

Hydrogenation of nitroarenes using polybenzimidazole-supported rhodium catalyst

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Abstract

Polybenzimidazole (PBI)-supported rhodium PBI-Rh(I) catalyst was prepared and characterised by chemical analysis, IR, TGA and X-ray photoelectron spectroscopy. Sodium borohydride was used to produce active species of the catalyst. The anchored catalyst PBI-Rh(I) was found to be effective for the reduction of nitrophenols, nitrobenzoic acids and nitroanilines in methanol at room temperature and at 1 atm hydrogen. The influence of temperature, concentrations of the catalyst and substrate and nature of the solvent on the reaction rates was investigated. The recycling efficiency of the catalyst was found to be good. A probable mechanism for the catalytic reaction has been suggested.
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1. Introduction

The preparation of catalysts by immobilizing active transition metal complexes on solid supports such as organic polymers and inorganic supports has attracted widespread attention [1]. The renewed interest in the field of polymer metal complexes as catalysts is partly due to the development of nitrogen-containing ligands. Polymer supports associated with nitrogen-containing ligands have been studied because of their stability to oxidation [2]. Though the field of polymer metal complexes as catalysts in organic synthesis has remained active over the last four decades, much of the research work has been mainly concentrated to the hydrogenation of alkenes, alkynes and dienes. Relatively, little attention has been paid to the reduction of nitro compounds [3].

Li and Frechet [4] have reported the catalytic hydrogenation of nitro compounds and alkenes at room temperature using polybenzimidazole (PBI)-supported Pd⁰ catalysts. Use of rhodium complexes containing benzimidazole ligands as homogeneous catalysts in the reduction of nitroarenes have

been reported from these laboratories [5]. Further, we have also reported the catalytic activity of PBI-RhCl₃ in the catalytic transfer hydrogenation of nitrophenols and nitrobenzoic acids using formic acid as hydrogen donor in methanol [6]. With this in view we have examined PBI-supported Rh(I) complexes for their catalytic activity in the reduction of nitro compounds. Herein we report the results obtained under ambient conditions of temperature and pressure.

2. Materials and methods

Polybenzimidazole (PBI; Fig. 1) resin (250–500 μm diameter, microporous Celanese Corporation, Charlotte) beads were used as such. Methanol, acetone and DMF were purified according to literature methods [7]. Nitrobenzoic acids and nitroanilines were recrystallised from methanol and nitrophenols were used as such. [RhCl(cod)]₂ (cod = cycloocta-1,5-diene) was prepared as per literature method [8].

The catalyst PBI-Rh(I) was prepared as follows: A mixture of [RhCl(cod)]₂ (0.375 g) with PBI (5.0 g) in acetone (150 cm³) under nitrogen atmosphere was refluxed for 5 h. Cream-coloured metal complex beads obtained were washed

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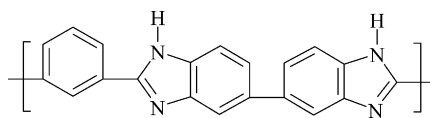


Fig. 1. PBI-unit.

with acetone followed by methanol. Subsequently, the beads were dried under vacuum. The rhodium content in the catalyst beads determined by spectrophotometry [9] was found to be 55 mg g^{-1} of dry polymer. From elemental analysis nitrogen content was found to be 8.78%. The N/Rh atomic ratio was found to be 11.7. The IR spectrum of the catalyst beads was recorded in KBr. The spectrum exhibited bands at 1626 and 1284 cm^{-1} and these were assigned to $\nu_{\text{C}=\text{N}}$ and $\nu_{\text{C}-\text{N}}$, respectively. The XPS of the catalytic species was recorded and the spectrum showed binding energies at 307.6 and 311.0 eV corresponding to Rh $3d_{5/2}$ and $3d_{3/2}$. These values are characteristic of Rh(I). The binding energy of 198.9 eV is assigned to Cl $2p$ and is suggestive of -1 oxidation state for the rhodium-bound chloride. Thus, the catalytic species predominantly contained rhodium in $+1$ oxidation state. Accordingly the polymer has remained neutral wherein PBI is co-ordinated to the metal via pyridine type of nitrogen ($-\text{N}=\text{C}$) and not the pyrrole type of nitrogen. The XPS data of the recycled species of the catalyst showed peaks at 306.9 and 311.8 eV assignable to Rh $3d_{5/2}$ and $3d_{3/2}$ in the zero oxidation state. It is likely that there is gradual reduction of Rh(I) to rhodium metal as the catalyst is recycled.

