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Application of polymer-bound Cu(II) complex of 2-phenylbenzimidazole towards oxidative bromination and oxidative esterification of organic substrates

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Application of polymer immobilized Cu(II)(PS-Cu(II)PBMZL) complex of 2-phenylbenzimidazole in oxidative bromination and oxidative esterification of organic compounds is reported. The complex has been characterized by CHNS analysis, UV-Vis/DRS, FT-IR, ESR spectroscopic studies, magnetic moment measurements and TG analysis. A shift in $\nu_{C=N}$ in the polymer-bound complex compared with the ligand indicates its complexation to Cu(II) center. A distorted octahedral coordination of Cu(II) in PS-Cu(II)PBMZL is confirmed by the electronic spectral data and the efficient binding of PBMZL is ascertained by adecrease in the intensity of ν_{CH2Cl} peak in the PS-PBMZL compared to the polymer support. An array of experiments has been carried out to assess the influence of various reaction parameters on the performance of PS-Cu(II)PBMZL. The activity of the polymer-bound complex is higher than the unbound complex. In the case of oxidative bromination, PS-Cu(II)PBMZLH displayed a 65% phenol conversion with 61% 2-bromophenol selectivity. The % benzaldehyde conversion and methyl benzoate selectivity in the case of oxidative esterification has been found to be 79 and 82%. Compiling all these results along with the knowledge obtained regarding the most probable reactive species, tentative mechanisms have been proposed.

Keywords: Cu(II) phenylbenzimidazole, Methyl benzoate, Oxidative bromination, Oxidative esterification

A transition metal complex will experience a significant change in its properties upon immobilization on polymer support owing to steric, electrostatic, hydrophobic, and conformational effects. Its catalytic activity depends on both the metal complex and the polymer support. Polymer support enhances thermal stability, selectivity,and recyclability of the bound complex[1,2]. Amongst polymer supports, chloromethylated polystyrene cross-linked with divinylbenzene is one of the most widely employed macromolecular supports for heterogenization of homogeneous catalysts[3–8].

Bromination of organic compounds is by and large accomplished with hazardous, noxious, and corrosive molecular bromine in the presence of chlorinated solvents. An oxidative bromination is an alternative approach necessitating the generation of electrophilic bromine in the presence of different oxidants. Among various oxidants involved, H_2O_2 is considereda green oxidant that is capable of oxidizing bromide on its own in a highly acidic medium (pH < 3) but is ineffective in the solution above *p*H > 5.0 and often requires activation by homogeneous or heterogeneous catalysts. This has provided a drift for the development of myriad useful catalysts containing vanadium, tungsten, molybdenum,and rhenium for oxidative bromination by H_2O_2[8–12] but most of them are found to be catalytically active only in the presence of an acid. They suffer from the drawbacks such as difficulty in separation from organic products and production of large volumes of hazardous wastes which are becoming increasingly conspicuous given the growing ecological awareness in recent years[13–18].

On the other hand, esterification is one of the most vital reactions in organic synthesis due to the application of esters as intermediates in organic synthesis and as flavoring agents, solvents, diluents,and extractants in the chemical industry. Esters are usually synthesized by the reaction of an activated carboxylic acid derivative with appropriate alcohol or via an esterification/trans-esterification protocol employing the stoichiometric use of toxic coupling reagents like DCC (N, N'-dicyclohexylcarbodiimide), HOBt (Hydroxybenzotriazole) with concurrent formation of by-products that can be difficult to remove during isolation. This is overcome by direct conversion of aldehydes to esters in the presence of alcohol by either oxidation of the aldehyde in the presence of alcohol employing stoichiometric oxidants or using N-heterocyclic carbenes (NHC) catalysts to activate aldehydes in-situ that in turn undergo esterification in the presence of the appropriate alcohol and stoichiometric oxidant.Electrochemical oxidation has also been used in conjunction with NHC activation or employing transition metals in the presence of oxidants[19-30], From a viewpoint of green chemistry, transition metal-catalyzed oxidative esterification is expected to be a versatile procedure directly giving esters from aldehydes and alcohols[31-33].

Hence, the present work is emphasized on synthesis and characterization of polymer anchored Cu(II) complex of 2-phenylbenzimidazole and its application towards oxidative bromination and oxidative esterification of organic compounds. The influence of external parameters on the catalytic activity of the anchored complex has been investigated for better performance of the catalyst.

Experiment Section

Chemicals and Reagents

Reagents like *o*-phenylenediamine, 4-aminophenol, nitrobenzene, anisole (S.d. fine chem. Ltd, India), diphosphorus pentoxide, *o*-phosphoric acid, 2,6-di-*tert*-butyl-4-methylphenol (BHT), salicylic acid, phenol, $CuCl_2.2H_2O$, aniline, toluene, benzene, benzaldehyde, 2-chlorobenzaldhyde, *o*-methoxybenzaldehyde, *p*-hydroxybenzaldehyde, salicylaldehyde, 3-chlorobenzaldehyde, 4-chlorobenzaldehyde, silica gel, ethyl acetate, petroleum benzene, *n*-hexane (Merck), methanol, ethanol, *n*-propanol, isopropanol, *n*-butanol, *t*-butanol, tetrabutylammonium bromide (Spectrochem. Pvt. Ltd, India),andmethyl-1-phenyl-2-propanol (Sigma Aldrich) were used as received. A solution of 2-methyl-1-phenyl-2-propyl hydroperoxide (MPPH) was prepared according to the literature method using 2-methyl-1-phenyl-2-propanol[34]. All the solvents were purified before use.

