



HIGHLY EFFICIENT AND RECYCLABLE ZSM-5 ANCHORED Pd (II) COMPLEXES AS CATALYST FOR THE DIHYDROGEN REDUCTION OF ORGANIC SUBSTRATES

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ABSTRACT

HZSM-5 was used to immobilize the homogeneous Pd (II) complexes of S-triazine derivatives and anthranilic acid. They were found very efficient towards the catalytic hydrogenation of alkenes, alkynes, nitrocompounds, benzaldehyde and benzil at 25°C and 1.38×10^3 KNm⁻² pressure of molecular hydrogen. At this temperature and pressure of molecular hydrogen, ZSM-5 anchored Pd (II) complexes could be used repeatedly. No diminished catalytic activity was observed even after 15-20 repeated catalytic runs. This indicated that almost negligible leaching out phenomenon of the metal or metal complexes. DMF-toluene (1 : 2) mixed solvents medium was found suitable for these complexes.

Key words: Pd (II) Complexes, ZSM-5, Nitrocompounds, Alkene, Alkyne, Catalytic hydrogenation.

INTRODUCTION

A good number of Pd (II) non-orthometallated and orthometallated complexes have 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 Pd (II) catalyst used for the dihydrogen reduction of various unsaturated organic substrates¹⁻¹¹ only few are found stable enough to reduce nitrocompounds, ketones and nitriles¹²⁻¹⁴ and in most of the cases the reduction mechanism could not be well established^{15,16}. In our previous communications, we have studied the catalytic activity of Pd (II) and Rh (I) complexes towards various unsaturated organic substrates in homogeneous phase^{17,18}. The heterogenise-homogeneous catalysts exhibit excellent catalytic activity for the hydrogenation of various organic substrates, over its homogeneous counterpart¹⁹⁻³². This paper introduces the excellent catalytic activity of ZSM-5 anchored Pd (II) complexes for the hydrogenation of wide variety of organic

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substrates. Immobilized Pd (II) complexes were found more stable, thermo potent, eco-friendly and industrially applicable as compared to its homogeneous counter part.

EXPERIMENTAL

Materials and methods

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 Anthranilic acid was used and purified by recrystallizing from benzene. S-triazines¹ OR-TH, DEt-ATH₃, DEt-ATH were prepared and purified using literature methods³³. Palladium chloride was used without further purification. Catalytic hydrogenation were carried out by using J. T. Baker (USA) analyzed DMF. Carbon, hydrogen and nitrogen of the complexes were recorded on Perkin Elmer 2400 CHN Elemental Analyzer. Palladium was estimated gravimetrically as Palladium-dimethylglyoximate. Chlorine was estimated by carius method. Molecular weight of the complexes was determined by using KNAUER Dampfedruck-Osmometer. UV/Vis, IR and NMR spectra were recorded on Pyeunicam PU8600, Pyeunicam SP3-300 and Bruker 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. Pd (II) complexes of S-triazine derivatives and anthranilic acid were prepared, purified and characterized by using literature methods¹⁷.

¹ORTH, 2-o-hydroxyphenyl-4-amino-6-alkoxy-1,3,5-triazine;

DEt-ATH₃, 2-o-hydroxyphenyl-4-amino-6-diethyleamino-1,2-dihydro-1,3,5-triazine;

DEt-ATH, 2-o-hydroxyphenyl-4-amino-6-diethyleamino-1,3,5-triazine

Preparation of complexes

Preparation of di-μ-chloro-bis(s-triazino) palladium (II) [Pd₂(OR-T)₂(Cl)₂] **1**

To the methanolic solution (25 mL) of palladium chloride (0.433 g), S-triazine (0.113 g) in benzene (8 mL) was added drop wise with constant stirring at 30°C. After complete addition of S-triazine the mixture was stirred for 1 h more. The greenish yellow precipitate of the subject compound appeared slowly. The palladium S-triazine complex was then filtered, washed several times with methanol and benzene. Finally, the compound was dried under vacuum. The other two palladium (S-triazine) complexes, i.e., [Pd₂(DEt-ATH₂)₂Cl₂] **2** and [Pd₂(DEt-AT)₂Cl₂] **3** were prepared following the same procedure.

Yield: **1** = 80%; **2** = 78%; **3** = 75%.

Preparation of bis(anthranilato)di- μ -chloropalladium (II) [Pd₂(An)₂(Cl)₂] 4

To the methanolic solution (25 mL) of PdCl₂ (0.086 g) anthranilic acid (0.133g) in methanol (10 mL) was added drop wise with constant stirring for 20 min. the stirring was continued for 1 h more. Greenish yellow subject compound was slowly precipitate out. Anthranilato complex was then filtered, washed several times with methanol and dried under vacuum desiccator.

