

HIGHLY ACTIVE AND RECYCLABLE ZSM-5 ANCHORED RHODIUM AZOBENZENE MIXED LIGAND COMPLEXES FOR THE HYDROGENATION OF ORGANIC SUBSTRATES

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ABSTRACT

The HZSM-5 were used to immobilize the homogeneous Rh(I) mixed ligand complexes of azobenzene. They were found very efficient towards the catalytic hydrogenation of alkenes, alkynes, nitrocompounds, benzaldehyde and benzil at 25°C and 2.07×10^3 KNm⁻² pressure of molecular hydrogen as compare to its homogeneous counter part. At this temperature and pressure of molecular hydrogen, ZSM-5 anchored Rh(I) complexes could be used repeatedly. DMF-toluene (1:2) mixed solvents medium was found suitable for these complexes. No diminished catalytic activity was observed even after 10-15 repeated catalytic runs. This indicated that zero almost negligible leaching out phenomenon of the metal or metal complexes.

Keyword: Rh(I) Complexes, Nitrocompounds, Alkene, Alkyne, Catalytic Hydrogenation.

INTRODUCTION

The transition metal complexes have long been used as catalysts for the dihydrogen reduction of organic substrates such as nitrocompound¹⁻¹³, alkenes¹⁴⁻²¹, alkynes²¹⁻²⁶, aldehydes²⁷⁻³⁰, ketones²⁹⁻³², Schiff bases³³ and nitriles³⁴. A good number of Rh (I) non-orthometallated and orthometallated complexes have also been found to exhibit very good catalytic activity towards dihydrogen reduction of wide variety of unsaturated organic compounds. Catalyst decomposition and poor reproducibility at the time of its repeated use was major disadvantage associated with these catalytic systems. Among the numerous homogeneous Rh (I) catalyst used for the dihydrogen reduction of various unsaturated organic substrates^{1-3, 15, 22, 33-38}, only few are found stable enough to reduce nitrocompounds, ketones and nitriles³⁹⁻⁴² and in most of the cases the reduction mechanism could not be well established⁴³⁻⁴⁴. In our previous communication we have studied the catalytic activity of Pd (II) and Rh(I) complexes towards various unsaturated organic substrates in homogeneous phase^{45,46}. The heterogenise-homogeneous catalysts exhibit excellent catalytic activity for the hydrogenation of various organic substrates, over its homogeneous counter part⁴⁷⁻⁵³. This paper introduce the excellent catalytic activity of ZSM-5 anchored Rh(I)-azobenzene mixed ligand complexes for the hydrogenation of wide variety of organic substrates. Immobilized Rh(I) complexes was found more stable, thermo potent, eco-friendly and industrially applicable as compare to its homogeneous counter part.

EXPERIMENTAL

Materials and Equipments

Analytical grade chemicals, dry and ultra pure quality of N₂, Ar and H₂ were always used. AR grade solvents and liquid substrates were purified by distillation and dried on molecular sieves (4A). Commercially available azobenzene (MERCK) was purified by recrystallizing with alcohol. RhCl₃.3H₂O of Arora-Matthey Ltd. was used without further purification. Catalytic hydrogenation were carried out by using J.T.Baker (U.S.A.) analyzed DMF. Carbon, Hydrogen and nitrogen of the complexes were recorded on Perkin Elmer 2400 CHN Elemental Analyser. Rhodium was not estimated rather it was calculated by difference. Molecular weight of the complexes was determined by using KNAUER, DAMPEFDRUCK-

Osmometer. UV/Vis., IR and NMR spectra were recorded on Pyeunicam PU8600, Pyeunicam SP3-300, Brucker AC-300F Spectrophotometer respectively. The product mixture were analyzed by TLC on silica gel coated plastic sheets (Merck Silica gel F₂₅₄) and by GLC (5700 Nucon gas chromatograph) using Apiezon.L, Carbowax 20M, SE-30 columns. Rh(I)- azobenzene mixed ligand complexes were prepared, purified and characterized by using literature methods⁴⁶.

