Synthesis and characterisation of a polymer-bound rhodium-benzimidazole complex as catalyst for the hydrogenation of nitroarenes

S. Alexander · V. Udayakumar · V. Gayathri

Received: 10 June 2011/Accepted: 19 September 2011/Published online: 20 October 2011 © Springer Science+Business Media B.V. 2011

Abstract A polymer-anchored rhodium complex was synthesised by sequential attachment of benzimidazole (BzlH) and RhCl₃ to chloromethylated poly(styrene-divinylbenzene) co-polymer (PSDVB) with 6.5% cross-linking. The catalyst was characterised by X-ray photoelectron spectroscopy, far-IR, UV-Vis, FTIR, SEM and thermogravimetric analysis. Various physico-chemical properties such as bulk density, surface area and swelling behaviour in different solvents were also studied. The polymer-anchored complex was tested as a catalyst for reduction of nitroarenes, namely o,m,p-nitrobenzoic acid, nitroaniline, nitrophenol and nitrotoluene. Kinetic measurements were carried for o-nitroaniline and p-nitrophenol by varying temperature, catalyst concentration and concentration of substrates. The rate of the reaction was found to be first order with respect to catalyst concentration and also with substrate concentration at low concentrations, becoming independent of substrate at higher concentrations. A plausible mechanism for the reaction is proposed. The energy and entropy of activation calculated from Arrhenius plots indicate high activity of the catalyst on the support. The recycling efficiency of the catalyst has been studied and there was no leaching of metal from the catalyst surface.

Introduction

Transition metal complexes have been used extensively as catalysts for homogeneous hydrogenation reactions due to their high selectivity under mild operating conditions [1-4]. However, homogeneous catalysis is associated with the problems of product contamination and catalyst loss when the products are not readily separated from the catalyst.

Immobilisations of metal complexes onto polymer supports for heterogeneous catalysis have been reported by many workers [5–7]. This has remained an area of considerable interest with a major objective of designing polymer supports with appropriate functional groups for attachment to the active metal centre. Poly(styrenedivinylbenzene) modified chemically into a ligand having a variety of coordination sites is the most commonly employed support. The preparation and characterisation of polymers incorporating N-heterocycles and their reactions with metal salts and complexes have been studied by Mahadevan et al. [8]. Magdalene et al. [9] and Frechet and et al. [10] have used polybenzimidazole-supported rhodium and palladium complexes respectively, for catalytic hydrogenation of nitro compounds. Recently, we have reported the hydrogenation of olefins, nitro compounds and Schiff bases using polymer-supported complexes [11–13].

Aromatic amines are important in the manufacture of a variety of chemicals such as dyes, pharmaceuticals, agricultural chemicals, surfactants and polymers [14]. Conventional hydrogenation involves the use of stoichiometric amounts of finely divided iron in the presence of acid [15]. Reports on the reduction of nitroaromatics using polymerbound metal complexes are relatively scarce and usually involve high pressure reactions [16]. In the present paper, we report the synthesis and characterisation of rhodium

Electronic supplementary material The online version of this article (doi:10.1007/s11243-011-9542-7) contains supplementary material, which is available to authorized users.

S. Alexander \cdot V. Udayakumar \cdot V. Gayathri (\boxtimes) Department of Chemistry, Bangalore University, Central College Campus, Bangalore 560 001, India e-mail: gayathrityr@yahoo.co.in

trichloride supported on polystyrene cross-linked with 6.5% divinylbenzene functionalised with benzimidazole and its catalytic activity towards reduction of nitroarenes at ambient temperature and pressure.

Experimental

Chloromethylated poly(styrene–divinylbenzene) co-polymer with 6.5% cross-linking was obtained as a gift from Thermax India Ltd, Pune, India. RhCl₃ was obtained from Arora Matthey Ltd. Nitro compounds were purified before use. Superdry methanol was prepared according to a literature method [17].

Elemental analyses were carried out using a Thermo Finnegan Eager 300 analyser at RRI, Bangalore. Rhodium was estimated spectrophotometrically by the tin chloride method [18] and chloride volumetrically by Volhard's method [19]. The FTIR spectra (in KBr) were recorded using a Shimadzu FT-IR–8400S spectrometer. Surface areas were measured using a Nova 1000 analyzer in N₂ atmosphere. TGA studies were carried out using a Perkin-Elmer 7 series instrument. Scanning electron micrographs were recorded on a Leica S440i. HPLC was carried out with a Shimadzu Prominence, 2A series instrument using a C-18 column.