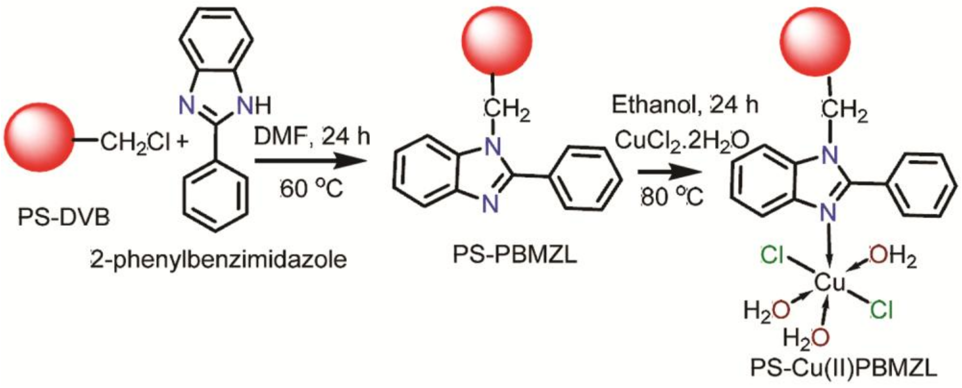
Physical methods and analysis

All the samples were vacuum dried before analysis. The elemental analyses were obtained with an Elementar Vario micro cube CHNS analyzer. The iron content wasdetermined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) Atomic Mineral Directorate, Southern region, Bangalore. The UV-visible-DRS spectra were measured using a Shimadzu UV-Vis-NIR model UV-3101P spectrophotometer having an integrating sphere attachment for the solid samples in $BaSO_4$. The IR spectra of the samples were recorded in the range 400-4000 cm^{-1} as KBr disks on a Shimadzu 8400 s FT-IR spectrometer. The ESR spectra were recorded using a Bruker EMX EPR spectrometer X-band, ν = 9.431GHz at room temperature (Indian Institute of Technology, Bombay). Thermograms were recorded on a TA instrument under a nitrogen atmosphere with a heating rate of 10 °C/min from 20 to 1000°C. The products were confirmed from GC/MS spectral analyses. The purity of the products was confirmed from ^1H NMR spectral analyses using a Bruker 400 MHz multinuclear NMR spectrometer. All the reaction products were analyzed using a Shimadzu 14B gas chromatograph (GC) fitted with a flame ionization detector using a BP-5 capillary column.

Synthesis

Synthesis of polymer-supported Cu(II) complex of 2-phenylbenzimidazole [PS-Cu(II)PBMZL]

The outline for the preparation of polymer-anchored Cu(II) complex of 2-phenylbenzimidazole [PS-Cu(II)PBMZL] is given in Scheme 1. Preparation of polymer anchored ligand (PS-PBMZL) is described in the previous report[35]. Polymer-anchored ligand (PS-PBMZL) (2.0 g) was allowed to swell in DMF (30 mL) for 2 h and filtered. A solution of



Scheme 1 ─ Preparation of PS-Cu(II)PBMZL

$CuCl_2.2H_2O$ (8.5 g, 50.0 mmoles) in ethanol (30 mL) was added to PS-PBMZL and the reaction mixture was stirred at refluxing temperature in ethanol for 24 h. The mixture was cooled to room temperature and brown beads were filtered off, washed thoroughly with hot DMF followed by washing by Soxhlet extraction using methanol:H_2O in 1:3 volume, and dried in an air oven around 120°C. The Cu content in [PS-Cu(II)PBMZL] was found to be 7.62 % (Table 1). The procedure of synthesis of unbound complexes is reported in the supplementary material.

Synthesis of Cu(II) complex of 2-phenylbenzimidazole [Cu(II)PBMZLH]

The unbound complex was synthesized by refluxing 20 mL ethanolic solution of PBMZLH (7.8 g, 40 mmoles) with 5 mL ethanolic solution of $CuCl_2.2H_2O$ (3.4 g, 20 mmoles) for 3 h[36](Scheme 2). The green-colored complex formed was filtered and washed with hot ethanol and dried at 120 °C for 12 h. The molar conductivity of the complex in methanol was found to be 62 $\Omega^{-1}cm^2mol^{-1}$, asserting its non-electrolytic behavior. Yield: 9.1 g; 87 %.