Synthesis of Complexes

Synthesis of DicarboxylChloro(2-Phenylazobenzene-N')Rhodium(I) [Rh(AzH)Cl(CO)₂] (where AzH is azobenzene)

RhCl₃.3H₂O (0.26 g; 1.242mmol) in deoxygenated DMF (10mL) was stirred with Azobenzene (0.300 g; 1.60mmol) in nitrogen atmosphere for half an hour. The solution was then refluxed under dinitrogen atmosphere for 2h on oil bath. During the first 10 minutes the solution changed its colour from dark red to brown. The same was cooled to room temperature and diluted with deoxygenated water (35 mL). A brown precipitate slowly appeared. The reaction mixture was kept at 5°C for 1h and then filtered in nitrogen atmosphere. The Precipitate was washed with deoxygenated water and acetone successively and finally dried in vacuum desiccators.

Yield: 0.35gm (75%)

m.p.-255°C (decomposition temperature). Anal.Data found: N,7.35 ; C,42.50 ; H,2.60 [Rh(AzH)Cl(CO)₂]. Calcd: N,7.43 ; C,44.64 ; H,2.67. IR(KBr) ν-CO 1940-1880cm⁻¹ ; ν-CO(DMF) 1640 cm⁻¹ ; N=N 1530-1470 cm⁻¹. UV/Vis(DMF) 22727cm⁻¹(d-d transition).

Synthesis of Dicarboxyl (2-Phenylazophenyl-C'N')Rhodium(I) [Rh(Az)(CO)₂]

[Rh(AzH)Cl(CO)₂] 2 (0.25 g; 6.619mmol) in deoxygenated DMF(50mL) was stirred under argon atmosphere for 8h. [Rh(AzH)Cl(CO)₂] 2 was slowly converted to the subject [Rh(Az)(CO)₂] 3 with the elimination of HCl. The course of conversion was monitored by measuring the conductance and pH of the solution. At the end of reaction the compound 3 was isolated by vacuum evaporation of DMF. Compound was finally purified by recrystallizing from DMF-Methanol medium.

Yield: 0.41gm (97%)

m.p.-225°C (decomposition temperature). Anal.Data found: N,8.20 ; C,49.31 ; H,2.62 [Rh(Az)(CO)₂]. Calcd: N,8.23 ; C,49.34 ; H,2.66 . IR(KBr) ν-CO 1945-1885cm⁻¹ ; ν-CO(DMF) 1640 cm⁻¹ ; N=N 1505-1470 cm⁻¹. UV/Vis(DMF) 22472cm⁻¹(d-d transition)

Synthesis of Carbonyl(2-Phenylazophenyl-C'N')(Triphenylphosphine) Rhodium(I) [Rh(Az)(CO)(PPh₃)]

Deoxygenated DMF (50mL) solution of [Rh(Az)(CO)₂] 3 (0.25g; 7.349mmol) was stirred with finely powdered triphenylphosphine (0.19g; 7.349mmol) in argon atmosphere for 4h. The course of the reaction was monitored by collecting and measuring the volume of displaced CO. At the end of the reaction subject compound [Rh(Az)(CO)(PPh₃)] 4 was isolated by evaporating DMF under reduced pressure. Compound was purified by recrystallizing the same from DMF-methanol medium.

