Liquid-phase catalytic oxidation of organic substrates by a recyclable polymer-supported copper(II) complex

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Abstract Chloromethylated polystyrene beads crosslinked with 6.5 % divinylbenzene were functionalized with 2-(2'-pyridyl) benzimidazole (PBIMH) and on subsequent treatment with Cu(OAc)₂ in methanol gave a polymersupported diacetatobis(2-pyridylbenzimidazole)copper(II) complex [PS-(PBIM)₂Cu(II)], which was characterized by physicochemical techniques. The supported complex showed excellent catalytic activity toward the oxidation of industrially important organic compounds such as phenol, benzyl alcohol, cyclohexanol, styrene, and ethylbenzene. An effective catalytic protocol was developed by varying reaction parameters such as the catalyst and substrate concentrations, reaction time, temperature, and substrateto-oxidant ratio to obtain maximum selectivity with high yields of products. Possible reaction mechanisms were worked out. The catalyst could be recycled five times without any metal leaching or much loss in activity. This catalyst is truly heterogeneous and allows for easy work up, as well as recyclability and excellent product yields under mild conditions.

Introduction

Application of transition metal complexes as homogeneous catalysts has been the focus of much research. The major

M. L. Shilpa · V. Gayathri (⊠) Department of Studies in Chemistry, Bangalore University, Central College Campus, Ambedkar Veedi, Bangalore 560 001, Karnataka, India e-mail: gayathritvr@yahoo.co.in drawback of homogeneous catalysts is the difficulty of separation of the catalyst from the reaction mixture. Immobilization of metal complexes onto a solid support has proved to be one of the most effective methods to overcome this problem. The search for environmentally benign synthesis has stimulated interest in developing polymer-supported catalysts that combine high activity and selectivity with easy workup and reusability.

Transition metal complexes based on nitrogen heterocycles with benzimidazole rings have been studied extensively [1–5]. Some of the Cu(II) complexes show good catalytic activity, particularly toward the synthetically important oxidation of substituted phenols [6]. The products of such reactions include high value-added chemicals of use in the pharmaceutical, agriculture, and perfumery industries [7].

The applicability of polymer-supported Cu(II) complexes as catalysts in the degradation of phenol is of current interest [8]. Styrene oxide has important applications as an intermediate in many organic syntheses. Several oxidizing reagents are used for such oxidation reactions. The use of TBHP (*tert*-butyl hydroperoxide) as oxidant in such reactions is convenient [9], and this reagent can selectively oxidize olefins, alcohols, ethers, and other organic compounds when transition metal catalysts are used [10–12]. Vanadium, molybdenum, and tungsten complexes of 2-(2'pyridyl)benzimidazole anchored onto a polymer support [13] were found to be active for the oxidation of both phenol and styrene. The conversion for phenol under optimized conditions was, however, only 34 % for the vanadium catalyst.

As a part of our interest in polymer-supported complexes [14, 15], our aim is to synthesize simple, selective, inexpensive, and environmental-friendly polymer-supported catalysts and develop their catalytic activity under

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mild conditions. Herein, we have synthesized a polymersupported diacetatobis(2-pyridylbenzimidazole)copper(II) complex [PS-(PBIM)₂Cu(II)] and investigated its catalytic activity toward oxidation of cyclohexanol, phenol, benzyl alcohol, ethylbenzene, and styrene using 70 % TBHP as oxidant in acetonitrile medium. The reaction conditions have been optimized for high activity and selectivity.

Experimental

Materials and methods

Chloromethylated polystyrene divinyl benzene copolymer with 6.5 % cross-linking (PS-DVB) obtained as a gift from THERMAX Ltd, Pune, India, was used as a support for anchoring the metal complex. Analytical-grade copper acetate and TBHP were purchased from Merck and used as such. Laboratory-grade solvents were purified according to the literature methods before use [16].