TGA studies were conducted on the catalytic species, according to which they are stable upto 360°C . The experimental details of hydrogenation were as reported earlier [10]. The hydrogenation rate was determined by measuring the uptake of hydrogen as a function of time at constant pressure. The reduced products of the substrate obtained in the molecular hydrogenation experiments were characterised based on their melting points, IR spectra and gas liquid chromatographic experiments (in a few cases).

3. Results and discussion

Physical properties of the polymer support and the catalyst are listed in Table 1. The surface area of the catalyst is observed to be higher than that of the polymer beads and this is attributed to complex formation with rhodium. The poly-

Table 1
Physical properties of PBI and PBI-Rh(I)

Property	PBI	PBI-Rh(I)
Surface area (NTP) ($\text{m}^2 \text{ g}^{-1}$)	30.2	41.7
Pore volume ($\text{cm}^3 \text{ g}^{-1}$)	0.045	0.067
Apparent bulk density (g cm^{-3})	0.24	0.23
Moisture content (wt.%)	–	4.3

Table 2
Swelling studies using different solvents and rates using *p*-nitrophenol [$0.066 \text{ mol dm}^{-3}$] and H_2 [1 atm] in methanol at 308 K

Solvent	Swelling (mol%)	Initial rate ($\times 10^4 \text{ mol dm}^{-3} \text{ s}^{-1}$)
Water	10.62	–
Methanol	6.93	0.18
Ethanol	3.72	0.25
Acetone	2.73	–
Benzene	2.49	–
THF	2.41	0.11

[PBI-Rh(I)]: $8.9 \times 10^{-4} \text{ g atom Rh dm}^{-3}$.

meric support showed swelling in different solvents but the extent of swelling is not found to influence the reaction rate. Though methanol is a better swelling solvent than ethanol, the rate of reduction of the substrate is higher in the latter solvent than in the former (Table 2). It is most probable that metal is on the surface of the catalyst. Polar protic solvents such as alcohols favour the reaction. For instance, non-polar solvents do not favour the reaction and thus the reduction of the substrate in benzene is almost negligible. In DMF, the catalyst, on addition of sodium borohydride dissolved to form a deep brown solution and this did not exhibit any catalytic activity. Among different solvents, methanol was selected to carry out reactions because of higher hydrogen solubility and polarity with its less complexing ability.

The catalytic hydrogenation of various aromatic nitrocompounds in presence of PBI-Rh(I) catalyst results in the formation of the corresponding amines. Turn-over numbers, the percentage of reduction of the substrates and time are given in Table 3.

The reduction reactions of *o*-nitrobenzoic acid were repeated with different concentrations of catalyst and substrate. The experiments were conducted under ambient conditions with respect to hydrogen pressure. The reaction solution was saturated with hydrogen and considered to be saturated with hydrogen at all times. The kinetic data obtained from each experiment could be fitted into a first-order plot of $\log(a-x)$ versus ' t ' where ' a ' is the initial substrate concentration in mol dm^{-3} and ' x ' is the amount of substrate reduced at time ' t ' (Fig. 2). The concentrations of the substrate were back calculated from the volume of hydrogen absorbed at different

Table 3
Reduction of selected nitro compounds with [PBI-Rh(I)]: $8.9 \times 10^{-4} \text{ g atom Rh dm}^{-3}$ and H_2 (1 atm) in methanol at 308 K for the hydrogenation of *p*-nitrophenol

Substrate	Turn-over number mol ($\text{g atom Rh})^{-1} \text{ h}^{-1}$	Reduction % (time (h))
<i>o</i> -Nitrophenol	110	100 (3.0)
<i>m</i> -Nitrophenol	54	37 (1.0)
<i>p</i> -Nitrophenol	73	100 (3.5)
<i>o</i> -Nitrobenzoic acid	110	100 (5.0)
<i>m</i> -Nitrobenzoic acid	90	80 (4.0)
<i>p</i> -Nitrobenzoic acid	72	87 (3.5)
<i>p</i> -Nitroaniline	73	84 (3.0)

[Nitro compound]: $0.066 \text{ mol dm}^{-3}$.

