ZSM-5 anchored Ru(II) complex of bipyridine: An efficient and reusable catalyst for oxidation of alkenes, alkanes, aromatic hydrocarbons and alcohols

Sharma Varsha[1] and Sagar Priyanka[2*]
1. Department of Chemistry, S.S. Jain Subodh P.G. College (autonomous), Jaipur, Rajasthan, INDIA
2. Department of Chemistry, S.S.J. Campus, Kumaun University, Almora, Uttarakhand, INDIA
*sagarpriyanka2006@gmail.com

Abstract

ZSM-5 anchored trans (Cl)-[Ru(II)(bpy)(CO)$_2$Cl$_2$] was found too proficient towards the catalytic oxidation of olefins, saturated and aromatic hydrocarbons and alcohols in CH_2Cl_2-C_2H_5OH (6:4) mixed solvent system at 60^OC and 6.2×10^3 KNm^{-2}. At this temperature and pressure, substantial amount of catalytic oxidation was observed and for this reason, the pressure was not increased above $6.2 \times 10^3 KNm^{-2}$.

Catalytic activity of ZSM-5 anchored catalyst did not declined even after repeated use up to 6-8 catalytic runs. It indicates that immobilized catalyst retains the stereochemistry around the catalytic active center as like its homogeneous counterpart.

Keywords: Ru(II) complexes; ZSM-5, catalytic oxidation, alkene, alkanes, aromatic hydrocarbons, alcohol.

Introduction

The variable oxidation state carried by the transition metal makes them more susceptible to interact with molecular oxygen in such a way that one can easily isolate the intermediates as well as oxygenated products.[3,6,8,13,15,43,46] Every form of metal whether in metallic state or in the form of salt or complex, is commonly but industrially used for the oxidation of a variety of organic substrates.[1,2,5,7,10,14,17,19,29,30,42,44,45,48,49] Large numbers of homogeneous and immobilized solid phase anchored complexes are also reported for their excellent catalytic activity towards oxidation of olefin, alkanes, aromatic hydrocarbons, alcohols and carbonyl compound.[4,11,12,20,22,25,26,27,31,32,47,50]

We previously reported the catalytic activity of homogeneous and ZSM-5 anchored Pd (II) and Rh(I) complexes towards oxidation and hydrogenation of various organic compounds.[33-40] In the present study, affluent use of ZSM anchored Ru(II) complex of bipyridine for the catalytic oxidation of olefins, alcohols, saturated and aromatic hydrocarbons has been reported.

Material and Methods

Materials and equipments: Analytical grade chemicals were used during the whole investigation. For experimental work we always used the ultra pure quality of N_2, Ar and O_2. Solvents preservation was always done by using molecular sieves (4A) which were kept under nitrogen / argon atmosphere. Commercially available bipyridine was used after recrystallising from aqueous ethanol.

Commercially available HZSM-5 {ZSM-5 is a zeolite having high silica content and much lower aluminum content, the structure of ZSM-5 embodied with two intersecting channel systems consist of ten member ring of tetrahedral[21]**}** was washed with dry methanol and activated prior to use. Ruthenium was estimated spectrophotometrically [41] using 5-nitro-2.4.6-triamino pyrimidino at pH 1.8. The absorbance was noted at λ max 540 nm.

Semi-micro analytical methods were used for the estimation of carbon, hydrogen and nitrogen. Estimation of halogen was confirmed by using literature method**[24].** Pye-Unicam PU-8600, Pye-Unicam SP3-300 and Bruker AC-300F spectrophotometer were used for electronic, vibrational and NMR spectral studies respectively. TLC using silica gel-coated plastic sheets (Merck silica gel F254) and GLC (5700 Nucon gas chromatograph, using SE-30, Carbowax-20M or OV-17 column) were used for the analysis of product mixture**.**

Preparation of catalysts

Preparation of trans (Cl)-2,2'-bipyridinedicarbonyldichlororuthenium(II) complex - Trans (Cl)- [Ru^{II}(bpy)(CO)$_2$Cl$_2$] {Where bpy = 2,2$^/$-bipyridine}: Complex was prepared and characterized as per reported method[23].