Elemental analyses were obtained with an Elementar Vario micro cube CHNS analyzer. Surface area measurements by the BET (Brunauer, Emmett and Teller) method were carried out with a Micromeritics surface area analyzer model ASAP 2,020. Copper content was determined using a Perkin-Elmer atomic absorption spectrometer, after digestion of the polymer-supported catalyst with concentrated sulfuric acid and subsequent decomposition with H₂O₂. 2-Methyl-1-phenyl-2-propyl hydroperoxide (MPPH) was prepared according to a literature method [17]. Thermogravimetric analysis of the polymer support and the anchored complex were carried out using a TA Instrument, SDT analyzer model Q 600, under nitrogen atmosphere with heating rate of 10 °C min⁻¹. Infrared spectra in the range 400-4.000 cm⁻¹ were recorded in KBr disks on a Shimadzu 8,400 s FTIR spectrometer. Diffuse reflectance spectra were recorded as BaSO₄ disks on a Shimadzu UV-Vis-NIR model UV-3101P spectrophotometer having an integrating sphere attachment for the solid samples. Magnetic moments of the supported and unsupported complexes were determined at room temperature using Guoy's method. ESR spectra were recorded using a Bruker EMX X-band ESR spectrometer at liquid nitrogen temperature. ESI-MS was recorded using a Thermo LCQ Deca XP Max instrument at the spectroscopy/analytical test facility, IISc., Bangalore. All the reaction products were analyzed using a Shimadzu 14B gas chromatograph fitted with flame ionization detector connected to a BP-5 capillary column.

Preparation of [Cu(OAc)₂(PBIMH)₂]

2-(2'-Pyridyl)benzimidazole (PBIMH) was prepared according to the literature method [18]. A solution of

2-(2'-pyridyl)benzimidazole (0.22 g, 1 mmol) in methanol (10 mL) was added to a solution of copper(II) acetate (0.10 g, 0.5 mmol) in methanol (10 mL), and the mixture was refluxed for about 7 h during which green precipitate separated out. This was filtered off, washed with water and then with ethanol, and dried in vacuum over P₂O₅ (yield 0.14 g, 52 %).

Functionalization of polymer support

Beads of chloromethylated polystyrene (5.0 g) cross-linked with 6.5 % divinyl benzene (5.12 mmol Cl g⁻¹) were washed with THF:water (4:1) and dried. They were then allowed to swell in DMF (50 mL) for 2 h. A DMF solution (100 mL) of PBIMH (6.5 g, 6.73 mmol) was added to the suspension, followed by the addition a solution of triethylamine (9.0 g, 20 mL) in ethyl acetate (150 mL), and the mixture was heated at 60 °C for 45 h. After cooling, the functionalized beads were filtered off, washed with ethanol, Soxhlet extracted with ethanol to remove any unreacted PBIMH, dried at 100 °C for 24 h, and then finally vacuum dried.

Preparation of the polymer bound complex

A sample of the functionalized polymer with PBIM (2.0 g, 4.3 % N) was soaked in toluene/acetonitrile mixture (100 mL, 1 : 1) for 1 h. A solution of copper(II) acetate (0.16 g, 0.8 mmol) in methanol (5 mL) was added, and the mixture was heated for 48 h at 60 °C, whereupon the beads turned green. The mixture was filtered, and the beads washed with hot ethanol were then Soxhlet extracted with ethanol to remove excess copper(II) acetate. The sample was dried in an oven for 24 h and vacuum dried over P_2O_5 (Scheme 1).

Typical procedure for the catalytic oxidation reaction

In a typical reaction, a mixture of catalyst (0.02 mmol with respect to copper) and 70 % aqueous TBHP (5.0 mmol) in acetonitrile (5 mL) was heated with continuous stirring at 60 °C. Substrate (5.0 mmol) was added, and the progress of the reaction was monitored by a Shimadzu 14B gas chromatograph with FID detector using BP-5 capillary column. When there was no further conversion of the reactants, the catalyst was filtered off and the products were analyzed.