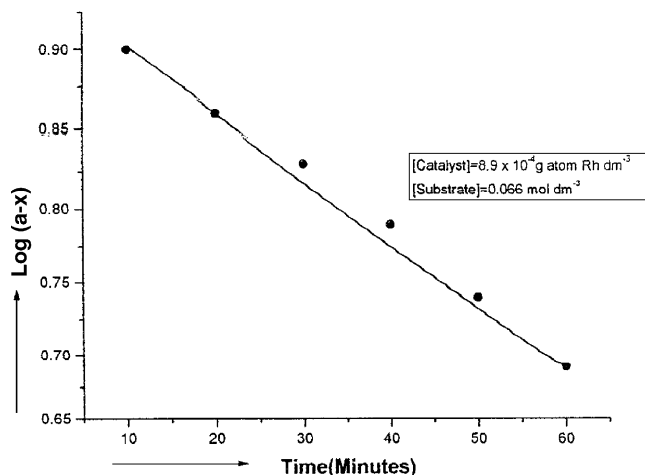


Fig. 2. First-order plot for hydrogenation of *o*-nitrobenzoic acid using PBI-Rh(I) catalyst at atmospheric pressure of hydrogen and 308 K.

time intervals taking that 3 moles of hydrogen were absorbed for every mole of the substrate. From the linear plots it can be concluded that the rate of consumption of the substrate is of the first-order. Experiments at different substrate concentrations show direct dependence of rate on the first power of substrate concentration (Fig. 3).

The influence of the catalyst concentration on the rate of reduction of *o*-nitrobenzoic acid in the range 7×10^{-4} to 9.6×10^{-4} g atom Rh dm^{-3} at a constant substrate concentration of $0.066 \text{ mol dm}^{-3}$ at 308 K and 1 atm. pressure was determined (Fig. 4). The order of the reaction calculated from the linear plot of $\log[\text{initial rate}]$ versus $\log[\text{catalyst}]$ was found to be fractional (plot not given). This might be due to the non-availability of catalytic sites or due to steric hindrance.

The PBI-Rh(I) complex behaves as active catalyst only upon addition of a small amount of sodium borohydride. The catalyst beads turned grey in presence of sodium borohydride on equilibration with hydrogen. This probably contained a hydrido complex in the solvated form [5,10]. A mechanism

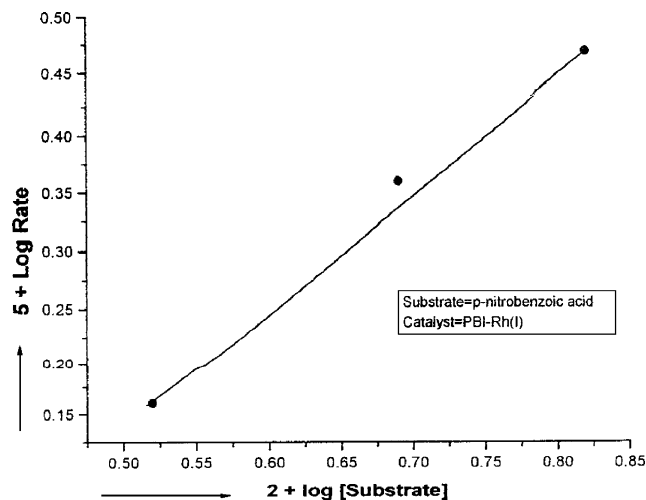


Fig. 3. Plot showing first-order dependence on [substrate].