Preparation of the catalyst

Beads of chloromethylated polystyrene cross-linked with 6.5% divinylbenzene polymer beads were first washed with a mixture of THF and H_2O (4:1) using a Soxhlet extractor for 10 h, then vacuum dried. The polymer was then functionalised with benzimidazole by treating the beads (5 g) with benzimidazole (2.845 g) in MeCN and toluene mixture (1:1) at 60 °C for 30 h. The beads were then filtered off. Soxhlet extracted with EtOH and dried.

The functionalised beads (5 g) were then treated with $RhCl_3$ (0.350 g) in 130 mL of MeOH, acetone and MeCN mixture (20:5:1). The mixture was refluxed for 60 h. During this time, the colour of the beads turned pink and the solution turned almost colourless. The beads were then filtered off, Soxhlet extracted and dried (Scheme 1). The supported Rh complex was activated by suspending in EtOH (25 mL) and NaBH₄ (2.64 mmol) was added. After 60 min the beads were filtered off, washed with MeOH, dried and used for hydrogenation reactions (Fig. 1).

Hydrogenation procedure

The polymer-supported Rh complex was added to 30 mL of deaerated superdry MeOH and allowed to saturate under atmosphere of H_2 for 2 h. The system was evacuated and



Fig. 1 Structure of polymer complex active towards hydrogenation of nitro compounds, *S* solvent

again saturated with H_2 gas. A known quantity of the nitro compound was dissolved in superdry MeOH and injected into the system, which was connected to a gas burette filled with H_2 . The reaction was monitored by the volume of H_2 absorbed with time. The reaction mixture was then filtered and the filtrate was evaporated to dryness. The residue was recrystallised, and the product was identified by IR, melting point and HPLC.

Results and discussion

Characterisation of the catalyst

Physico-chemical properties of the supported catalyst are given in Table 1. A decrease in the surface area of the beads after loading of the metal ions may be due to blocking of pores in the polymer support [20, 21]. The elemental analyses at different stages of preparation of the catalyst indicate successful functionalisation of the polymer. Rhodium content in the functionalised beads was found to be 1.6%; on activation with sodium borohydride this value reduced to 1.4%.

In order to ascertain the mode of attachment of benzimidazole and rhodium on the polymer support, IR spectra were recorded. The intensity of the peak due to v_{C-CI} of the -CH₂Cl group at 1,261 cm⁻¹ was found to decrease after functionalisation with benzimidazole (Fig. S-1 of Supplementary Material). A peak at 1,612 cm⁻¹ was assigned to $v_{C=C}$ and $v_{C=N}$ in the functionalised polymer. The rhodium contents of the catalyst and recycled beads imply that there is no leaching of the metal ions even after recycling them six times.

Reduction using NaBH₄ usually changes the oxidation state of rhodium from +3 to +1 and in some cases from +3 to zero [8, 22, 23]. To ascertain the oxidation state of the polymer anchored catalyst before and after treatment with NaBH₄, Far-IR, diffuse reflectance and XPS studies were carried out. The far-IR spectrum of the catalyst before activation shows a band at 340 cm⁻¹ assigned to v_{Rh-Cl} which on activation, shifted towards lower frequency by

 Table 1 Elemental analysis and physical properties of polymer and polymer-bound complex

	Metal (%)	C (%)	H (%)	N (%)	Pore volume (cm ³ /g)	Surface area (m ² /g)	Apparent bulk density (g/cm ³)	Pore diameter (Å)
Polymer support (PSDVB)	_	69.5	6.0	_	0.045	35.5	0.42	84.79
Benzimidazole functionalised beads (PSDVB-BzlH)	-	68.0	5.5	6.3	0.039	35.4	0.45	43.44
PSDVB-BzlH-RhCl ₃	1.6	64.0	6.0	6.0	0.051	30.7	0.46	66.26
PSDVB-BzlH-RhCl ₃ activated with NaBH ₄	1.4	67.0	5.0	6.0	0.043	30.2	0.46	45.20
Recycled beads	1.4	69.7	5.9	5.30	0.039	35.6	0.45	44.30

16 cm⁻¹ (Fig. 2). The diffuse reflectance spectrum of PSDVB-Bzl-RhCl₃ exhibited a weak band at ca. 400 nm assigned to a d–d transition. This was absent after peak on treatment of the beads with NaBH₄, indicating a change in oxidation state of rhodium. For rhodium(I) the d–d transitions may be obscured in the intense bands of the polymer and benzimidazole [24].