Yield: **4** = 85%

Immobilization of homogeneous Pd (II) complexes with ZSM-5

Immobilizations of homogeneous Pd (II) complexes were carried out by using Literature methods³⁴⁻³⁹. 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 2 h and then at 300°C in muffle-furnaces for 6 h. Pre-heated and pre-activated HZSM-5 was then dipped into the respective solution of soluble Pd (II) complexes. Solution was stirred mechanically with the help of shaker in argon atmosphere for 48 h. When almost all the Pd (II) complexes were 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 and finally calcined below the decomposition temperature of the respective complexes for 8-48 h. Extent of impregnated (% in w/w) was determined both by weighing the residue left after vacuum evaporation of filtrate and by estimating palladium, chloride and nitrogen in the impregnated ZSM-5. Extent of impregnation was varied from 0.005-0.012% (w/w with respected to ZSM-5).

Experimental procedure for high pressure hydrogenation

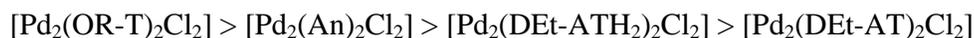
High pressure hydrogenation was carried out in high pressure autoclave. The substrate solution in DMF-toluene mixed solvent system containing immobilized complex was taken in the autoclave and the reaction was conducted at a constant temperature in the range 25°-60°C by immersing the autoclave in a constant temperature oil-bath. The autoclave was first evacuated and then purged several times with hydrogen. The hydrogen gas was introduced till the desired pressure (1.38 x 10³ 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 Pd (II) complexes the reductions of alkenes were performed at 25°C while those of nitroaromatics were studied at different temperature ranging from 25°-60°C to obtain substantial rate of hydrogen.

RESULTS AND DISCUSSION

HZSM-5 was used to immobilize the homogeneous Pd (II) complexes of S-triazine derivatives and anthranilic acid. HZSM-5 is an aluminum silicate with high silica content. It consists of two intersecting channel systems defined by ten member ring of tetrahedral. The channels are ellipsoidal with ten ring openings having approximate free dimensions $5.4 \times 5.5 \times 10^{-8}$ cm (straight channel) and $5.1 \times 5.4 \times 10^{-8}$ cm (sinusoidal channel). A gram of so of this type of catalyst support has an internal surface area equal to that of a standard tennis court.

The ZSM-5 anchored Pd (II) complexes were found to be highly active towards reduction of alkenes, alkynes, nitroaromatics and benzyl under normal pressure conditions. ZSM-5 anchored complexes drastically increase the rate of hydrogenation, turn over number and yield of products. The optimum conditions, nature and % of yield of various products with recycling activity of the ZSM-5 anchored $[\text{Pd}_2(\text{OR-T})_2\text{Cl}_2]$ 1 and $[\text{Pd}_2(\text{DEt-ATH}_2)_2\text{Cl}_2]$ 2 have given in Table 1 and 2, 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 be dependent on the nature of the catalyst. In our previous communication¹⁷, it was found that homogeneous $[\text{Pd}_2(\text{OR-T})_2\text{Cl}_2]$ 1 was found highly but not equally active as compared to other Pd (II) complexes. Likewise homogeneous Pd (II) complexes, the ZSM-5 anchored Pd (II) complexes may be placed in the following order according to their catalytic activities –



In case of homogeneous $[\text{Pd}_2(\text{OR-T})_2\text{Cl}_2]$ complexes, the maximum initial turn over number of was found only 87 min^{-1} but in ZSM-5 anchored $[\text{Pd}_2(\text{OR-T})_2\text{Cl}_2]$ complexes the turn over number increases to 92 min^{-1} . A comparative graph of the efficiency of ZSM-5 anchored $[\text{Pd}_2(\text{OR-T})_2\text{Cl}_2]$ complex over the homogeneous one with various organic substrates is shown in Fig. 1.

The greater activity of ZSM-5 anchored Pd (II) complexes over its homogeneous counterpart may be due to higher internal surface area. In spite of that the higher amount of more electronegative silicon and lower alumina content which make the ZSM-5 stronger acid and so the complexes become more catalytically active. In homogeneous phase the Pd (II) complexes were decomposed when exposed to open environment but ZSM-5 anchored Pd (II) complexes has more environmental tolerance. DMF-toluene (1 : 2) mixed solvents medium was found suitable for these complexes.