The typical procedure for the oxidative bromination and oxidative esterification of organic substrates

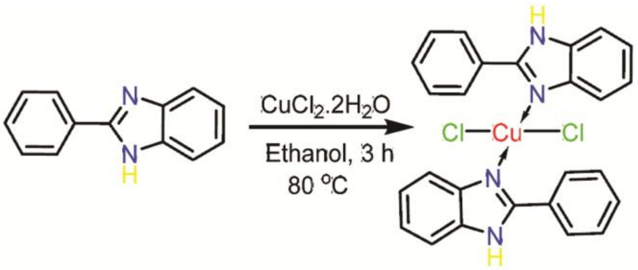
Oxidative bromination

The polymer-bound complexes were used in catalytic oxidative bromination of organic substrates. The reaction conditions were optimized for phenol. In a conventional procedure, aqueous 30% H_2O_2 (2.27 g, 20 mmoles) was added dropwise to the mixture of phenol (1.22 g, 10.0 mmoles) and KBr (2.38 g, 10.0 mmoles) taken in 10 mL of water at 30°C. 0.050 g of catalyst was added to it and the reaction mixture is stirred at room temperature. After the specified time of the reaction, the catalyst was filtered and the solid was washed with ether. The combined filtrates were washed with a saturated sodium bicarbonate solution. The ether extract was dried over anhydrous sodium sulphate and the solvent was evaporated. The products were purified by column chromatography using ethylacetate/petroleum benzene and analyzed by GC and confirmed by ^1H NMR spectral analysis.

Table 1 —Influence of nature of oxidants on the oxidative bromination of phenol

Oxidant	[KBr]	% Substrate conversion	% Product selectivity		
			OBP	PBP	DBP
TBHP	10.0	75	33	37	30
H_2O_2	10.0	65	61	20	19
H_2O_2	20.0	65	31	32	37
H_2O_2	30.0	66	21	36	43

Reaction conditions: [phenol] = 10 mmole; phenol: H_2O_2 = 1:2; T = 30 °C; 10 mL water



Scheme 2 ─ Preparation of Cu(II)PBMZLH

Oxidative esterification

PS-Cu(II)PBMZL (0.050 g) and aldehyde (30 mmoles) were taken in 10 mL of methanol. After stirring for 5 minutes at room temperature, H_2O_2 (6.84 g, 60 mmoles) was added dropwise to the solution, followed by the addition of K_2CO_3 (4.1 g, 3 mmoles). The reaction mixture was stirred at 60 °C for 3.5 h and quenched with saturated NH_4Cl (5 mL). The mixture was extracted using ether (15 mL in 3 portions). The combined organic extract was dried over anhydrous $CaCl_2$. After evaporation of the solvent, the crude residue was purified by column chromatography and confirmed by GC-MS analysis.

Results and Discussion

FT-IR spectral studies

The FT-IR spectra of polymer-anchored ligand and its complexes are presented in Fig. 1. PBMZLH exhibits the ν_{NH} at 3463 cm^{-1} as a broad peak and the $\nu_{C=N}$ at 1630 cm^{-1} (Fig. 1, right).The peak at 1264 cm^{-1} due to ν_{CH2Cl} in PS is decreased in intensity after functionalization of PS with PBMZLH[37,38].The disappearance of the ν_{NH} peak in PS-PBMZL suggests the covalent bond formation of the ligand through imine nitrogen. The $\nu_{C=N}$ peak in PS-PBMZL appears at 1627 cm^{-1}. A shift of the $\nu_{C=N}$ to lower frequency in PS-Cu(II)PBMZL (1617 cm^{-1}) suggests the coordination of the tertiary nitrogen of the ligand to the metal. The position of the ν_{NH} peak remains nearly unchanged in the unbound complex as compared to PBMZLH. In the unbound complex, the $\nu_{C=N}$ peak has been found to shift to lower frequencies compared to PBMZLH indicating the coordination of tertiary nitrogen of benzimidazole moiety to Cu(II) ion.

UV-Vis-DRS spectral studies

The electronic spectral data of complexes is presented in Fig. 2. The ligand exhibits bands at 205,

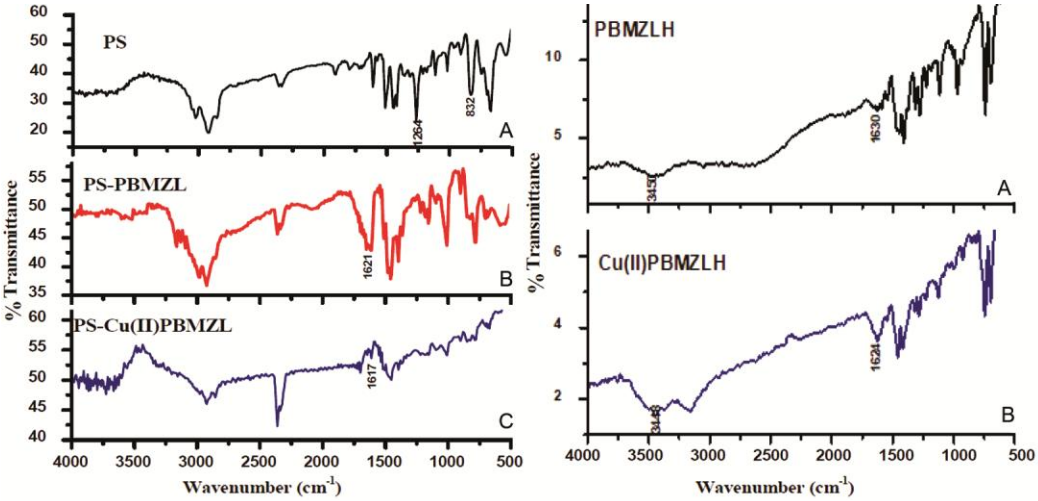


Fig. 1 — FT-IR spectra of (A) PS, (B) PS-PBMZL, (C) PS-Cu(II)PBMZL (Left) and (A)PBMZLH (B) Cu(II)PBMZLH (Right).