The XPS spectrum of the catalyst prior to activation showed peaks at 309.7 and 315.4 eV corresponding to $3d_{5/2}$ and $3d_{3/2}$ respectively, confirming the +3 oxidation state for rhodium (Fig. 3). Upon activation with NaBH₄ these peaks shift to 308.9 and 311.3 eV, corresponding to rhodium(I). A similar change in oxidation state of rhodium from +3 to +1 upon treatment with NaBH₄ was observed by Selvaraj and Mahadevan [8] when a copolymer containing amino and heterocyclic N-vinylpyrrolidinone (N-VP) loaded with rhodium trichloride was activated using NaBH₄. The XPS data for some rhodium catalysts found by other workers are listed in Table 2. Based on these values and from our data, we assign the +3 and +1 oxidation states to rhodium for the polymer anchored PSDVB-BzIH-RhCl₃ before and after activation, respectively. The recycled catalyst exhibited



Fig. 2 Far-IR spectra of *A* PSDVB-BzlH-RhCl₃ *B* Activated PSDVB-BzlH-RhCl₃



Fig. 3 XPS spectra of A PSDVB-BzlH-RhCl₃ B Activated PSDVB-BzlH-RhCl₃. C Recycled beads

Table 2 List of $3d_{5/2}$ and $3d_{3/2}$ values for various rhodium catalysts with reference to C_{1s} peak at 285 eV

Species	Binding er	References	
	3d _{5/2}	3d _{3/2}	
Rh(0) (metal)	307.1	311.8	[25]
Rh(CO)PPh ₃ (H)	308.1	312.9	[26]
RhCl ₃ (PPh ₃) ₂	308.2	312.7	[8]
RhCl ₃ ·3H ₂ O	309.7	314.4	[27]
Rh ₂ (OAc) ₄ 2(DMSO)	308.5	313.4	[22]
Rh ₂ (OAc) ₄ 2(Py)	308.5	313.3	[22]
PS-Rh(III)	310.1	315.0	[8]
PS-Rh(II)	308.1	313.0	[8]
PS-Rh(I)	308.1	312.1	[28]
4-VP-Rh(III)	310.2	314.0	[8]
4-VP-Rh(I)	307.6	312.5	[8]
N-VP-Rh(III)	310.0	314.1	[8]
N-VP-Rh(I)	308.0	312.2	[8]

peaks at 308.9 and 311.4 eV assignable to $3d_{5/2}$ and $3d_{3/2}$ indicating +1 oxidation state and there was no change in the oxidation state of the metal after six reaction cycles.

Scanning electron micrographs (SEM) were recorded to understand the morphological changes occurring on the surface of the polymer at various stages. The initially smooth surface of the polymer bead was roughened on functionalisation with benzimidazole and anchoring of the metal. TGA of the activated catalyst indicated that it was stable up to 250 °C. Some weight loss (5.0%) was also observed below 100 °C due to loosely bound water molecules. Swelling was fond to increase with polar solvents compared to nonpolar solvents. Though maximum swelling of the beads is in H₂O which may be attributed to hydrogen bonding, methanol appears to be better suited for carrying out hydrogenation reactions since the solubilities of both substrates and hydrogen are greater in the latter solvent.

Kinetics of hydrogenation

Hydrogenation of various nitro compounds produced the corresponding amines in good yields. Table 3 shows the initial rate and relative rates of hydrogenation of nitro compounds. Our earlier results with polymer-supported palladium Schiff base catalysts indicated that the rate of hydrogenation of nitro groups is enhanced by the presence of electron donating substituents [13] and a similar trend has been observed in the present study. The ortho and para isomers are generally reduced much faster than the meta isomers. Saha and Islam reported the hydrogenation of nitro compounds with a polymer-supported Ru(II) complex [29]. They observed that nitrobenzene and *p*-substituted derivatives are reduced at a higher rate, followed by meta and ortho-substituted ones in order and they attributed this to the steric factors. Our observation that the reduction rate follows the order ortho > para > meta in most cases may be due to the dominance of electronic factors over steric factors.

