Catalyic Activity of Ruthenium(III) and Palladium(II) Complexes of 2-Methylbenzimidazole (Mebzlh) Encapsulated in Zeolite-Y and ZSM-5 for Liquid Phase Hydroxylation of Phenol

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Abstract

Ruthenium(III) and palladium(II) complexes of 2-methylbenzimidazole (Mebzlh) ligand encapsulated in the super cages of zeolite-Y and ZSM-5 have been synthesized and characterized by various physico-chemical measurements. A suitable reaction condition has been optimized for [Ru(Mebzlh)]-Y by considering the effect of various parameters such as different solvents, concentration of substrate, reaction time and amount of oxidant etc., for the maximum conversion of phenol to a mixture of catechol and hydroquinone. The results obtained showed that selectivity for the catechol formation is ca. 85%, even though the conversion of phenol varies in the order [Ru(Mebzlh)]-Y (35%) >

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[Pd(Mebzlh)]-Y (15 %) > [Ru(Mebzlh)]- ZSM-5(10 %) > [Pd(Mebzlh)]- ZSM-5 (2 %) after 6 h of reaction time.

Keywords: Encapsulation; zeolite-Y; ZSM-5; hydrogen peroxide decomposition; oxidation of phenol

1. **Introduction**

Nowadays the research in the area of heterogeneous catalysts is gaining importance because of the problems involved with homogeneous catalysts. The optimization of already known synthetic procedures by the possibility of performing reactions with very high yield by reducing by-products and with limited use of solvents is gaining lot of importance [1]. Generally such a reaction requires the presence of a catalyst which can selectively break the chemical bonds and form the new chemical bonds. Homogeneous catalysts were designed for such type of organic reactions but they require large quantities of solvents and difficult to recover the products. The substitution of such homogeneous catalysts with anchored solid supports is economical and reduces the environmental problems [2]. A great deal of research has been done on solid catalysts by considering their chemical and thermal stability, micro and mesoporosity. A heterogeneous catalyst can be obtained by encapsulating [ship-in-a-bottle] inside the pore of zeolite or by anchoring or tethering them to inert supports [3]. The ship-in-a-bottle approach is convenient and ideal, because the complex, once formed inside the cages of zeolite, is too large to diffuse out and is not lost in the liquid phase reaction. These encapsulated zeolites are the most important heterogeneous catalysts used in the petrochemical industry and in the synthesis of fine chemicals. Various transition metal complexes of Schiff bases and phthalocyanines have been encapsulated in zeolite-Y and their catalytic activity has been studied in the decomposition of H_2O_2 and tert-butyl hydroperoxide, oxidation of phenols, cyclohexanol, cyclohexene and other related reactions [4-9]. The liquid phase hydroxylation of phenol using simple oxidant like molecular oxygen and H_2O_2 is industrially important reaction. Both homogeneous and heterogeneous processes were known for the hydroxylation of phenol. The zeolite encapsulated metal complexes have considerable importance in this regard.

In the present work, ruthenium(III) and palladium(II) complexes of 2-methylbenzimidazole (Mebzlh, I) are encapsulated in zeolite-Y and ZSM-5 and their catalytic activity for the liquid phase hydroxylation of phenol has been studied. To our knowledge, there are no reports so far of using encapsulated benzimidazole complexes of ruthenium and paladium inside H-Z-Y and H-ZSM-5 for the hydroxylation of phenol. A suitable reaction condition has also been optimized to get maximum conversion of phenol.

2 Experimental

2.1 Materials

Zeolite H-Y and H-ZSM-5 were purchased from Sud-Chemie, Mumbai. LR−Grade acetone was purified according to literature methods [10]. Analytical grade ruthenium chloride and palladium chloride, Phenol and hydrogen peroxide (30%) were purchased from Merck and were used as such.   The ligand,   2-methyl benzimidazole was prepared according to the literature method [11].

2.2 Characterisation

Metal contents in the encapsulated complexes were measured by using Perkin-Elmer model ICP instrument.   Surface area measurements were carried out by the BET method on a NOVA-1000 Ver.3.70 instrument. TGA was recorded on a NETZSCH STA 409 PG/PC in flowing air and He atmosphere.   X-ray diffraction patterns were recorded on a Philips Analytical X-ray instrument with CuKα target.   FT-IR spectra of the complexes were recorded as KBr pellets on a Nicolet 4000 spectrophotometer.   UV−Vis spectra were recorded for the ligand in DMF and by diluting with $BaSO_4$ for the neat complex and encapsulated complex on a Shimadzu UV-Vis-NIR model UV-3101P instrument.   Products formed from the reactions in the catalytic activity studies were analyzed using a Shimadzu 14B gas chromatograph fitted with FID detector and BP-5 capillary column.