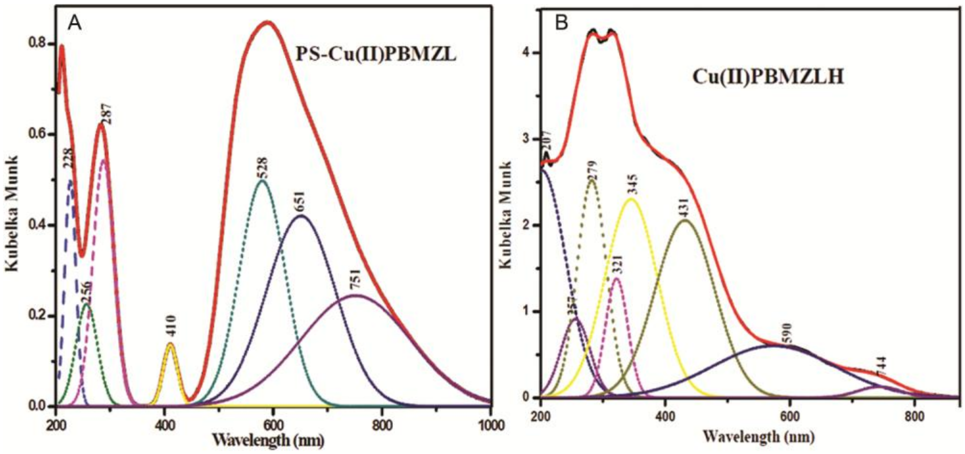


Fig. 2 —UV-Vis/DRS spectra of A) PS-Cu(II)PBMZL; B) Cu(II)PBMZLH (Recorded at room temperature in solid mode using $BaSO_4$).

218, 240, 264, 294, 301, and 316 nm in the UV region due to φ→φ*, π→π* and n→π* transitions [32]. In addition to intra-ligand transition bands, PS-[Cu(II)PBMZL] displays d-d transition around 528, 651, and 751 nm due to d_{x2-y2}→d_{z2}, d_{x2-y2}→d_{xz},d_{yz}, d_{x2-y2}→d_{xy}transitions [39], consistent with axially distorted octahedral coordination around Cu(II) center. The unbound Cu(II)PBMZLH complex exhibits d-d transition bands at 431, 590, 744 nm due to square planar coordination around Cu(II).

ESR spectral studies

The ESR spectra of PS-Cu(II)PBMZL and PS-VO(IV)PBMZL are presented in Fig. 3. PS-Cu(II)PBMZL exhibits a rhombic ESR spectrum with g_{II} = 2.242 and $g_{\perp}$ = 2.081 with A_{II} = 51mT and $A_{\perp}$ = 16 mT, characteristic of axially distorted octahedral environment around Cu(II).

Magnetic moment measurements

The magnetic moment of PS-Cu(II)PBMZLhas been determined by using vibrating sample magnetometer (Fig. 4). PS-Cu(II)PBMZL, exhibits a saturation magnetization (M_s) of 246.21 $\times 10^{-6}$ emu from which the magnetic moment is 0.98 BM. The plot of magnetic moment (emu) versus magnetic field (G) is found to display a typical paramagnetic character for Cu(II) ion in PS-Cu(II)PBMZL.

TG analysis

The thermograms of polymer-supported and unsupported complexes are presented in Fig. 5. The PS-Cu(II)PBMZL shows three step decomposition profile from 150°C to 1000 °C. The first step was due to the loss of 3 H_2O molecules (~6.84 %, 150°C to 248°C), which has beenfollowed by ~32.68 % weight loss due to $2Cl^-$ and PBMZL (248 to 496°C). The