Table 3 Initial rate of hydrogenation of various substituted nitro compounds with [catalyst] = 22.35×10^{-4} M and [substrate] = 0.033 M at 30 °C in 30 mL methanol

Substrate	Initial rate $\times 10^{-4}$ (mol/dm ³ /s)	Relative rate	
o-nitrophenol	9.78	9.3	
<i>m</i> -nitrophenol	5.29	5.0	
p-nitrophenol	8.33	7.9	
o-nitrobenzoicacid	2.24	2.1	
m-nitrobenzoicacid	1.92	1.8	
p-nitrobenzoicacid	2.08	2.0	
o-nitroaniline	8.08	7.7	
<i>m</i> -nitroaniline	1.05	1.0	
<i>p</i> -nitroaniline	3.18	3.0	
o-nitrotoluene	3.89	3.7	
<i>m</i> -nitrotoluene	4.94	4.7	
<i>p</i> -nitrotoluene	6.66	6.3	

Kinetic measurements were carried out for hydrogenation of *o*-nitroaniline and *p*-nitrophenol. The reduced products were characterised by melting points, IR spectra and HPLC. The free complex RhCl(BzlH)₂(H₂O) was synthesised by the literature method [30] and also used for reduction of nitro compounds under similar conditions. However, as soon as the methanolic solution of the complex was saturated with hydrogen, metal precipitated out making it unsuitable for the reaction. In contrast, the polymer-supported rhodiumbenzimidazole catalyst retained its activity over six cycles with no loss of metal.

The influence of substrate concentration [S] on the rate of hydrogenation was studied for *o*-nitroaniline and *p*-nitrophenol over a range of concentration from 0.03 to 0.07 mol/dm³ at 30 °C and 1 atmosphere pressure of H₂ at a constant catalyst concentration of 22.35×10^{-4} mol/dm³. The rate of hydrogenation (R) increases with increase in substrate concentration at lower concentrations, becoming independent at higher concentration (Fig. S-2 of Supplementary Material). The catalyst concentration was varied between 4.47×10^{-4} and 22.35×10^{-4} mol/dm³ of rhodium at 30 °C, 1 atmosphere pressure and a constant substrate concentration of 0.033 mol/dm³. The initial rate showed a direct dependence on catalyst concentration. A plot of $-\log(initial rate)$ versus $-\log(catalyst)$ showed first order kinetics (Fig. 4).

Based on the experimental data and the literature [31-33], the tentative mechanism shown in Scheme 1 is suggested for the reaction.



Scheme 1 Proposed mechanism for the reduction of nitro compounds using polymer-bound rhodium catalyst, S solvent



Fig. 4 Logarithmic plot of initial rate versus catalyst concentration

The rate law derived for the above mechanism is as follows:

$$Rate = \frac{K_0 K k_1 [H_2]^2 [RNO_2] [Catalyst]}{1 + K_0 [H_2] + K_0 K [H_2] [RNO_2]}$$
(1)

Since all reactions were carried out at fixed hydrogen pressure of 1 atmosphere, Eq. 1 reduces to

$$Rate = \frac{K_0 K k_1 [RNO_2] [Catalyst]}{1 + K_0 + K_0 K [RNO_2]}$$
(2)

At low concentrations of the substrate, the rate equation reduces further to Rate α [RNO₂] [Catalyst]. At higher concentration, it becomes zero order with respect to substrate, i.e. Rate α [Catalyst]. This is consistent with the observed behaviour.

Hydrogenation reactions were carried out in the range of 298–318 K to determine the influence of temperature at a fixed catalyst concentration of 22.35×10^{-4} mol/dm³ of rhodium, 1 atmosphere of H₂ and a nitroarene concentration of 0.033 mol/dm³. An increase in rate was observed with increase in temperature. The energy of activation was calculated from a plot of log(initial rate) versus 1/*T* (Fig. 5). The values of E_a (39.2 kJ/mol for *o*-nitroaniline and 21.8 kJ/mol for *p*-nitrophenol) indicate high activity of the catalyst, while the high activation entropies ΔS^{\ddagger} (217 J/K for *o*-nitroaniline and 275 J/K for *p*-nitrophenol) indicate that there is no significant penalty in entropy upon fixation of the catalyst molecule on the polymer support [12].