Results and discussion

Characterization of the materials

Polymer beads were functionalized with PBIMH, followed by the reaction with Cu(OAc)₂. Elemental analysis showed



Polymer Support (PS-DVB)

Functionalised PS-DVB

PS-(PBIM),Cu(II) complex

Scheme 1 Synthesis of PS-(PBIM)₂Cu(II) complex

Table 1 Physical properties and analytical data of polymer beads, functionalized beads, $PS-(PBIM)_2Cu(II)$ complex, recycled supported complex, and $Cu(OAc)_2(PBIMH)_2$

Parameters	Color	Analytical d	ata		Apparent bulk	Surface	Pore	
		C %	Н %	N %	Cu %	density (g cm ⁻³)	area $(m^2 g^{-1})$	volume $(cm^3 g^{-1})$
PS-DVB	White	73.9	6.2	-	-	0.3	20.8	0.2
Functionalized beads with PBIM	Yellow	66.9	8.9	4.3	-	0.4	17.8	0.2
Functionalized PBIM beads anchored with Cu(OAc) ₂	Olive green	72.7	8.6	3.8	2.3	0.5	16.4	0.1
Recycled supported complex	Olive green	71.4	8.1	3.9	2.3	0.5	16.2	0.1
Cu(OAc) ₂ (PBIMH) ₂ *	Green	57.7 (58.0)	4.2 (4.2)	14.9 (14.5)	10.8 (10.4)	_	-	-

* Calculated values are in parentheses

that the functionalized beads had 4.3 % nitrogen content, which indicated that the PBIM had bonded on to the polymer support. Metal estimation by AAS indicated 2.3 % Cu in the immobilized catalyst (Scheme 1). The equivalent complex Cu(OAc)₂(PBIMH)₂ was also synthesized by reacting copper acetate with PBIMH in methanol. It was characterized by IR, electronic, ESR, ESI mass spectral methods, and magnetic susceptibility measurements (supplementary data). Surface area and pore volume were determined by the BET method, and the values are tabulated along with apparent bulk density in Table 1. Swelling studies are an important method to study the mechanical properties of the swollen beads, effects of cross-linking, and their interaction with the solvents, which in turn influences the rate of the catalytic reaction. The swelling of the polymer-supported complex was in the order: acetonitrile > methanol > THF > ethanol > ethylacetate > benzene. Maximum swelling occurred in acetonitrile; hence, it was chosen as the solvent for the oxidation reactions.

Thermogravimetric analysis of the polymer support and the anchored complex was carried out in a nitrogen atmosphere with heating rate of 10 °C min⁻¹ up to 600 °C. The results indicated that the polymer support was stable up to 330 °C, but on anchoring the metal complex, its stability decreased to 210 °C.

The IR spectrum of the chloromethylated polystyrene beads exhibited bands at 1,263 and 829 cm⁻¹ due to v_{CH_2-Cl} and v_{C-Cl} (Fig. 1). On functionalization, these bands decreased in intensity, indicating the bonding of PBIM onto the polymer support. The free PBIMH exhibited a band around 3,400 cm⁻¹ due to v_{N-H} , which was absent in the functionalized polymer, as the bonding of the ligand to the polymer beads is accomplished through the nitrogen.

The functionalized beads exhibited a band at 1,616 cm⁻¹ due to $v_{C=N}$, which was shifted to 1,609 cm⁻¹ in the anchored beads, indicating that the nitrogen atoms of the pyridine and benzimidazole moieties of the ligand are coordinated to copper. The anchored beads displayed bands at 1,520 and 1,484 cm⁻¹ due to $v_{C=O}$ and v_{C-O} , respectively, characteristic of monodentate coordination of the acetate group to the metal [19]. The IR spectra of the anchored complex before and after recycling were similar. The unsupported complex (E) exhibited a band due to v_{N-H} at 3,253 cm⁻¹, which was absent in the polymer-supported metal complex, confirming that the 2-(2'-pyridyl)benzimidazole is bonded through nitrogen to the polymer support.