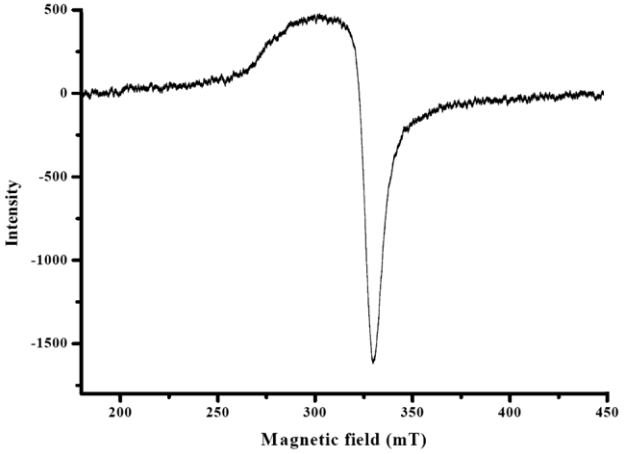


Fig. 3 — ESR spectrum of PS-Cu(II)PBMZL

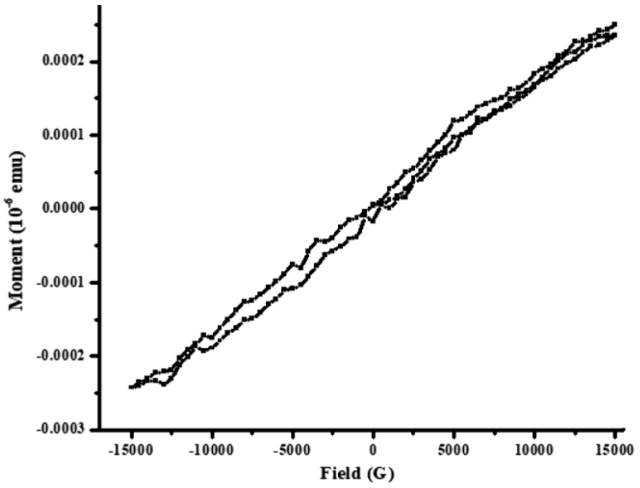


Fig. 4 — VSM plot of PS-Cu(II)PBMZL

polymer matrix is decomposed from 496 °C. The PS-VO(IV)PBMZL exhibits ~2.58 % weight loss due to H_2O (120 to 128 °C) followed by ~9.29 % loss corresponding to sulphate (128 to 174 °C) and 25.37 % loss due to PBMZL (174 to 414 °C). This has been followed by the decomposition of polymer support from 414°C. The PS-Cu(II)PBMZL is found to be stable up to 150 °C whereas the unbound complex Cu(II)PBMZLH is stable up to 110 °C. It is observed that the polymer-bound complex is more stable than the corresponding unbound complex.

Catalytic applications

Oxidative bromination

The effect of temperature on oxidative bromination has been investigated by carrying out the reaction in the temperature range of 30–60°C using 10 mmoles of phenol, 0.05 g of catalyst, 20 mmoles of H_2O_2 in 10 mL water in the presence of 10 mmoles of KBr as the brominating agent for 3 h (Fig, 6A). The conversion of phenol is not much influenced by variation in temperature (30°C; 65 % and 60°C; 70 %), but the selectivity to 2-bromophenol (30°C; 61 % and 60°C; 32 %) and 4-bromophenol decreases (30°C; 33 % and 60°C; 15 %). It is also observed that with an increasein temperature, the selectivity towards 2,4-dibromophenol increases (30°C; 6 % and 60°C; 53 %).

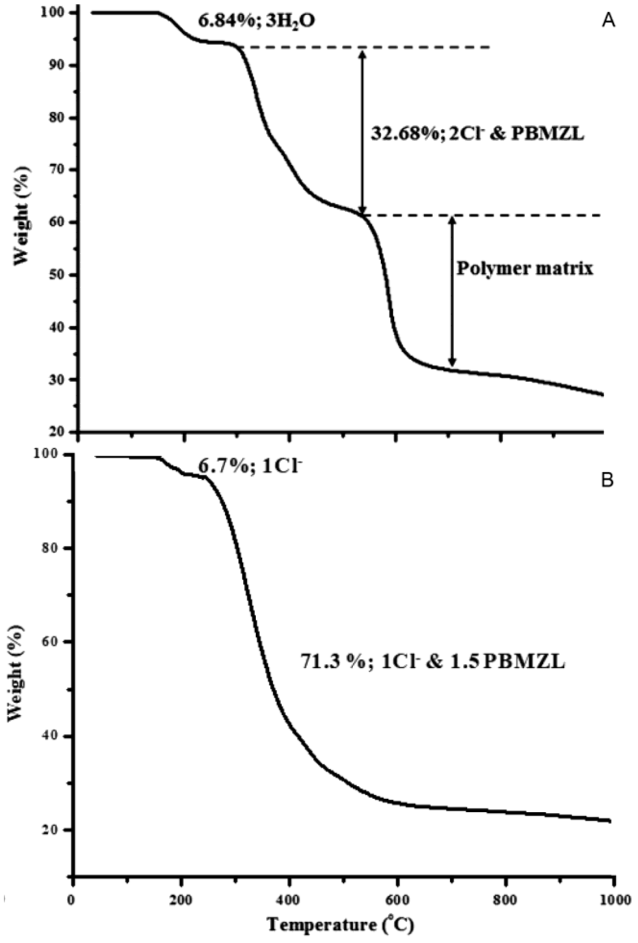


Fig. 5 — TG of A) PS-Cu(II)PBMZL; B) Cu(II)PBMZL

Oxidative bromination of phenol has been carried out using H_2O_2 and TBHP as oxidants (Table 1). The order of phenol conversion and 2-bromophenol selectivity is found to be: TBHP (75 %, 33 %) >H_2O_2 (65 %, 61 %). H_2O_2has been chosen as an oxidant, as the selectivity towards 2-bromophenol is greater in TBHP. TBHP being a strong oxidizing agent, can have resulted in the higher % phenol conversion, but due to its bulkiness, bromination at the *o*-position of phenol will be hindered.