Yield: 0.65gm (92%)

m.p.-235°C (decomposition temperature). Anal.Data found: P,5.30 ; N,4.79 ; C,64.80 ; H,4.19 [Rh(Az)(CO)(PPh₃)]. Calcd: P,5.39 ; N,4.87 ; C,64.81 ; H,4.21. IR(KBr) ν-CO 1950-1890cm⁻¹ ; ν-CO(DMF) 1640 cm⁻¹ ; δP-C₆H₅ 1060 ; N=N 1505-1475 cm⁻¹. ³¹P (NMR)-Ph₃ 35δ. UV/Vis(DMF) 21739cm⁻¹(d-d transition)

Immobilization of Homogeneous Rh(I) Complexes With ZSM-5

Immobilizations of homogeneous Rh (I) complexes were carried out by using Literature methods⁵⁴⁻⁵⁹. Commercially available HZSM-5 was used through out the investigation. The HZSM-5 was washed thoroughly with methanol and then dried in oven first at 60°C for 2hr and then at 300°C in muffle-furnaces for 6hr. Pre-heated and pre-activated HZSM-5 was then dipped into the respective solution of soluble Rh(I) complexes. Solution was stirred mechanically with the help of shaker in argon atmosphere for 48hr. when almost all the Rh (I) complexes was absorbed/adsorbed by ZSM-5 as marked by the appearance of a colourless clear solution. The impregnated ZSM-5 was filtered and washed thoroughly

with appropriate solvent to remove the surface adhered solution of the complexes. Impregnated ZSM-5 was dried under vacuum a finally calculated below the decomposition temperature of the respective complexes for 8-48hr. Extent of impregnated (% in w/w) was determined both by weighing the residue left after vacuum evaporation of filtrate and by estimating Rhodium, Chloride and Nitrogen in the impregnated ZSM-5. Extent of impregnated was varied from 0.005-0.012% (w/w with respect to ZSM-5).

Experimental Procedure for High Pressure Hydrogenation

High pressure hydrogenation was carried out in high pressure autoclave. The substrate solution in DMF-toluene mixed solvent system containing immobilized complex was taken in the autoclave and the reaction was conducted at a constant temperature in the range 25⁰-60⁰C by immersing the autoclave in a constant temperature oil-bath. The autoclave was first evacuated and then purged several times with hydrogen. The hydrogen gas was introduced till the desire pressure ($2.76 \times 10^3 \text{ KNm}^{-2}$) was attained. Stirring of the reaction mixture was started only when it attained a constant desired temperature and pressure. At regular time interval, the product mixture was taken out by hot release. By using these immobilized Rh(I) complexes the reductions of alkenes were performed at 25⁰C while those of nitroaromatics were studied at different temperature ranging from 25⁰-60⁰C to obtain substantial rate of hydrogen.

Separation, Identification and Estimation of the Hydrogenated Products

At the end of the catalytic run, the colour of impregnated ZSM-5 was found to change depending upon the nature of substrates used and the reaction conditions. After the catalytic run the impregnated ZSM-5 was filtered off, washed thoroughly and dried while the filtrate was used for the separation of the different components. The components were separated and identified by following the same general procedure. Finally they were estimated by glc using SE-30, carbowax-20M, Sebaconitrile-25% column. The choice of column was made according to the nature of the components to be estimated.

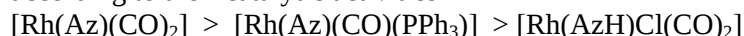
Recycle of the Catalyst

It was always found possible to recycle the ZSM-5 anchored Rh(I) complexes from the reaction mixture at the end of each catalytic run. At the end of catalytic run impregnated ZSM-5 was usually washed well with dry DMF and CCl₄ successfully. It could be used several times (10-15 Times) without any diminished catalytic activity.

RESULTS AND DISCUSSION

The ZSM-5 anchored Rh(I) azobenzene complexes were found to be highly active towards reduction of alkenes, alkynes, nitroaromatics and benzyl under high pressure conditions. ZSM-5 anchored complexes were increase the rate of hydrogenation, turn over number and yield of products drastically. In case of homogeneous Rh(I) azobenzene complexes the maximum initial turn over number of is only 27 min⁻¹ ⁴⁶ but in ZSM-5 anchored Rh(I) azobenzene complexes the turn over number increases to 45 min⁻¹. A comparative graph of the efficiency of ZSM-5 anchored complex over the homogeneous ones is shown in Fig-1. The optimum conditions, nature and % of yield of various products with recycling activity of the ZSM-5 anchored [Rh(Az)(CO)₂], [Rh(Az)(CO)PPh₃], and [Rh(AzH)Cl(CO)₂] have given in Table-1,2 and 3 respectively.