% Transmittance

3253 cn

D

C

complex and E Cu(OAc)₂ (PBIMH)₂

4000 3500 3000 2500 2000 1500 1000 500 Wavenumber (cm⁻¹) Fig. 1 Infrared spectra of A PS-DVB, B functionalized polymer, C polymer-supported Cu(II) complex, D recycled polymer-supported

The diffuse reflectance spectra of the unsupported and polymer-supported metal complexes were similar. PBIMH exhibited an absorption band at 314 nm due to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. The electronic spectra of both supported and unsupported complexes showed bands around 414, 623 and 823 nm, which are assigned to ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$, ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$ and ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ transitions [20] of Cu(II) with d⁹ configuration in a distorted octahedral geometry.

The magnetic moments of the polymer-supported and unsupported complexes at room temperature were found to be 1.72 and 2.14 BM, respectively. The ESR spectra of the $Cu(OAc)_2(PBIMH)_2$ and $PS-(PBIM)_2Cu(II)$ complexes at liquid nitrogen temperature exhibited one peak, with calculated *g* values of 2.12 and 2.14, respectively. Hence, both the magnetic moment and ESR spectral studies indicated that the copper is paramagnetic with one unpaired electron.

Catalytic activity

The catalytic activity of the polymer-supported complex was initially tested for the oxidation of cyclohexanol, phenol, and styrene at 60 °C using both H_2O_2 and TBHP as oxidants. The catalyst decomposed when H_2O_2 was used. Hence, TBHP was chosen for further catalytic studies. In search of suitable reaction conditions to achieve maximum conversion, variations of the catalyst and substrate concentration, reaction temperature, and substrate-to-TBHP ratio were investigated. Use of the unsupported complex as a catalyst under similar conditions gave low yields (30 %).



Fig. 2 Effect of the amount of oxidant on the oxidation of styrene

Oxidation of styrene

The oxidation of styrene catalyzed by PS-(PBIM)₂Cu(II) using TBHP as oxidant gave styrene oxide as the major product and benzaldehyde as minor product. The activity of PS-(PBIM)₂Cu(II) in the oxidation of styrene was evaluated using four different molar ratios of styrene : TBHP, with fixed amounts of styrene (5 mmol) and PS-(PBIM)₂Cu(II) (0.02 mmol) at 60 °C in acetonitrile. Using a 1:0.5 styrene:TBHP molar ratio, only 61 % conversion of styrene (Fig. 2) occurred, with 47 % selectivity to styrene oxide. At 1:1 styrene:TBHP ratio, nearly 95 % conversion of styrene with 93 % of styrene oxide and 2 % of benzaldehyde was obtained. Further increases in styrene:TBHP ratio (1:2 and 1:3) gave only 2 % increase in conversion, with decrease in selectivity for styrene oxide (93–88 %) and increase of benzaldehyde (2–6 %).

The concentration of catalyst was also varied from 0.01 to 0.05 mmol, keeping all other parameters constant. At 0.01 mmol of catalyst, 64 % conversion of styrene was observed (Fig. 3), and at 0.02 mmol of catalyst, there was 92 % conversion of styrene. At higher catalyst concentrations (0.03–0.05 mmol), the conversion of styrene remained almost constant. Hence, 0.02 mmol of the catalyst was chosen for the oxidation of styrene, which gave 88 % conversion to styrene oxide and 3 % benzaldehyde.

The oxidation of styrene was also carried out by varying the substrate concentration from 2.5 to 10 mmol. At 2.5 mmol, there was 97 % conversion of styrene with 95 % selectivity to styrene oxide. With further increase in styrene concentration up to 10 mmol, the conversion and the selectivity to styrene oxide gradually decreased. At 10 mmol of styrene concentration, there was only 87 % conversion of styrene. Hence, 5 mmol of styrene was



Fig. 3 Effect of catalyst concentration on the oxidation of styrene

optimal for the effective oxidation of styrene. The effect of temperature on the performance of the catalyst was studied in the range from 30 to 70 °C. At 30 °C, low conversion (79 %) of styrene was observed. The optimum temperature was found to be 45 °C, giving maximum conversion of styrene (95 %) with 93 % selectivity to styrene oxide. At higher temperatures, the selectivity decreased. The optimized operating conditions for the oxidation of styrene were therefore 0.02 mmol of catalyst plus 5 mmol of styrene and TBHP at 45 °C in acetonitrile.