Immobilization of soluble complex with ZSM-5: Immobilization of the complex by ZSM-5 was conducted by reported literature methods [9,16,28]. ZSM-5 is a zeolite having high silica content and much lower aluminum content. The structure of ZSM-5 embodied with two intersecting channel systems consists of ten member ring of tetrahedral.

The ZSM-5 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)[18,21].

Dry methanol was used for washing the commercially available HZSM-5. After washing it was dried in oven at 120^0C for 2h and dried in Muffle-furnace at 350^0C for 6h. Preheated and activated HZSM-5 was then dipped into the deoxygenated solution of soluble transition metal complex trans(Cl)-2,2$^/$-bipyridinedicarbonyldichlororuthenium(II) in a 50 ml round bottom flask which was connected with gas inlet and outlet assembly.

Mechanical shaker was used to stirrer round bottom flask mechanically in nitrogen atmosphere for 48 h. Absorption/adsorption of all the metal complex by the ZSM-5 was confirmed by the remaining colorless clear solution in round bottom flask. The impregnated ZSM-5 was filtered and washed properly with dry alcohol for removing the adhering surface particles of the complex.

Under vacuum condition, impregnated ZSM-5 was dried and was kept under reduced pressure of argon at the temperature below the decomposition temperature of the respective complexes for 8-48 hours. After that weighing of the residue left after vacuum evaporation of filtrate and weighing and estimation of metal, halogen and nitrogen in the impregnated ZSM-5 were done to determine the extent of impregnation (% in w/w).

Procedure for high pressure oxidation: High pressure oxidation procedure was discussed in our previous communication[38]. Immobilized complex and substrate with solvent system was taken in a non-magnetic stainless steel high pressure autoclave which was kept in a constant temperature oil-bath (at 55^0C-70^0C). First of all, the evacuation of autoclave was done and then depurated several times with oxygen.

The autoclave was connected with oxygen cylinder till the desirable pressure (~ 6.20×10^3 KNm^{-2}) was obtained. After attaining the constant desired temperature and pressure, stirring of the reaction mixture was started. Time to time at regular interval, the product mixture was taken out by product release assembly for analysis of intermediate products.

Results and Discussion

The ZSM-5 anchored Ru(II) complex was found active under both normal and high pressure conditions towards the catalytic oxidation of olefins, alcohols, saturated and aromatic hydrocarbons. But at high pressure of molecular oxygen, the remarkable increase in the rate of oxidation was found.

As a consequence of this catalytic oxidation using ZSM-5 anchored complex was carried out mainly at high temperature (60^0C) and at high pressure (~6.20×10^3 KNm^{-2}). Catalytic oxidation was carried out in different solvents namely in DMF, CH_3CN, C_2H_5OH and CH_2Cl_2. In the present investigation CH_2Cl_2-C_2H_5OH (7:3) was found best solvent system when oxidation was carried out with ZSM-5 anchored trans (Cl)-[Ru(bpy)$(CO)_2(Cl)_2$] catalyst. The operating condition, nature and percentage of yield of major products with recycling activity of ZSM-5 anchored trans (Cl)-[Ru(bpy)$(CO)_2(Cl)_2$] have been given in table 1.

A significant increase in the rate of oxidation of different organic substrates was observed with the increase of temperature while keeping other conditions constant. The rate of oxidation at 28^0C was very slow but increased slowly and significantly at higher temperature up to 65-70^0C. The rate of oxidation was found to decrease sharply above 70^0C, possibly the emergence of some inactive stable species inside the cavities of ZSM-5. No diminished catalytic activity was observed even after 6-7 repeated catalytic runs. In the present investigation no leaching out phenomenon was observed in any cases.