2.3 Preparation of zeolite encapsulated complexes

5 g of metal chloride salt was dissolved in acetone. To this solution taken in a 100 ml round bottom flask, 11g of calcined H-Y or H-ZSM-5 was added. The mixture was refluxed with stirring for 12 h in an oil bath. The solid was filtered out and then washed with water till the washings were free of metal ions. It was dried in a hot- air oven at 150 ℃ for 24 h. Then M-Y was treated with an acetone solution of 2.5 g of 2-methyl benzimidazole and refluxed with stirring for 24 h in an oil bath. The residue was filtered and extracted first with DMF then with acetone using the Soxhlet apparatus to remove the unreacted ligand and any free metal complex adsorbed on the zeolite surface. The resulting solution was treated with aq. 0.01M NaCl solution and then stirred for 15 h to exchange the uncomplexed metal ions with sodium ions. Then, the zeolite- encapsulated complex was filtered, washed with distilled water to remove the chloride ions present and dried in a hot- air oven at 150 ℃ for 24 h.

3 Catalytic Activity Measurements

3.1 Decomposition of H_2O_2

An aqueous solution of standard 30% H_2O_2 (3.95 ml, 5.53 g) was added to 0.025 g catalyst and the reaction mixture was stirred for 1 and 2 h respectively, at room temperature. The catalyst was then separated out by filtration and washed with distilled water. The filtrate containing partially decomposed H_2O_2 and the washings were collected in a 250 ml volumetric flask, and the contents were made up to 250 ml with distilled water. Then 10 ml of this solution was titrated with standard $KMnO_4$ solution to estimate the unreacted H_2O_2 [12].

3.2 Hydroxylation of phenol

The catalytic reactions were carried out in a 50 ml double-necked round bottom flask fitted with a water condenser and heated on an oil bath using a magnetic stirrer. In a typical reaction, Phenol (2.35 g, 0.025 mol) and 30% aqueous H_2O_2 (19.8 ml, 0.25 mol, 27.7g) were mixed in 2ml of MeCN solvent and the reaction mixture was heated in an oil bath with continuous stirring at 80 ℃. Then 2

mmol catalyst was added and the reaction was considered to begin. Aliquots were withdrawn from the reaction mixture and analyzed, using a gas chromatograph.

4 Results and Discussion

4.1 Synthesis and characterization of catalysts

Synthesis of the metal complex in the cages of H-Y and H-ZSM-5 was carried out by the flexible ligand method [13]. The percentage of metal content in the encapsulated complex was measured by using ICP instrument.   The percentages of metal content along with the colour and formulae of the complexes and surface area measurements are given in Table 1. Simple complexes of Mebzlh were also prepared for comparison of the physico-chemical properties of encapsulated complexes.

Compound	Colour	Metal (Wt %)		*S_{BET}	Total Pore volume
H-Z-Y	White		-	25.8	0.105
H-ZSM-5	White		-	258.7	0.179
[Ru(Mebzlh)]-Y	Dark grey	0.192		14.5	0.025
[Ru(Mebzlh)]-ZSM-5	Light grey	0.030		122.6	0.081
[Pd(Mebzlh)]-Y	Off white	0.006		18.4	0.028
[Pd(Mebzlh)]-ZSM-5	White	0. 008		64.1	0.092

*S_{BET} = Specific surface area measured by BET method

Table 1: Percentage of metal, colour of encapsulated complex and their surface area measurement data

Thermal stability of the catalyst   Thermal stability of the encapsulated complex was studied using TGA and DTG. Representative TGA and DTG graphs of [Ru(Mebzlh)]-Y complex is shown in Fig. 1. The weight loss and the group lost is also tabulated in Table 2. The weight loss of the encapsulated complexes is observed to be in two to three major stages in the broad temperature range, which is clearly evident from DTG curve. The first stage weight loss starts on increasing the temperature above