Oxidation of ethylbenzene

Oxidation of ethylbenzene is difficult to achieve under normal conditions. Generally, oxidation of ethylbenzene yields three products, namely acetophenone, benzaldehyde, and styrene. PS-(PBIM)₂Cu(II) catalyzed the oxidation of ethylbenzene to acetophenone, with 90 % selectivity under mild conditions. The influence of TBHP concentration on the oxidation of ethylbenzene was studied by using ethylbenzene-to-TBHP ratios of 1:0.5, 1:1, 1:2, and 1:3 with 5 mmol of ethylbenzene plus 0.02 mmol of PS-(PBIM)₂Cu(II) at 60 °C in 10 ml of acetonitrile. As the 1:2 molar ratio gave higher conversion of ethylbenzene, this ratio was chosen for further reactions. Catalyst concentration was varied from 0.01 to 0.05 mmol, showing that 0.04 mmol gave highest selectivity to acetophenone (78 %, Fig. 4). Substrate variation studies at 60 °C (Fig. 5) indicated that 5 mmol of ethylbenzene was the suitable concentration with 90 % conversion to acetophenone plus 7 % of benzaldehyde. The reaction was also carried out at 45, 60, and 70 °C; maximum conversion occurred at 60 °C. Hence, the optimum conditions for ethylbenzene oxidation were 0.04 mmol of PS-(PBIM)₂Cu(II) plus 5 mmol of



Fig. 4 Effect of catalyst concentration on the oxidation of ethylbenzene



Fig. 5 Effect of substrate concentration on the oxidation of ethylbenzene

ethylbenzene at 60 °C with 1:2 ethylbenzene:TBHP mole ratio in acetonitrile.

Oxidation of alcohols

PS-(PBIM)₂Cu(II) also proved to be capable of catalyzing the oxidation of cyclohexanol, benzyl alcohol, and phenol. Oxidation of phenol gave catechol as the major product with hydroquinone as a minor product. The optimal conditions for phenol oxidation (Table 2) were 0.03 mmol of the catalyst with 5.0 mmol of phenol at 60 °C with 1:2 molar ratio of substrate:TBHP, resulting in complete conversion with 95 % catechol and 3 % hydroquinone (Entry 15). Oxidation of cyclohexanol gave cyclohexanone, with the best conditions identified as 0.02 mmol of the catalyst plus 20 mmol of cyclohexanol at 60 °C with 1:1 substrate:cyclohexanol molar ratio. Benzylalcohol (25 mmol) on oxidation with PS-(PBIM)₂Cu(II) catalyst (0.02 mmol) gave benzaldehyde with 98 % selectivity, using a 1:2 substrate to TBHP ratio at 60 °C. Further details of the optimization experiments are given in the Supplementary Data.

Reaction mechanism

Catalytic oxidation reactions using TBHP can proceed by either homolytic or heterolytic decomposition of the alkyl hydroperoxide [21]. The oxidation reaction of styrene was carried out in the presence of 50 equivalents of 2,6-di-tbutyl-4-methyl phenol (BHT) with 0.03 mmol of the PS-(PBIM)₂Cu(II) catalyst plus 5.0 mmol of styrene in 5 mL of acetonitrile in the presence of TBHP (Substrate:TBHP = 1:1) at 60 °C. BHT acts as a scavenger for free peroxy radicals. The results showed that conversion of styrene (96 %) and formation of the reaction products were not altered in presence of BHT, indicating that the reaction does not involve free radicals.