The main drawback of polymer-supported catalysts tend to be leaching of metal ions from the support. In order to test the stability of the polymer-bound catalyst, a known quantity of the substrate was reduced and its initial rate was determined. The beads were then filtered off, washed, dried



Fig. 5 Arrhenius plot:logarithmic plot of initial rate versus reciprocal of temperature

and reused for six cycles. The activity of the catalyst remained essentially unaltered during these experiments.

Acknowledgments The authors would like to thank UGC for DRS programme, Prof. Sadashiva, Liquid Crystal Lab. RRI for CHN analysis and DST, Central Facility, Physics Department, IISc Bangalore for recording far-IR spectra.

References

- 1. Molnar A, Sarkany A, Varga M (2001) J Mol Catal 173:185-221
- Parshall GW (1980) Homogeneous catalysis—the application and chemistry of catalysis by soluble transition metal complexes, chapter 1. Wiley-Interscience Publication, Wiley, New York
- 3. Santra PK, Sagar P (2003) J Mol Catal A 197:37-50
- 4. Gupta KC, Sutar AK (2008) Coord Chem Rev 252:1420-1450
- 5. Gupta KC, Sutar AK, Lin CC (2009) Coord Chem Rev 253: 1926–1946
- 6. Leadbeater NE, Dixon MJ, Bradely M (2002) Chem Rev 102: 3275–3300
- 7. Lu J, Toy PH (2009) Chem Rev 109:815-836
- 8. Selvaraj PC, Mahadevan V (1997) J Polym Sci Polym Chem 35:105–122
- Magdalene RM, Leelamani EG, Gowda NMN (2004) J Mol Catal A 223:17–20
- 10. Li NH, Frechet JMJ (1987) React Polym 6:311-321
- Alexander S, Udayakumar V, Gayathri V (2009) J Mol Catal 314: 21–27
- Udayakumar V, Alexander S, Gayathri V, Shivakumaraiah B, Patil KR, Viswanathan B (2010) J Mol Catal 317:111–117
- Alexander S, Udayakumar V, Nagaraju N, Gayathri V (2010) Transition Met Chem 35:427–435
- Jospeh T, Kumar KV, Ramaswamy AV, Halligudi SB (2007) Catal Commun 8:629–634
- Corma A, lez-Arellano CG, Iglesias M, Saonchez F (2009) Appl Catal 356:99–102
- Zheng Y, Ma K, Wang H, Sun X, Jiang J, Wang C, Li R, Ma J (2008) Catal Lett 124:268–276

- 17. Perrin DD, Armarego WCF, Perrin (1966) Purification of laboratory chemicals, chapter-3, 1st edn. Pergamon Press, New York
- Beamish FE (1966) The analytical chemistry of the noble metals, chapter-5, Pergamon Student edition
- Mendham J, Denncy RC, Barnes JD, Thomas M (2000) Vogel's Text book of quantitative chemical analysis, chapter-10, 6th edn. Pearson Education Ltd
- 20. Dalal MK, Ram RN (2001) Bull Mater Sci 24:237-241
- 21. Anthony R, Tembe GL, Ravindranathan M, Ram RN (2003) J Appl Polym Sci 90:370–378
- 22. Holy N (1979) J Org Chem 44:239-243
- 23. Parameshwaran VR, Vancheesan S (1991) React Kinet Catal Lett 45:55–60
- 24. Lever ABP (1984) Inorganic electronic spectroscopy, chapter 7, 2nd edn. Elsevier, Amsterdam

- Hammer AD, Tisley DG, Walton RD (1973) J Chem Soc Dalton (1):116–120
- 26. Bruner H, Bailer JC Jr (1973) Inorg Chem 12:1465-1470
- 27. Card RJ, Neckers DC (1978) Isr J Chem 17:269–273
- 28. Mathew J, Mahadevan V (1990) J Mol Catal 60:189-207
- 29. Islam SM, Saha CR (2004) J Mol Catal 212:131-140
- Ghosh SP, Bhattacharjee P, Dubey L, Mishra LK (1977) J Indian Chem Soc 54:230–238
- Islam SM, Tuhina K, Mubarak M, Mondal P (2009) J Mol Catal 297:18–25
- 32. Patel DR, Ram RN (1998) J Mol Catal 130:57-64
- 33. John J, Dalal MK, Ram RN (1999) J Mol Catal 137:183-191