The nature of products obtained for a particular substrates using different complexes as catalyst were almost same but the rate of hydrogenation, turn over number and yield of different products was found to depend on the nature of the catalyst. [Rh(Az)(CO)₂] was found highly but not equally active as compared to other Rh(I) complexes. The ZSM-5 anchored Rh(I) complexes may be placed in the following order according to their catalytic activities –



The greater activity of ZSM-5 anchored Rh(I) complexes over its homogeneous counterpart may be due to the higher amount of more electronegative silicon and lower alumina content which make the ZSM-5 stronger acid and so the complexes are more catalytically active. In homogeneous phase the Rh(I) complexes were found susceptible to aerobic oxidation leading to Rh(III) species but ZSM-5 anchored Rh(I) complexes has more environmental tolerance. DMF-toluene (1:2) mixed solvents medium was found suitable for these complexes.

The final products in case of alkenes reduction were mainly the corresponding alkanes. The extent of isomerization was far less as compared to the homogeneous catalyst and thereby increases the yield of hydrogenated products. This was probably due to the very good reactant shape selectivity, transition state shape selectivity and product shape selectivity of ZSM-5. Fig.2 and 3 clearly shows the hydrogenation of Hex-1-ene by using homogeneous $[\text{Rh}(\text{Az})(\text{CO})_2]$ and ZSM-5 anchored $[\text{Rh}(\text{Az})(\text{CO})_2]$ complexes respectively. It requires a particular type of orientation of the coordinated alkene so that linear alkyl complex formation was preferred.

The reduction of nitroaromatics was found to be depending substantially on the reaction temperature provided other conditions remained same. The rate of reduction at room temperature was very slow and increased with temperature upto 60°C and then decreased sharply with increasing temperature. This fall in rate might be due to formation of some stable species inside the cavities of ZSM-5 at comparatively higher temperature. The products obtained from these nitrocompounds were always the corresponding amines and to partially reduced compounds were possible to isolate anywhere. The partially reduced nitrocompounds such as phenylhydroxyamines, nitrosobenzene, etc. could be reduced completely to the corresponding amines but azo and azoxy compounds could not be reduced to the corresponding amines. Hence it may be concluded that nitroaromatics were reduced without the formation of any coupled product.

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Table-1: Optimum conditions, nature and % yield of products with recycling activity of ZSM-5 anchored $[\text{Rh}(\text{Az})(\text{CO})_2]$

Substrate	Rh content (before use) gm.Atom/lit.x 10^{-3}	Products	Ist CYCLE		Ind CYCLE		IIRD CYCLE		Rh content (after use) gm.Atom / lit. x 10^{-3}
			Initial turn over no.	% of yield	Initial turn over no.	% of yield	Initial turn over no.	% of yield	
Styrene ^a	3.02	Ethylbenzene	45	98	44	98	43	98	3.02
1-Hexene ^a	3.02	1-Hexane	30	97	29	97	28	97	3.02
cyclohexene ^a	3.02	Cyclohexane	20	97	19	97	18	97	3.02
Fumaric acid ^a	3.02	Succinic acid	15	95	14	95	13	95	3.02
Phenyl acetylene ^a	3.02	Ethylbenzene	25	96	24	96	23	96	3.02
Nitrobenzene ^b	3.02	Aniline	20	98	19	98	18	98	3.02
p-Chloro nitrobenzene ^b	3.02	p-Chloroaniline	18	96	17	96	16	96	3.02
p-Dinitro benzene ^b	3.02	p-Phenylene diamine	15	97	14	97	13	97	3.02
1-Nitro naphthalene ^b	3.02	1-Amino naphthalene	12	94	11	94	10	94	3.02
Benzaldehyde ^c	3.02	Benzylalcohol	15	97	14	97	13	97	3.02