Table 1: Optimum conditions, nature and % yield of products with recycling activity of ZSM-5 anchored [Pd₂(OEt-T)₂Cl₂]

Substrate	Pd content (before use) g A tom/lit. x 10 ⁻³	Products	I st Cycle		III rd CYCLE		V th CYCLE		Pd content (after use) g A tom/lit. x 10 ⁻³
			Initial turnover No.	% of yield	Initial turnover No.	% of yield	Initial turnover No.	% of yield	
Styrene ^a	2.85	Ethylbenzene	92	98	91	98	90	98	2.85
1-hexene ^a	2.85	1-hexane	60	96	59	96	58	96	3.85
Cyclohexene ^a	2.85	Cyclohexane	42	97	41	97	40	97	2.85
Fumaric acid ^a	2.85	Succinic acid	16	95	15	95	14	95	2.85
Phenylacetylene ^a	2.85	Ethylbenzene	35	97	34	97	33	97	2.85
Nitrobenzene ^b	2.85	Aniline	30	98	29	98	28	98	2.85
p-chloro- nitrobenzene ^b	2.85	p-chloro- aniline	25	97	24	97	23	97	2.85
p-dinitro- benzene ^b	2.85	p-phenylene- diamine	18	96	17	96	16	96	2.85
1-nitro- naphthalene ^b	2.85	1-amino- naphthalene	15	95	14	95	13	95	2.85
Benzaldehyde ^c	2.85	Benzylalcohol	18	97	17	97	16	97	2.85

[Subs] = 0.50 mol/lit, medium = DMF-Toluene, Total Vol. = 15 mL., Pressure of H₂ = 1.38 x 10³ KNm⁻² [a at 25°C, b at 60°C, c at 50°C]

Table 2: Optimum conditions, nature and % yield of products with recycling activity of ZSM-5 anchored [Pd₂(An)₂Cl₂]

Substrate	Pd content (before use) g A tom/lit. x 10 ⁻³	Products	I st Cycle		III rd CYCLE		V th CYCLE		Pd content (after use) g A tom/lit. x 10 ⁻³
			Initial turnover No.	% of yield	Initial turnover No.	% of yield	Initial turnover No.	% of yield	
Styrene ^a	3.99	Ethylbenzene	87	98	86	98	85	98	3.99
1-hexene ^a	3.99	1-hexane	50	97	49	97	48	97	3.99
Cyclohexene ^a	3.99	Cyclohexane	35	96	34	96	33	96	3.99
Fumaric acid ^a	3.99	Succinic acid	12	94	11	94	10	94	3.99
Phenylacetylene ^a	3.99	Ethylbenzene	22	97	21	97	20	97	3.99
Nitrobenzene ^b	3.99	Aniline	25	97	24	97	23	97	3.99
p-chloro- nitrobenzene ^b	3.99	p-chloro- aniline	20	96	19	96	18	96	3.99
p-dinitro- benzene ^b	3.99	p-phenylene- diamine	12	95	11	95	10	95	3.99
1-nitro- naphthalene ^b	3.99	1-amino- naphthalene	10	94	9	94	8	94	3.99
Benzaldehyde ^c	3.99	Benzylalcohol	15	96	14	96	13	96	3.99

[Subs] = 0.50 mol/lit, medium = DMF-Toluene, Total Vol. = 15 mL, Pressure of H₂ = 1.38 x 10³ KNm⁻² [a at 25°C, b at 60°C, c at 50°C]

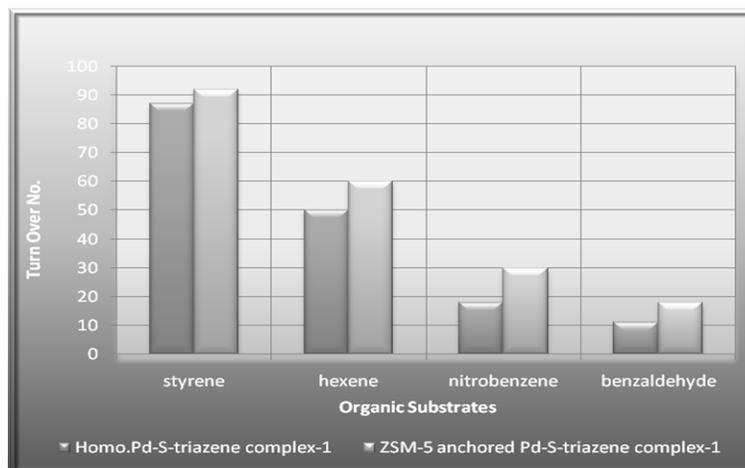


Fig. 1: Comparative graph of the efficiency of ZSM-5 anchored $[Pd_2(OR-T)_2Cl_2]$ complex over the homogeneous one with various organic substrates

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. It requires a particular type of orientation of the coordinated alkene. This was probably due to the very good shape selectivity of ZSM-5.