100°C and continues till around 250°C until the loss of all intrazeolite water. The second step weight loss starts immediately after first step and continues around 450°C until the loss of all coordinated water molecules along with the chloride ions. The presence of several water molecules in these encapsulated complexes is expected even after drying them to 150°C. The second step weight loss occurs in a wide temperature range of about 400 to 700°C and is due to the slow decomposition of the ligand.
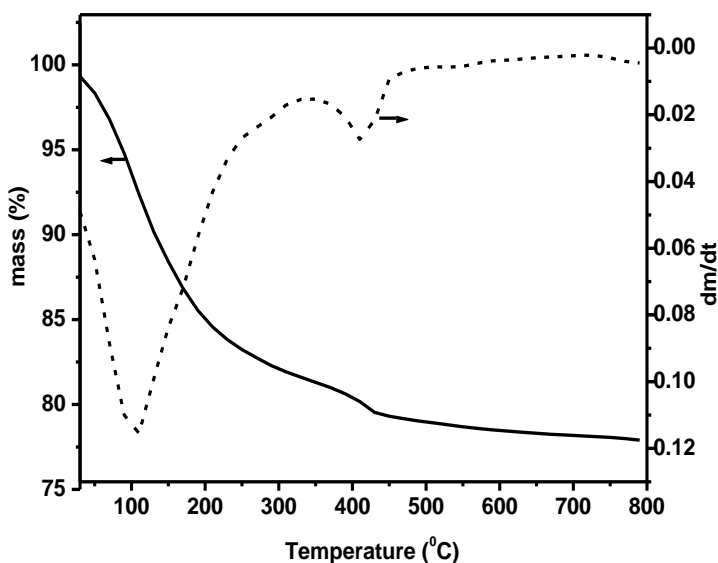

Fig. 1. TGA(___) and DTG(- - - -) Curves for [Ru(Mebzlh)]-Y

A very small weight percentage loss indicates the presence of only small amounts of metal complex in the zeolite cavities [14]. This is in agreement with the low percent of metal content measured.

Catalyst	Temperature range (°C)	weight loss (%)	Group lost
[Ru(Mebzlh)]-Y	90-230	14.0	nH_2O
	230-450	4.0	H_2O+Cl^-+L
[Ru(Mebzlh)]-ZSM-5	90-200	4.0	nH_2O
	200-390	2.5	H_2O+Cl
	390-850	1.0	L
[Pd(Mebzlh)]-Y	90-220	20.0	nH_2O
	220-600	5.0	H_2O+Cl^-+L
[Pd(Mebzlh)]-ZSM-5	90-230	4.0	nH_2O
	230-450	2.5	H_2O+Cl^-
	450-650	1.2	L

Table 2: Thermogravimetric analysis data of catalysts

Powder X-Ray diffraction studies

The powder X-ray diffraction patterns of H-Y, H-ZSM-5 and of the encapsulated complexes were recorded at 2θ values between 5 to 80°. Essentially similar patterns were noticed for the encapsulated complexes as compared to H-Y and H-ZSM-5, though a slight change in the intensity of the bands was seen. These observations indicate retainment of the crystalline nature of the zeolite even after the encapsulation of the complex. No new peaks were detected in the encapsulated complex due to low percent loading of metal complexes.

Infrared spectral studies

The IR spectra (in KBr) of the neat complex and encapsulated complexes are similar to the spectra of the uncoordinated ligand, except for minor shifts in the positions of some of the bands and some changes in their intensities due to coordination (Table 3). The complex shows a broad band around 3193 cm^{-1} assign to υ_{N-H}. The $\upsilon_{C=N}$ and $\upsilon_{C=C}$ vibrations are very close and occur around 1626 cm^{-1}, this band is at a slightly lower frequency when compared to that observed in the ligand spectrum (1631 cm^{-1}). The band around

1584 cm^{-1} is assigned to the N-H inplane bending. υ_{C-N} and δ_{N-H} appear around 1326 cm^{-1}. The bands around 1414, 1275, 1062, 752, 633 and 447 cm^{-1} are assigned to benzimidazole ring vibrations. The assignments are tentative and have been made on the basis of similar assignments described earlier[15, 16].

Compound	υ_{N-H}	$\upsilon_{C=N}$ / $\upsilon_{C=C}$	N-H inplane bending	$\upsilon_{C-N}/\delta_{N-H}$
Mebzlh	3210	1631	1512	1310
[Ru(Mebzlh)]	3193	1626	1584	1326
[Ru(Mebzlh)]-Y	-	1625	1529	1452
[Ru(Mebzlh)]-ZSM	3115	1652	1558	1378
[Pd(Mebzlh)]	2787	1619	1563	1450
[Pd(Mebzlh)]-Y	3133	1642	1515	1452
[Pd(Mebzlh)]-ZSM	3105	1631	1574	1412