[Subs] = 0.50 mol/lit, medium = DMF-Toluene, Total Vol.=15 ml., Pressure of H₂ = 2.07 x 10³KNm⁻² [a at 25⁰C, b at 60⁰C, c at 50⁰C]

Table-2:Optimum conditions, nature and % yield of products with recycling activity of ZSM-5 anchored [Rh(Az)(CO)PPh₃]

Substrate	Rh content (before use) gm.Atom /lit x 10 ⁻³	Products	Ist CYCLE		Ind CYCLE		IIRD CYCLE		Rh content (after use) gm.Atom /lit. x 10 ⁻³
			Initial turn over no.	% of yield	Initial turn over no.	% of yield	Initial turn over no.	% of yield	
Styrene ^a	2.63	Ethylbenzene	35	97	34	97	33	97	2.63
1-Hexene ^a	2.63	1-Hexane	20	95	19	95	18	95	2.63
Cyclohexene ^a	2.63	Cyclohexane	10	94	9	94	8	94	2.63
Fumaric acid ^a	2.63	Succinic acid	8	92	7	92	6	92	2.63
Phenylacetylene ^a	2.63	Ethylbenzene	17	95	16	95	15	95	2.63
Nitrobenzene ^b	2.63	Aniline	13	97	12	97	11	97	2.63
p-Chloro nitrobenzene ^b	2.63	p-Chloroaniline	10	95	9	95	8	95	2.63
p-Dinitro benzene ^b	2.63	p-Phenylene diamine	8	94	7	94	6	94	2.63
1-Nitro naphthalene ^b	2.63	1-Amino naphthalene	7	93	6	93	5	93	2.63
Benzaldehyde ^c	2.63	Benzylalcohol	9	95	8	95	7	95	2.63

[Subs] = 0.50 mol/lit, medium = DMF-Toluene, Total Vol.=15 ml., Pressure of H₂ = 2.07 x 10³KNm⁻² [a at 25⁰C, b at 60⁰C, c at 50⁰C]

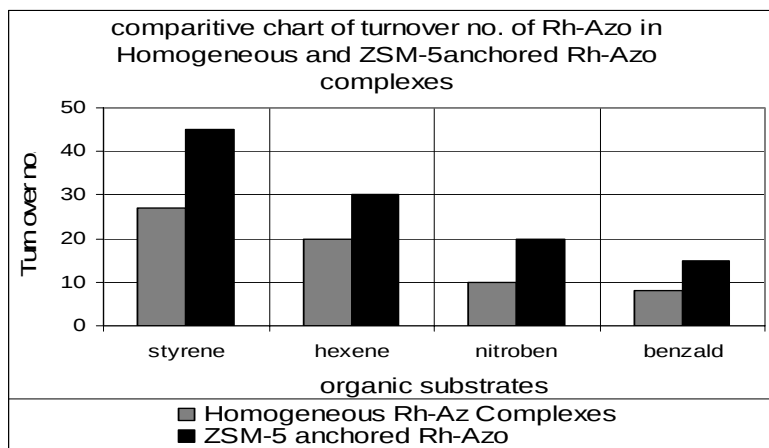


Fig.-1: Comparative study of Homogeneous Rh-Az and ZSM-5 anchored Rh-Az Complexes

Table-3: Optimum conditions, nature and % yield of products with recycling activity of ZSM-5 anchored $[\text{Rh}(\text{AzH})\text{Cl}(\text{CO})_2]$