The oxidation of styrene under the optimized reaction conditions was also carried out using methyl-1-phenyl-2-propyl hydroperoxide (MPPH) as a mechanistic probe, to check for homolytic versus heterolytic scission of the peroxide O–O bond. According to Sorokin et al. [22], if the reaction proceeded via heterolytic cleavage of the O–O bond, then the reaction with MPPH and the catalyst should give 2-methyl-1-phenyl-2-propanol. On the other hand, homolytic cleavage of the hydroperoxide leads to a radical mechanism yielding acetone, benzyl alcohol, and benzaldehyde as some of the β -scission fragmentation products. The reaction was carried out using MPPH (1.7 g) with 0.01 mmol of catalyst in acetonitrile (5 mL) for 5 h, and the reaction products analyzed by GC revealed the presence of 2-methyl-1-phenyl-2-propanol. Under the same reaction conditions, when styrene was used as the substrate, the product analysis showed the presence of styrene oxide, benzaldehyde, unreacted styrene, and 2-methyl-1-phenyl-2-propanol. Thus, in this case, products arising from the homolytic cleavage of MPPH were not detected [23], indicating that the oxidation of styrene occurred by heterolytic cleavage of the O-O bond of hydroperoxide and not by homolytic cleavage.

Based on these results, tentative mechanisms can be proposed for the oxidation of styrene (Scheme 2) and ethylbenzene (Scheme 3). The reaction mechanism for the phenol had been discussed earlier [24].

Heterogeneity and recycling tests

A heterogeneity test was performed by taking 0.02 mmol of the catalyst plus 5.0 mmol of cyclohexanol with 1:1 substrate:TBHP ratio at 60 °C in acetonitrile solvent. The reaction was carried out for 30 min, giving a conversion of 37 %. The catalyst was then filtered off from the reaction mixture, and the filtrate was stirred for a further 1 h at

Table 2 Effect of catalyst and phenol concentration, phenol:TBHP ratio, temperature, reaction time on the oxidation of phenol	Entry	Catalyst	Temp	Phenol	Substrate	Reaction	%	Selectivity (%)	
		conc. (mmol)	(°C)	conc. (mmol)	: TBHP ratio	time (h)	Conversion of phenol	Catechol	Hydroquinone
	1	0.01	60	5.0	1:1	5	65	62	35
	2	0.02	60	5.0	1:1	5	84	80	16
	3	0.03	60	5.0	1:1	5	96	95	1
	4	0.04	60	5.0	1:1	5	93	87	7
	5	0.05	60	5.0	1:1	5	92	84	8
	6	0.03	30	5.0	1:1	5	68	65	32
	7	0.03	45	5.0	1:1	5	95	89	5
	8	0.03	70	5.0	1:1	5	98	94	2
	9	0.03	60	2.5	1:1	5	99	98	1
	10	0.03	60	7.5	1:1	5	53	39	47
	11	0.03	60	10	1:1	5	50	42	46
	12	0.03	60	10	1:1	10	57	47	43
	13	0.03	60	10	1:1	24	66	53	34
	14	0.03	60	5.0	1:0.5	5	75	87	5
	15	0.03	60	5.0	1:2	5	100	95	3
	16	0.03	60	5.0	1:3	5	100	96	3



Scheme 3 Plausible reaction mechanism for the oxidation of ethylbenzene

60 °C. The GC analysis indicated there was no further conversion of cyclohexanol. The filtrate was tested for metal content by AAS. The absence of copper in the filtrate confirmed that there was no leaching of the metal from the polymer support during the catalytic reaction, and the polymer-supported complex was truly heterogeneous.

The recyclability of the catalyst was tested for oxidations of cyclohexanol, phenol, and styrene under the optimized conditions. The results are shown in Table 3. After the reaction, the catalyst was separated by simple filtration, washed with ethanol and dried before use, and recycled five times. The catalytic activity of the supported complex toward oxidation of substrates remained almost constant. Analytical and spectral studies of the recycled catalyst indicated that the metal did not leach out from the support,

Table 3 Recycling ability of the $PS-(PBIM)_2Cu(II)$ catalyst for the oxidation of styrene, ethylbenzene, and phenol

Conversion* (%)	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
Styrene	92	90	90	89	89
Ethylbenzene	87	87	87	85	85
Phenol	84	84	83	82	82