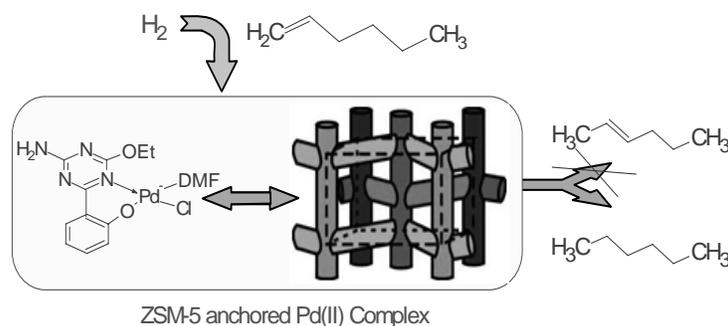


Fig. 2

Fig. 3 and 4 clearly shows the hydrogenation of Hex-1-ene by using homogeneous $[Pd_2(OR-T)_2Cl_2]$ and ZSM-5 anchored $[Pd_2(OR-T)_2Cl_2]$ complexes, respectively.

The reduction of nitroaromatics was found to be substantially dependent on the reaction temperature and the other conditions were same. The rate of reduction at room temperature was very slow and increased with temperature upto $60^\circ C$ 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 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.

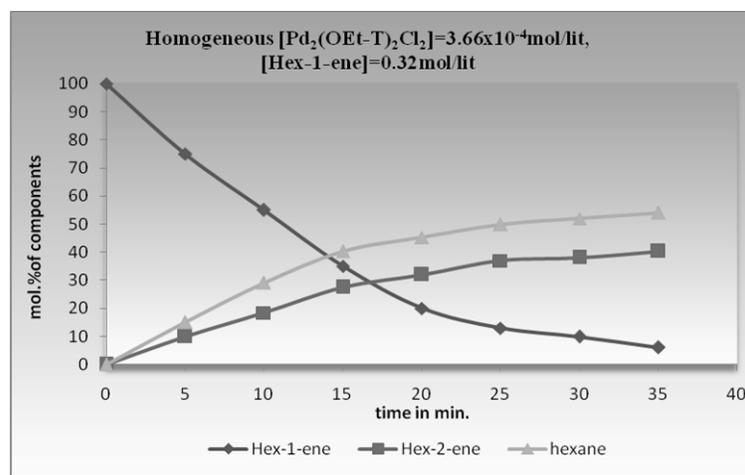


Fig. 3: Hydrogenation of Hex-1-ene by using homogeneous $[Pd_2(OR-T)_2Cl_2]$ complex

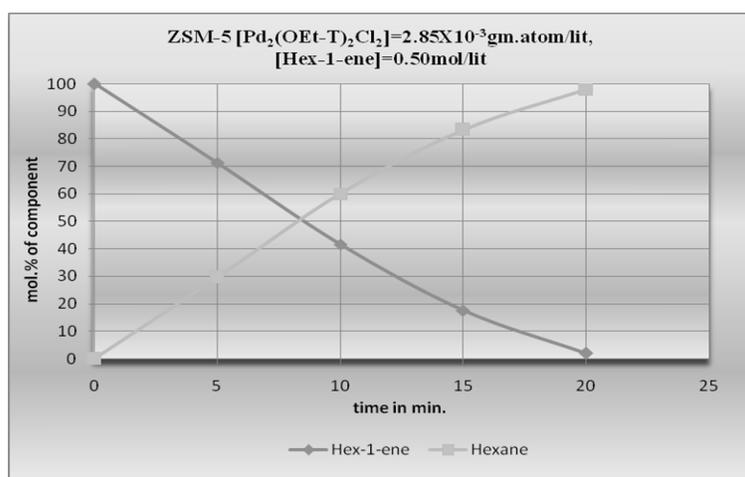


Fig. 4: Hydrogenation of Hex-1-ene by using ZSM-5 anchored $[Pd_2(OR-T)_2Cl_2]$ complex

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 by fractional distillation. The separated components were 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 Pd (II) 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 (15-20 times) without any diminished catalytic activity.

CONCLUSION

The ZSM-5 anchored Pd (II) complexes of S-triazine derivatives and anthranilic acid exhibit excellent catalytic activity for the hydrogenation of various organic substrates. These immobilized complexes are more efficient as compared to its homogeneous counterpart. In case of alkenes, the yield of hydrogenated products was increased by decreasing isomerization due to shape selectivity of immobilized catalyst. DMF-toluene (1 : 2) mixed solvents medium was found suitable for these complexes. No diminished catalytic activity was observed even after 15-20 repeated catalytic runs.

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