Table 1
Recycling activity of ZSM-5 anchored trans(Cl)-[Ru^{II}(bpy)$(CO)_2(Cl)_2$] towards the catalytic oxidation of organic substrates

Substrate	Ru content (before use) (10^3g.atom/ lit.)	Product[a]	Ist cycle		IIIrd cycle		VIth cycle		Ru content (after use) (10^3g.atom/lit)
			Initial turn over no.	% of yield	Initial turn over no.	% of yield	Initial turn over no.	% of yield	
Styrene	2.60	Benzaldehyde	35	90	34	89	34	89.5	2.60
Cyclo-hexene	2.60	2-cyclohexen-1-ol	30	73	30	73.5	29.5	73.5	2.58
1-octene	2.60	2-octanone	20	92	20	92	20	91.5	2.58
Benzene	2.60	Phenol	21	88	20.5	87	20.5	87	2.59
Benzyl-alcohol	2.60	Benzaldehyde	18	62[b]	17.7	62[b]	17.5	61[b]	2.59
p-chloro benzyl alcohol	2.60	p-chloro benzaldehyde	16	60[b]	16	60[b]	16	59[b]	2.55

[subs] = 0.5 mol/lit., Medium = CH_2Cl_2-C_2H_5OH (6:4) mixed solvent, Total volume =15ml,
Pressure of oxygen = 6.20×10^3 KNm^{-2}, Temperature = 80^OC, [a]Only major products are reported,
[b] % yield after 4 h.

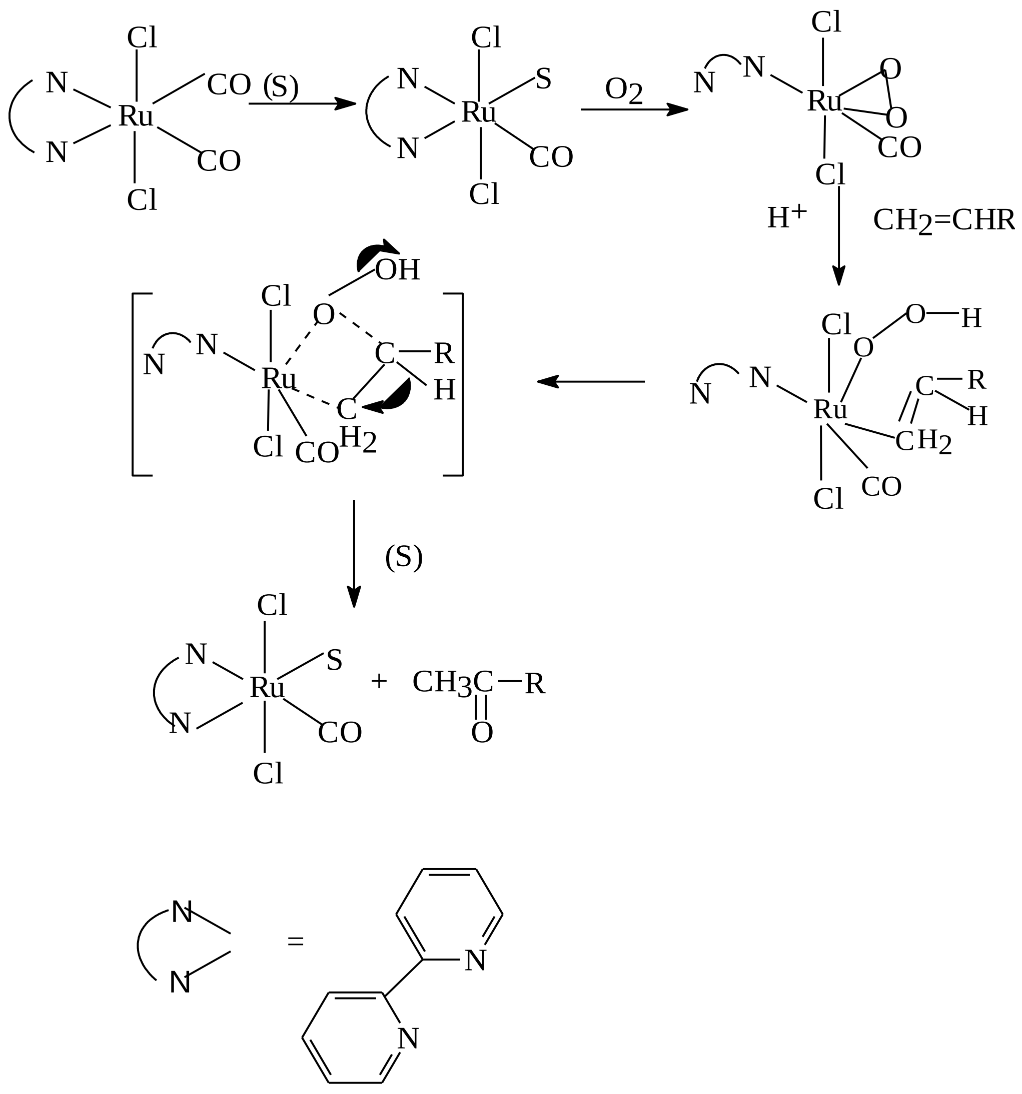
This was confirmed by estimating Ru content in ZSM anchored catalyst before and after use as in table 1. On the grounds of initial turn over number, the substrate may be organize in the following order:

