrum C) revealed that, palladium continues to be in the +2 oxidation state even after recycling the catalyst for six times although the broadening of the peaks observed in spectrum C could be due to the presence of palladium in zero oxidation state formed during usage.

Hydrogenation reaction: When the homogeneous analogue of the polymer-supported catalyst; [Pd(MeImz)₂Cl₂] was used as catalyst for the hydrogenation of nitro compounds in methanol, it resulted in the separation of metal from the reaction mixture during the course of the reaction, making it unsuitable for reaction. On the other hand, when the polymer-supported complex was used for the hydrogenation reaction it was found that metal does not leach out from the support. The reaction was monitored by hydrogen uptake at different intervals of time. The rate of hydrogenation reaction was calculated from the slope after plotting the volume of hydrogen uptake by the substrate as a function of time.

Reactivity of aromatic nitro compounds: The reactivity of the nitro group in substituted nitro aromatics may depend both on the presence of electron-releasing or electron-donating groups attached to the aromatic ring and the steric effect contributed by the substituted group (Scheme 2). When the hydrogenation of nitrobenzene was studied by varying the *para* substituents with electro-donating groups like -NH₂, -OH and -CH₃, and electron-withdrawing groups like -COOH and -NO₂, rate of hydrogenation followed the order: nitro compounds with electron-donating groups > nitrobenzene > nitro compounds with electron-withdrawing groups. Initial rates and relative reactivities are tabulated in Table 2. Different trends are reported by Baralt and Holy¹⁴, and Werner.³² Baralt and Holy reported that the hydrogenation reaction of nitro compounds was not highly dependent on electronic effects, whereas Werner observed the order of initial rate of hydrogenation of nitro compounds as nitrobenzene > electron-donating group substituted >> electron-withdrawing group substituted nitrobenzenes. The comparative study for hydrogenation of different isomers of nitroaniline and nitrobenzoic acid showed that the hydrogenation rate was in the order of *para*- > *ortho*- > *meta*- substituted isomers. Wan *et al.* have reported the order of reactivity as *ortho* and *meta* isomers higher than the *para* one.³³ These observations reveal that the type of catalyst used, the electronic effect as well as the steric effect of the substituent controls the rate of hydrogenation of the nitro group in the substrates studied. When PCNB was used as a substrate, dechlorination was observed during hydrogenation giving aniline as the product.^{34,35} Hence the effect of the chloro group on the rate could not be determined.

Sequential hydrogenation of *m*-dinitrobenzene: When the hydrogenation of *m*-dinitrobenzene (MDNB) was carried out with catalyst concentration 5.93 × 10⁻³ mol dm⁻³ Pd and 33.3 × 10⁻³ mol dm⁻³



Scheme 2 Hydrogenation of aromatic nitro compounds.

Table 2 Initial rates of hydrogenation and relative rates for various nitro compounds

Reaction condition: 5.92 × 10⁻³ mol dm⁻³ Pd, 33.3 × 10⁻³ mol dm⁻³ substrate concentration, 30 °C temperature, 30 mL methanol, 596 mm Hg hydrogen pressure.

Substrate	Initial rate x10 ⁻³ /mol dm ⁻³ min ⁻¹	Relative rate
<i>p</i> -Nitroaniline	1.33	1.15
<i>p</i> -Nitrophenol	1.26	1.09
<i>p</i> -Nitrotoluene	1.25	1.08
Nitrobenzene	1.15	1.00
<i>p</i> -Nitrobenzoic acid	0.93	0.80
<i>p</i> -Dinitrobenzene	0.85	0.73

Table 3 Percentage conversion of various nitro compounds with supported palladium-2-methylimidazole complex catalyst

Substrates	Products	Percentage conversion ^a	Time /min
Nitrobenzene	Aniline	72	100
<i>p</i> -Nitroaniline	<i>p</i> -Phenylenediamine	70	80
<i>o</i> -Nitroaniline	<i>o</i> -Phenylenediamine	70	120
<i>m</i> -Nitroaniline	<i>m</i> -Phenylenediamine	82	130
<i>p</i> -Nitrophenol	<i>p</i> -Aminophenol	79	100
<i>m</i> -Nitrophenol	<i>m</i> -Aminophenol	80	120
<i>p</i> -Nitrotoluene	<i>p</i> -Toluidine	72	100
<i>p</i> -Nitrobenzoic acid	<i>p</i> -Aminobenzoic acid ^b	75	110
<i>o</i> -Nitrobenzoic acid	<i>o</i> -Aminobenzoic acid	80	110
<i>m</i> -Nitrobenzoic acid	<i>m</i> -Aminobenzoic acid	80	120
<i>m</i> -Dinitrobenzene	<i>m</i> -Phenylenediamine	84	180

^a Conversion based on the HPLC analysis. ^b Isolated yield 72%.

MDNB sequential hydrogenation of nitro groups was observed. MDNB was first converted into *m*-nitroaniline before *m*-phenylenediamine was formed.^{1,36,37}

The percentage conversions of various nitro compounds are listed in Table 3. All the reactions were carried out with a constant 5.92 × 10⁻³ mol dm⁻³ Pd and 33.3 × 10⁻³ mol dm⁻³ substrate concentration at a temperature of 30 °C with 596 mm Hg hydrogen pressure using methanol as solvent.