Substrate	Rh content (before use) gm.Atom/lit $\times 10^{-3}$	Products	Ist CYCLE		Ind CYCLE		IIRD CYCLE		Rh content (after use) gm.Atom /lit. $\times 10^{-3}$
			Initial turn over no.	% of yield	Initial turn over no.	% of yield	Initial turn over no.	% of yield	
Styrene ^a	2.63	Ethylbenzene	34	97	33	97	32	97	2.63
1-Hexene ^a	2.63	1-Hexane	19	94	18	94	17	94	2.63
Cyclohexene ^a	2.63	Cyclohexane	9	93	8	93	7	93	2.63
Fumaric acid ^a	2.63	Succinic acid	7	92	6	92	5	92	2.63
Phenylacetylene ^a	2.63	Ethylbenzene	16	95	15	95	14	95	2.63
Nitrobenzene ^b	2.63	Aniline	12	97	11	97	10	96	2.63
p-Chloronitrobenzene ^b	2.63	p-Chloroaniline	9	94	8	94	7	94	2.63
p-Dinitrobenzene ^b	2.63	p-Phenylenediamine	7	93	6	93	5	93	2.63
1-Nitronaphthalene ^b	2.63	1-Aminonaphthalene	6	92	5	92	4	92	2.63
Benzaldehyde ^c	2.63	Benzylalcohol	8	95	7	95	6	95	2.63

[Subs] = 0.50 mol/lit, medium = DMF-Toluene, Total Vol.=15 ml., Pressure of $\text{H}_2 = 2.07 \times 10^3 \text{ KNm}^{-2}$ [a at 25°C, b at 60°C, c at 50°C]

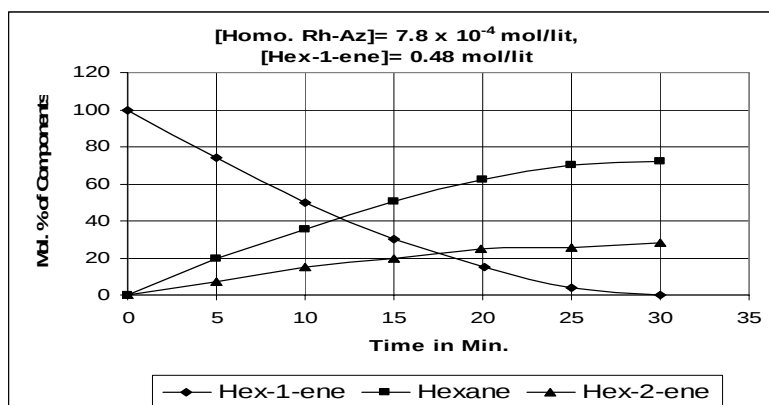


Fig.-2: Catalytic hydrogenation of hex-1-ene with $[\text{Rh}(\text{Az})(\text{CO})_2]$ in DMF at 25°C and 1 atm. Pressure of hydrogen

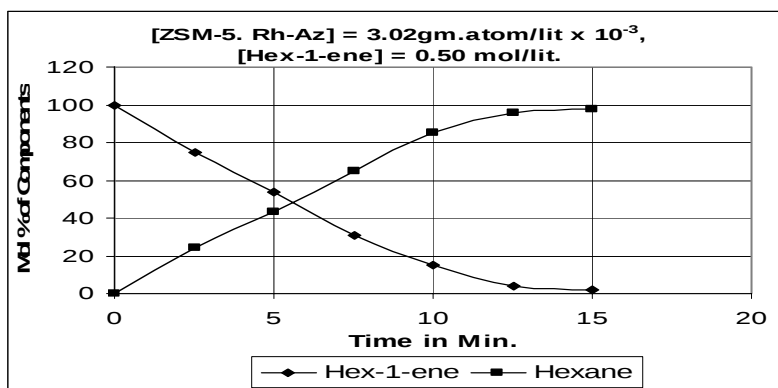


Fig.-3: Catalytic hydrogenation of hex-1-ene with ZSM-5 anchored $[\text{Rh}(\text{Az})(\text{CO})_2]$

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