* Reaction condition: 0.02 mmol catalyst, 5 mmol of the substrates at 60 °C with 1:1 substrate:TBHP ratio in acetonitrile

and the structure of the polymer-supported complex remained unchanged, even after recycling it for five times. We conclude that the catalyst is purely heterogeneous in nature. Comparison of the catalytic activity of PS-(PBIM)₂Cu(II) with other reported systems (Table 4)

Catalyst		Oxidant	Temperature (°C)		Time	%	5	Selectivity (Ref	
					(h)	Convers of Styre	ion 9 ne 9	Styrene oxide	Benzaldehyde	
Styrene										
PS-(PBIM) ₂ Cu(II) catalyst		TBHP	45		4	95	Ģ	93	2	This work
Polymer-anchored Cu(II) Schiff base complex		TBHP	50		7	53	-	52	48	25
Polymer-anchored Schiff bas complex	e copper	TBHP	60		8	79	7	79	21	26
PS-[Cu(hpbmz) ₂] ^a		H_2O_2	80		7	59		2	58	27
PS-[Cu(Hfsal-aepy)Cl] ^b		TBHP	70		6	87	7	78	16	28
Polymer-anchored Cu(II) azo	complex	TBHP	60		6	74	1	12	57	29
Catalyst	Oxidant	Temperature (0 C) Time (h) %		% Con	% Conversion of pheno		ol Selectivity (%)		Ref	
								Catechol	Hydroquinone	
Phenol										
PS-(PBIM) ₂ Cu(II) catalyst	TBHP	60		5	100			95	3	This work
PS-(QBIM) ₂ Cu(II) catalyst ^c	TBHP	70		5	99			89	4	24
(P-HPHZ-Cu) ^d	H_2O_2	70		24	43			89	-	30
(P-HPPn-Cu) ^e	H_2O_2	70		24	53			89	-	31
Catalyst	Oxidant	Temperature	(°C)	Time (h)	% Coi	nversion of	Selec	electivity (%)		Ref
						Ethylbenzene		Acetophenone Benzaldehyde		
Ethylbenzene										
PS-(PBIM) ₂ Cu(II) catalyst	TBHP	60		6	99		90		7	This work
PS-[Cu(tmbmz) ₂] ^f	H_2O_2	70		8	15		5		71	32
(PS-PAR-Cu) ^g	O ₂	90		10	11		68		_	33

^a $PS[Cu(hpbmz)_2] = polymer-supported 2-(2'-hydroxyphenyl)benzimidazole copper complex$

^b PS-[Cu(Hfsal-aepy)Cl] = polymer-supported[(3-formyl salicylic acid) with 2-(2-aminoethyl)pyridine] copper complex

^c $PS-(QBIM)_2Cu(II) = polymer-supported diacetatobis(2-quinolylbenzimidazole)copper(II) complex$

^d (P-HPHZ-Cu) = polymer-supported [N,N'-bis(o-hydroxy acetophenone)hydrazine Schiff base]copper complex

^e (P-HPPn-Cu) = polymer-supported [N,N'-bis(o-hydroxy acetophenone) propylene diamine Schiff base]copper complex

^f PS-[Cu(tmbmz)₂] = polymer-supported [2-thiomethylbenzimidazole]copper complex

^g (PS-PAR-Cu) = polymer-supported 4-(2-pyridylazo)rosorcinol-copper complex

reveals that the present catalyst exhibits higher conversion and selectivity compared to other systems [24–33].

Conclusion

The polymer-supported (PBIM)₂Cu(II) catalyst described in this paper is recyclable, selective, efficient, stable, and can be reused without appreciable decrease in the activity. Hence, this material is a prospective heterogeneous catalyst for the oxidation of various organic compounds. Further efforts are being carried in our laboratory for the efficient oxidation of other substrates. Acknowledgments Authors wish to thank UGC, New Delhi, India, for Major Research Project [F no. 39-741/2010(SR)]; Department of Chemistry, Bangalore University, Bangalore, for instrumentation facilities; Thermax Ltd., is gratefully acknowledged for providing PS-DVB.

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