The influence of phenol concentration has been examined using 4 different concentrations; 5, 10, 20,

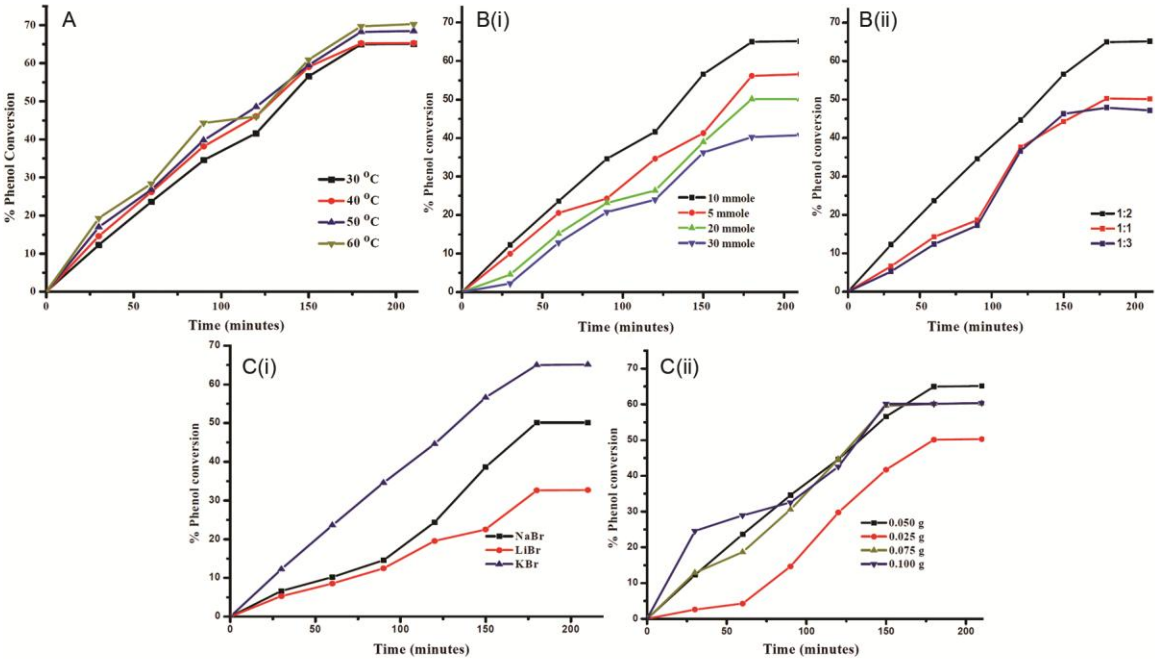


Fig. 6A — Effect of temperature on % phenol conversion; 6B — (i) Effect of phenol concentration; 6B (ii) Influence of phenol:H_2O_2 molar ratio on % phenol conversion and 6C — (i) Effect of nature of brominating agents on % phenol conversion; (ii) Effect of catalyst concentration on % phenol conversion

30 mmoles (Fig. 6B(i)). The % phenol conversion is higher with an increase in concentration from 5mmoles (56 %) to 10 mmoles (65 %) but decreases thereafter which can be attributed to the competition between the substrate molecules for the active sites. The selectivity towards 2-bromophenol has been found to be 5 mmoles (61 %) > 10 mmoles (56 %) > 20 mmoles (47 %) > 30 mmoles (45 %).

Oxidative bromination of phenol has been carried out by varying the phenol:H_2O_2(from 1:1 to 1:3) molar ratio by maintaining the other parameters constant (Fig. 6B (ii)). Bromination is maximum for 1:2 molar ratio. With a further increase in a molar ratio to 1:3, both phenol conversion (48 %) and selectivity towards 2-bromophenol decrease. It (26 %) may be due to preferential binding of H_2O_2 to the Cu(II) center compared to phenol.

The effect of the brominating agent has been also studied for the oxidative bromination of phenol using H_2O_2 as oxidant using LiBr, NaBr, and KBr as bromine sources (Fig. 6C (i). Among them, KBr is the most efficient bromine source (65 % conversion) with better regio-selectivity towards *o*-product (61%), while with NaBr, conversion of 50 % is observed with a decrease in regio-selectivity (32 % 2-bromophenol, 34 % 4-bromophenol, and 33 % 2,6-dibromophenol) and LiBr shows very poor conversion (33 %).

To investigate the effect of the concentration of KBr on oxidative bromination, three different concentrations have been employed (10, 20, and 30 mmoles). The % phenol conversion and product selectivity are maximum for 10 mmoles of KBr (65 %). With further increase in KBr, the phenol conversion remains almost the same but the selectivity towards dibromophenol is enhanced (43 % for 30 mmole of KBr). The influence of catalyst concentration on oxidative bromination has been investigated by taking four different concentrations of catalyst, 0.025, 0.050, 0.075, and 0.100 g (Fig. 6C(ii). The conversionis thehighest for 0.050 g of catalyst (65 %) and decreases slightly above this concentration (60 % for 0.100 g). With the increase in the concentration of catalyst, the number of active sites also increases resulting in higher conversion. When the concentration has been increased to 0.075 g, a decrease in the conversion is noticed which can be due to the binding of the oxidant and substrate to different active sites. For effective conversion, both substrate and oxidant have to bind to the same active site.