Table 3:   IR spectral data (cm^{-1}) of ligand, neat and encapsulated complexes

Electronic spectral studies

Electronic spectra for the ligand and the neat complex have been recorded in DMF and DRS were recorded in BaSO$_4$ for the encapsulated complex and the data are listed in Table 4. The electronic spectrum of the ligand exhibited a split peak at 274 and 279 nm due to the n-π^* transitions of the benzimidazole moiety. The neat ruthenium complex showed adsorption bands at 409, 521 and 609 nm that are assigned to $^2T_{2g} \rightarrow {}^4T_{1g}$, $^2T_{2g} \rightarrow {}^4A_{2g}$ and $^2T_{2g} \rightarrow {}^2T_{1g}$ transitions, respectively. Their positions are typical of ruthenium(III) complexes with octahedral geometry [17]. The spectrum of [Ru(Mebzlh)] encapsulated complexes in BaSO$_4$ displayed three bands. The neat palladium complexes showed absorption bands at 280 nm and 483 nm and are assigned to ligand to metal charge transfer transition and $^1A_{1g} \rightarrow {}^1B_{1g}$ transition respectively. In case of encapsulated Pd(Mebzlh) complex there is no absorption band in the visible region because of less metal content present.

Compound	medium	λ_{max} (nm)
Mebzlh	DMF	241, 274, 279
[Ru(Mebzlh)]	$BaSO_4$	243, 267, 274, 363, 456, 523
[Ru(Mebzlh)]-Y	$BaSO_4$	241, 269, 296, 366, 461, 544
[Ru(Mebzlh)]-ZSM	$BaSO_4$	245, 287, 274, 372, 468, 506
[Pd(Mebzlh)]	$BaSO_4$	243, 271, 280, 293, 384, 483
[Pd(Mebzlh)]-Y	$BaSO_4$	241, 268, 274, 311, 397
[Pd(Mebzlh)]-ZSM	$BaSO_4$	242, 269, 275, 295, 381

Table 4: Electronic spectral data of ligand and complexes

4.2 Catalytic activity studies

Decomposition of H_2O_2

Encapsulated complexes were tested for their catalytic activity towards the decomposition of H_2O_2. The percentage of H_2O_2 that reacted and the turnover frequency (TOF) at two different time intervals (1 and 2 h) were measured. The results showed that the decomposition of H_2O_2 is slow up to 1 h (0.53 to 2.18 %) in all the cases and increases after 2 h with different trends. The percentage decomposition of H_2O_2 and the turn over frequency (TOF) are tabulated in Table 5.   The data indicate that the encapsulated complex requires a relatively longer time to attain maximum equilibrium. Hence, increasing time of reaction is a very effective method of carrying out the oxidation reaction, with H_2O_2 as the source of oxygen.

| *Catalyst	Percentage of H_2O_2 reacted After 1 h	#TOF (h-1)	Percentage of H_2O_2 reacted After 2 h	#TOF (h-1)
[Ru(Mebzlh)]-Y	2.18	7.42	3.66	6.32
[Ru(Mebzlh)]-ZSM-5	0.53	11.45	3.0	32.66
[Pd(Mebzlh)]-Y	0.58	68.59	0.75	43.32
[Pd(Mebzlh)]-ZSM-5	1.00	81.75	1.16	47.53

#TOF = moles of the substrate converted per mole of the (metal) in the solid catalyst

Table 5:   Turnover number for the decomposition of H_2O_2

Hydroxylation of Phenol

The catalytic hydroxylation of phenol using different encapsulated complexes was studied as a function of time using H_2O_2 as oxidant and acetonitrile as solvent. Catechol and hydroquinone were obtained as the major products [Retention times for phenol, catechol and hydroquinone 8, 13 and 15 min respectively) as shown below.

The minor products if any, was not detected in GC under the condition used herein.

Phenol   Catechol   Hydroquinone
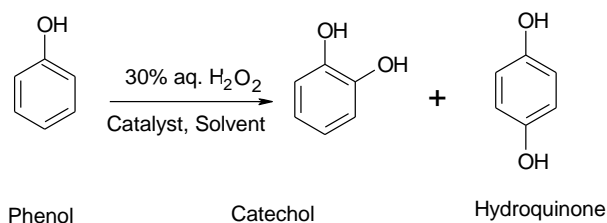
To have maximum transformation of phenol and better selectivity for catechol, the different parameters were optimized using [Ru(Mebzlh)]-Y.