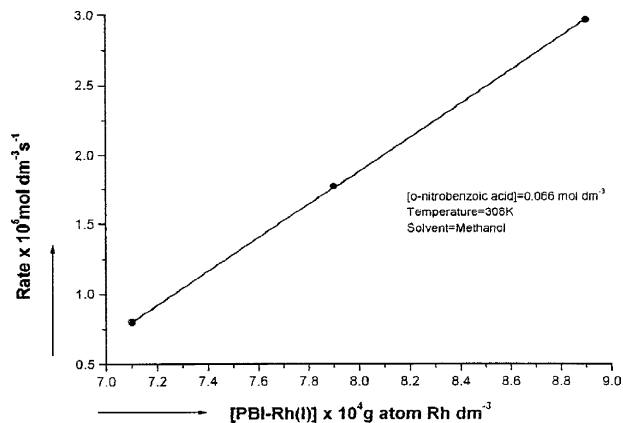


Fig. 4. Dependence of rate of hydrogenation of *o*-nitrobenzoic acid on PBI-Rh(I) concentration.

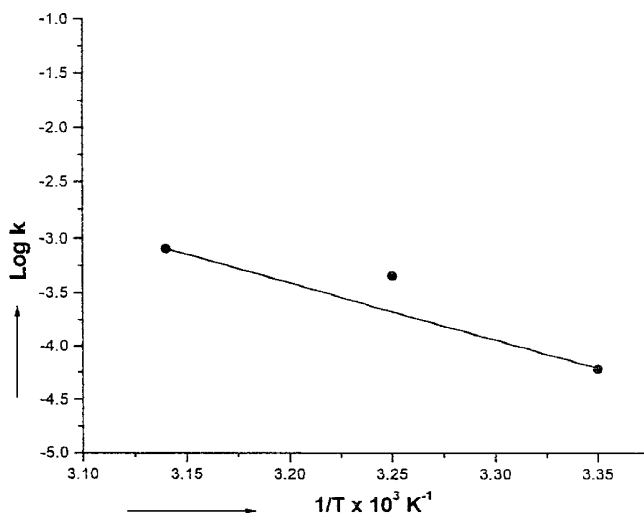
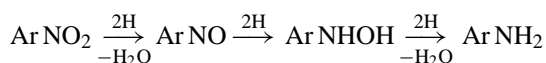


Fig. 5. Arrhenius plot for catalyst PBI-Rh(I).

similar to that proposed for the reduction of nitro group in nitroaryls in presence of homogeneous catalyst RhCl(cod) bzIH (bzIH = benzimidazole) can be envisaged [5]. One can therefore visualize the following steps for the reduction of nitroaryl to amine in presence of the catalyst.



Similar observation has been made by other workers [11].

The kinetics of hydrogenation of *p*-nitrophenol in the temperature range 298–318 K at a constant concentration of substrate and a fixed amount of the catalyst was studied. The rate of reaction was found to be dependent on the temperature of the system. The energy of activation calculated from the slope of the plot of $\log k$ versus $1/T$ was 76.5 kJ mol^{-1} (Fig. 5).

4. Recycling efficiency

The recycling efficiency of the catalyst was assessed taking *p*-nitrophenol as the substrate. The observed rates of

Table 4
Recycling efficiency of the catalyst in methanol at 1 atm. H₂ and 308 K

	Number of cycles			
	Fresh	Recycled		
		1	3	5
PBI-Rh(1)				
Rh content mg g ⁻¹	55	54	50	48
Rate × 10 ⁴ mol dm ⁻³ s ⁻¹	7.1	6.8	6.1	5.8

[*p*-Nitrophenol]: 0.066 mol dm⁻³.

reduction are given in Table 4. The activity of the catalyst dropped to 82% of its initial value when it was recycled five times. Thus, the catalyst has a good recycling efficiency. The XPS data of the recycled catalyst indicated the presence of Rh(0) and chloride-free surface. Therefore, it could be inferred that rhodium metal was formed on the polymer as a result of H₂ reduction of the supported rhodium under reaction conditions [12].

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