Oxidative bromination of a few aromatics has also been carried out under optimized conditions of phenol (Table 2). Aromatic substrates like phenol, anisole, aniline, and toluene show more selectivity towards

Table 2 — Oxidative bromination of various organic substrates catalyzed byPS-Cu(II)PBMZL

Substrates	Conversion (%)	Product Selectivity (%)
Aniline	63	2-bromoaniline (37 %); 4-bromoaniline (44%); 2,4dibromoaniline (19 %)
Phenol	65	2-bromophenol (61 %); 4-bromophenol (33 %); 2,4dibromophenol (7 %)
Anisole	59	2-bromoanisole (34 %); 4-bromoanisole (48 %); 2,4dibromoanisole (17 %)
Toluene	60	2-bromotoluene (42 %); 4-bromotoluene (50 %); 2,4dibromotoluene (8 %)
4-aminophenol	63	2-bromo-4-aminophenol (100 %))
Benzene	10	Bromobenzene (100 %))
Nitrobenzene	7	3-bromo-nitrobenzene (100 %)

Reaction conditions: 0.05 g of catalyst, 10 mmole of substrate, 1:1 phenol:H_2O_2 *ratio, 10 mmole of KBr at 30 ℃*

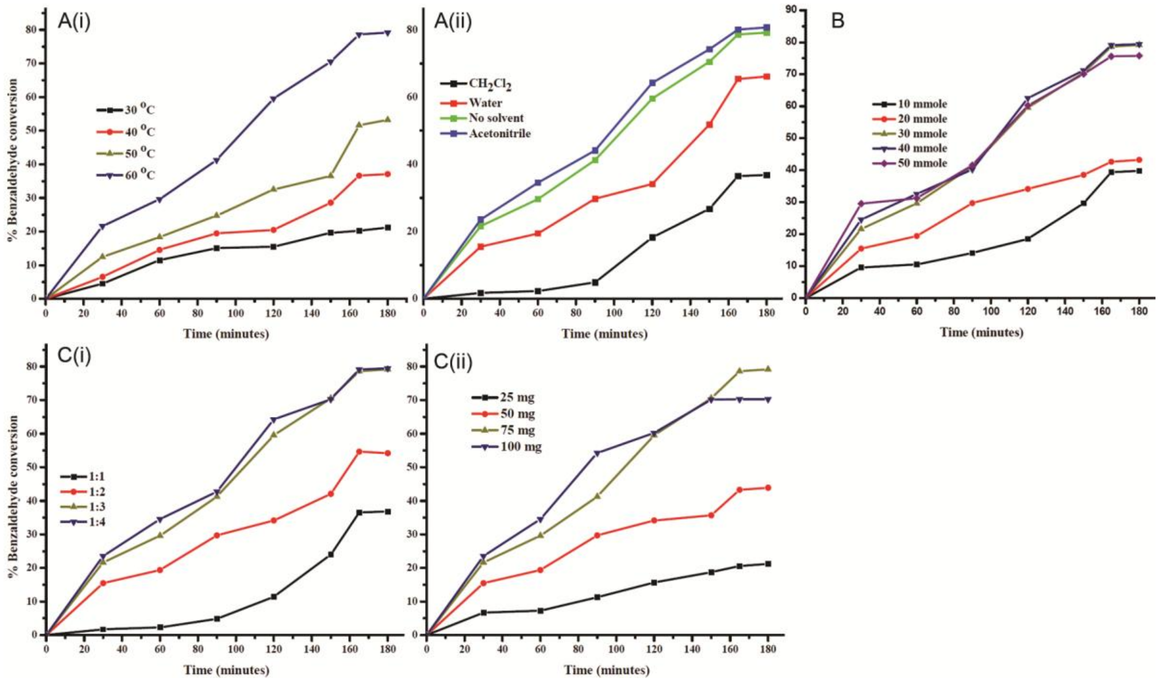


Fig. 7A — (i) Influence of temperature, 7A(ii) Influence of nature of solventson % benzaldehyde conversion; 7B — Effect of benzaldehyde concentration on its % conversion and 7C— (i) Effect of benzaldehyde:H_2O_2 ratio, (ii) Effect of catalyst concentration on % benzaldehyde conversion

ortho- and *para*-positions with high conversion whereas benzene being less active towards electrophilic substitution reaction, shows lower conversion (10%), while a deactivated aromatic ring such as nitrobenzene also shows lower conversion under optimized reaction conditions (7%).

The PS-Cu(II)PBMZL displays better activity than Cu(II)PBMZLH. Cu(II)PBMZLH shows 54% phenol conversion with 35 % selectivity towards 2-bromophenol.

Influence of various parameters on oxidative esterification

To investigate the effect of temperature, oxidative esterification has been carried out at 30, 40, 50, and 60°C using 30 mmoles of aldehyde, 10 mL methanol, H_2O_2 (10.26 g, 90 mmoles) and K_2CO_3 (4.1 g, 3 mmoles) (Fig. 7A(i). With the increase in temperature, the % benzaldehyde conversion also increases with a simultaneous increase in the formation of methyl benzoate. The selectivity towards benzoic acid formation is greater at a lower temperature (30 °C) which decreases with an increase in temperature Thus, at a higher temperature, the condensation coalesces between benzoic acid and methanol leading to methyl benzoate is more feasible. The order of % benzaldehyde conversion and methyl benzoate selectivity is; 30°C (20, 18 %) < 40°C (37, 34 %) < 50°C (52, 62 %) < 60°C (79, 82 %).