Kinetic studies: The influence of catalyst concentration on rate of hydrogenation was investigated for NB, PNA and PNT over a range of 1.46 × 10⁻³ to 5.92 × 10⁻³ mol dm⁻³ Pd at constant substrate concentration of 33.3 × 10⁻³ mol dm⁻³ at a temperature of 30 °C with 596 mm Hg hydrogen pressure using methanol as solvent. The order of reaction determined from the slope of the plot of log(initial rate) against log[Catalyst] showed that all the substrates followed first order kinetics.³⁸ The influence of substrate concentration on the rate of the reaction was studied in the range of 3.33 × 10⁻³ to 33.3 × 10⁻³ mol dm⁻³ of substrate at 30 °C and at 596 mm Hg hydrogen pressure with a constant catalyst concentration of 5.92 × 10⁻³ mol dm⁻³ Pd for all the substrates in methanol. The order of reaction found by plot of log(initial rate) against log[substrate] was first order.³⁹ Based on the results obtained, a probable reaction pathway is proposed for the hydrogenation of nitro compounds (Scheme 3).²¹

According to the proposed reaction pathway, after oxidative addition of a hydrogen molecule to the catalyst, a nitro group is hydrogenated to produce a hydroxylamine intermediate in two steps which finally undergoes reductive elimination to yield the corresponding amine. Krathy *et al.* have also proposed a similar plausible reaction mechanism for the hydrogenation of aromatic nitro compounds using a polymer supported palladium catalyst where the reaction route is via formation of a hydroxylamine intermediate.⁴⁰ A rate law proposed for the reaction pathway (Scheme 3) is given in equation (1).

$$\text{Rate} = K_1 k [\text{Catalyst}] [\text{Substrate}] [\text{H}_2] \quad (1)$$

Where K_1 is the equilibrium constant for addition of hydrogen to the catalyst, and k is the velocity constant for the rate determining step (Step 2) Since the reactions were carried out at constant hydrogen pressure, equation (1) can be modified as given in equation (2).

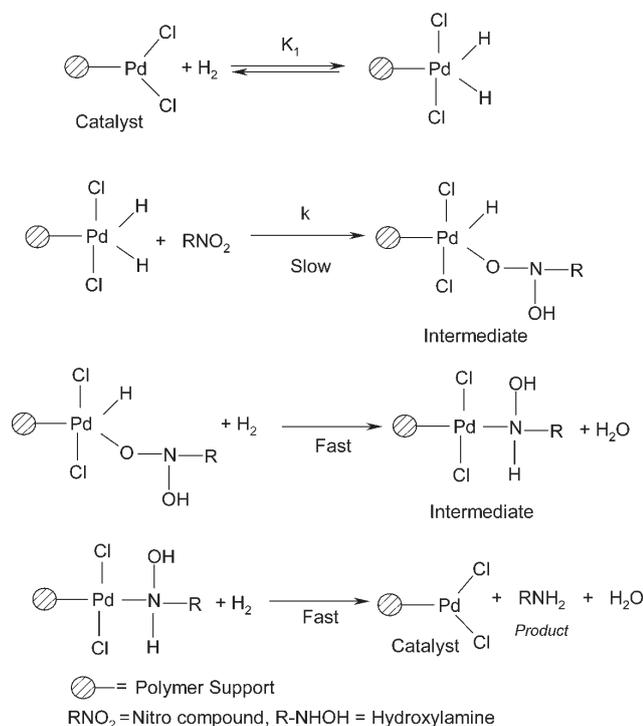
$$\text{Rate} = K' k [\text{Catalyst}] [\text{Substrate}] \quad (2)$$

Where $K' = K_1 [\text{H}_2]$. The rate equation was found to be in agreement with the experimental results where the reaction was first order in the catalyst and first order in the substrate concentration at constant hydrogen pressure.

Test for metal leaching from the polymer support and the recycling efficiency of the catalyst

One of the main objectives of synthesising polymer-supported metal complex catalysts is to recycle the catalyst efficiently. The catalyst was reused for six cycles at a constant catalyst concentration of 59.2 × 10⁻⁴ mol dm⁻³ Pd, PNBA concentration of 33.3 × 10⁻³ mol dm⁻³ at 30 °C with 596 mm Hg of hydrogen pressure. The initial rate remained almost constant for over six cycles without any loss in the efficiency of the catalyst. There was no change in the percentage of palladium in the catalyst when metal estimation was carried out at the end of first and sixth cycle. No traces of palladium were found in the

Received 19 September 2010; accepted 15 December 2010
 Paper 1000365 doi: 10.3184/174751911X556855
 Published online: 10 February 2011



Scheme 3 Probable pathway for hydrogenation of aromatic nitro compounds.

reaction mixture at the end of the reaction. These results support the conclusion that metal did not leach from the catalyst support.

Conclusion

A synthesised polymer-supported palladium-2-methylimidazole complex can be used successfully under ambient conditions to hydrogenate nitrobenzene and a few of its derivatives to their corresponding amines. Recycling experiments showed that no metal leaching occurred and the catalyst maintained its activity for six cycles. The reactivity of nitro group is dependent on the nature and position of the substituent in the benzene ring. When PCNB was used as a substrate, both hydrogenation and dechlorination proceeded simultaneously resulting in the formation of aniline. Sequential hydrogenation of nitro groups was observed when MDNB was used as a substrate.

The authors wish to thank UGC for the DSA-SAP and DST for FIST programme, Thermax India Ltd, Pune, India for providing the PS-DVB, Prof. B. K. Sadashiva, Liquid Crystals Lab, RRI, Bangalore and CDRI, Lucknow for C, H and N analyses and STIC, Cochin for TGA. V.Udayakumar thanks Sree Siddaganga Education Society, Sree Siddaganga Math, Tumkur, Karnataka, India, for extending support for doctoral studies.

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