The reaction was carried out for 6 h of reaction time with the optimized condition (2.35 g phenol, 4 ml H_2O_2, 2.5 mmol catalyst in 2 ml of acetonitrile at 80 ℃) for all the catalysts. The effect of different catalysts for the conversion of phenol is represented in Fig. 2.
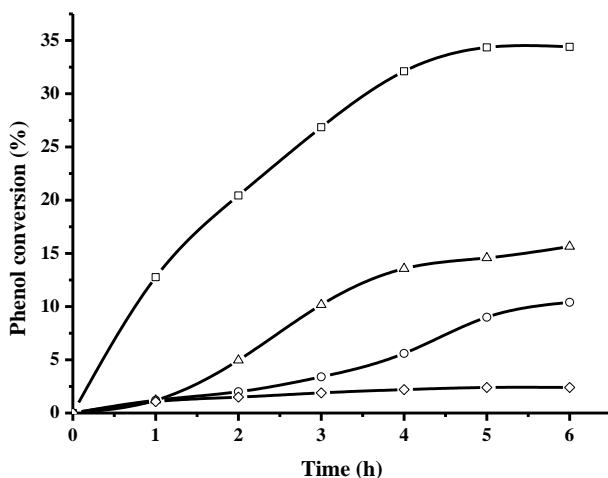
Fig. 2.   Effect of various catalysts on phenol hydroxylation (□) [Ru(Mebzlh)]-Y,   (O) [Ru(Mebzlh)]- ZSM-5 , (Δ) [Pd (Mebzlh)]- Y   and (◊) [Pd (Mebzlh)]- ZSM-5

Recycling efficiency

The recycling efficiency of the catalyst [Ru(Mebzlh)]-Y is checked for hydroxylation of phenol under optimized reaction conditions. The observed percentage of phenol conversion and selectivity to catechol and hydroquinone are given in Table 6. The catalytic activity of the catalyst decreased very slowly due to very slow leaching of the metal complex. Thus, the catalyst has a good recycling efficiency.   The metal estimation test showed very negligible amount of metal concentration loss in the reaction mixture.

Catalyst	Number of cycles			
[Ru(Mebzlh)]-Y	Fresh	1	2	3
Phenol conversion (%)	35	33	34	32
Catechol selectivity (%)	85	83	85	82
Hydroquinone selectivity (%)	15	17	15	18

Table 6: Recycling efficiency

5 Conclusions

Encapsulation of ruthenium(III) and palladium(II) complexes in Z-Y and ZSM-5 zeolite cavities can be conveniently carried out by the flexible ligand method.   Physical and spectral studies of the encapsulated zeolites clearly indicate that the encapsulation of complex occurs in the cages of zeolite. The encapsulated complexes are active catalysts for the decomposition of H_2O_2 and for the oxidation phenol with good selectivity for catechol and hydroquinone. A blank reaction was also conducted with the optimized condition and a very less percentage of phenol conversion (2%) was observed. In all the catalysts the selective is much more for catechol than hydroquinone (Table 7). Fig.3. indicates the percentage formation of catechol and hydroquinone products. The IR and UV spectra of fresh and used catalysts are nearly identical with not much loss in intensity of the peaks, which indicates that these zeolite encapsulated catalysts can be reused for catalytic study.
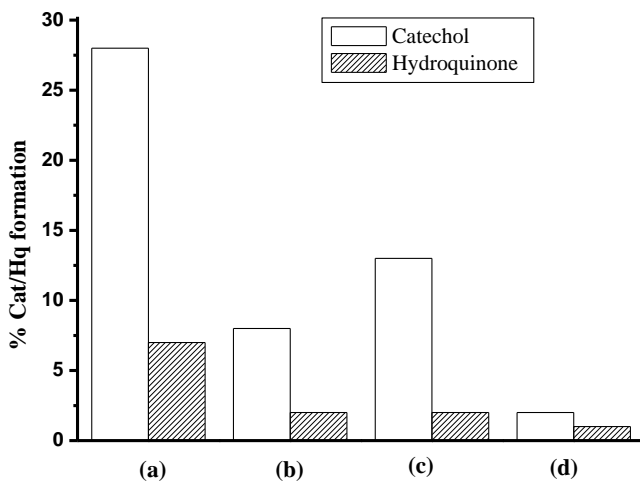
Fig 3:   Percentage formation of Catechol and hydroquinone for (a) [Ru(Mebzlh)]-Y, (b) [Ru(Mebzlh)]- ZSM-5 , (c) [Pd (Mebzlh)]- Y and (d) [Pd (Mebzlh)]- ZSM

Sl. No	Catalyst used	Phenol conversion (%)	Diphenol formation (%)	
			Catechol (%)	Hydroquinone (%)
1	[Ru(MeBzlH)]-Y	35.05	28.07	6.98
2	[Pd(MeBzlH)]-Y	14.85	12.92	1.93
3	[Ru(MeBzlH)]-ZSM	10.01	8.08	1.93
4	[Pd(MeBzlH)]- ZSM	2.09	1.06	1.03

Table 7: Percentage formation of Catechol and hydroquinone

Dedication

This paper is dedicated to Late Dr. N. Shashikala, Reader, Dept. of Chemistry, Bangalore University, Bangalore.

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