Styrene > cyclohexene > 1-octene > benzene > benzyl alcohol > p-chloro benzyl alcohol.

In the present investigation, the genre, yield and turnover of products obtained for a variety of substrates using ZSM-5 anchored catalyst were found comparable to that of their soluble counterpart. It indicates that in ZSM-5 anchored catalyst, the stereochemistry around catalytic centre was not changed substantially (Mechanism 1).

Separation, identification and estimation of the oxygenated products: After the completion of each catalytic reaction, the colour of impregnated ZSM-5 was observed to change which was depending upon the nature of substrate and catalyst. At the end of catalytic run, the impregnated ZSM-5 was separated from the reaction mixture simply by filtration which was then ready to recycle after washing and drying. The filtrate of reaction mixture was ready to analyze after doing for the separation and estimation of the different oxygenated products. Separation and identification of different oxygenated products were performed by the same general procedure as mentioned previously. They were analyzed by GLC using SE-30, Carbowax-20M and OV-17 column. The column was selected on the basis of the nature of the oxygenated products to be analyzed.

Recycle of the catalyst: After each catalytic run, it was always tried to recycle the ZSM-5 supported Ru(II) complex from the reaction mixture. After each catalytic run, impregnated ZSM-5 was washed properly with dry alcohol. ZSM-5 was then dried and could be used many times (almost 6-7 times) without showing any diminished catalytic activity.



S = Solvent

Mechanism 1: The tentatively proposed mechanism for the oxidation of 1- alkene in presence of molecular oxygen as oxidant

Conclusion

ZSM-5 anchored Ru(II) complex was used as effective catalyst for oxidation of a variety of organic compounds. Ru(II)-bipyridine complex was effective in homogeneous phase but additional advantages i.e. separation and stability were achieved in impregnated form. The best suitable solvent for these catalytic reactions is CH_2Cl_2-C_2H_5OH (6:4) mixed solvent at 65^0C and 6.2 x 10^3 KNm^{-2}.

In the present investigation, genre and percentage of yield of products obtained for different substrates using ZSM-5 anchored catalyst were found comparable to that of their soluble counterpart. It indicates that in ZSM-5 anchored catalyst the stereochemistry around catalytic centre was not changed substantially if anyone compared with its homogeneous counterpart which is a highly potential application in the field of green chemistry to save our environment from chemicals.

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