The influence of solvents on the % conversion of benzaldehyde has been investigated using acetonitrile, CH_2Cl_2, water, and in CH_3OH alone (without any other solvent) maintaining the other conditions constant (Fig. 7A(ii)). The % benzaldehyde conversion follows the order; acetonitrile (80%) > solvent-free (79%) > water (65 %) > CH_2Cl_2 (36%). Though the conversion is higher in acetonitrile, the selectivity towards methyl benzoate decreases (34%) as compared to solvent-free conditions (52%).

The influence of the nature of oxidants on the reaction rate has been investigated for H_2O_2 and TBHP (Table 3). The blank reaction shows 15% of methyl benzoate yield in the absence of the catalyst. Meanwhile, no methyl benzoate can be detected when no oxidant is involved in the reaction. Oxidants such as hydrogen peroxide (H_2O_2, 30 %, 90 mmoles) and TBHP (90 mmoles) have been compared keeping all other parameters constant. However, with H_2O_2 (79, 82%), though the benzaldehyde conversion was low, methyl benzoate selectivity is higher than with TBHP (85, 36%). This can be due to the steric hindrance caused by the bulky oxidant moiety.To investigate the effect of K_2CO_3 and Na_2CO_3 on the reaction, oxidative esterification has been carried out under optimized conditions using these two bases (Table 3). It is observed that the % benzaldehyde conversion and methyl benzoate selectivity are the highest for K_2CO_3. Na_2CO_3 as a base gives only 52% conversion and 35% selectivity towards the ester formation.

The effect of benzaldehyde concentration has been studied by varying the concentration of benzaldehyde maintaining all other parameters constant (Fig. 7B). It is observed that at lower aldehyde concentration (10 mmoles), the formation of benzoic acid is high which diminishes with further increase in concentration to 30 mmoles. The formation of methyl benzoate has been increased gradually upon an increase in benzaldehyde concentration from 10 to 30 mmoles, but later, it decreased. The order of % benzaldehyde conversion and methyl benzoate formation for PS-Cu(II)PBMZL was found to be: 10 mmoles (39 %, 26 %) < 20 mmoles (43, 32 %) < 30 mmoles (79, 82 %) ~ 40 mmoles (79, 86 %) > 50 mmoles (76, 86 %). This trend can be due to enhanced competition between the substrates molecules at higher concentrations for the active sites resulting in lower conversion.

Table 3 — Effect of nature of oxidants and base on oxidative esterification

Oxidant	Base	% Benzaldehyde Conversion	% Product Selectivity	
			MB	BA
TBHP	K_2CO_3	85	36	64
H_2O_2	K_2CO_3	79	82	18
H_2O_2	Na_2CO_3	52	35	65

Reaction conditions: [benzaldehyde] = 30 mmole; 10 mL of methanol; 50 mg of catalyst at 60 °C for 3 h

To see the effect of the mole ratio, the reaction has been performed by varying the mole ratio of benzaldehyde:H_2O_2(Fig.7C (i)). According to the chemical dynamics, the oxidative-esterification can be improved by increasing the amount of H_2O_2. The conversion increased with an increase in the molar ratio and reaches 79% at mole ratio of 1:3 with 52 % selectivity towards methyl benzoate. With a further increase in the mole ratio to 1:4, there is no significant increase in conversion (79%), however,a noticeable increase in selectivity to benzoic acid has been observed (56%) whereas selectivity towards methyl benzoate decreases (22%).

The effect of the amount of catalyst on conversion has been studied by varying the catalyst amount in the range from 0.025 to 0.100 g (Fig. 7C (ii). Oxidative esterification of aldehyde is significantly affected by Lewis-acidity of Cu(II) in the catalyst. The increase in the conversion can be attributed to an increase in the number of available catalytically active sites. It has been observed that the conversion increases with an increase in the amount of catalyst and reaches a maximum of 79% at 0.050 g. The selectivity to ester product increases on increasing the amount of the catalyst and major ester product (82%) has been observed using 0.050 g of the catalyst.

The oxidative esterification has been evaluated by using different aldehydes with methanol under optimized reaction conditions (Table 4). Benzaldehyde derivatives bearing different functional groups,

Table 4 — Influence of nature of substituent on benzaldehyde on oxidative esterification

Substrates	Ester formed	Ester selectivity	% Benzaldehyde conversion
Benzaldehyde	methyl benzoate	82	79
o-methoxybenzaldehyde	*o*-methoxy methylbenzoate	47	80
o-chlorobenzaldehyde	*o*-chloro methylbenzoate	21	45
p-chlorobenzaldehyde	*p*-chloro methylbenzoate	29	52
m-chlorobenzaldehyde	*m*-chloro methylbenzoate	25	49
p-hydroxybenzaldehyde	*p*-hydroxy methylbenzoate	40	70
salicylaldehyde	methyl salicylate	35	65

Reaction conditions: [benzaldehyde] = 30 mmole, [K_2CO_3] = 30 mmole, 10 mL of methanol, 50 mg of PS-Cu(II)PBMZL for 3.5 h at 60 °C including hydroxyl ($^-$OH), methoxy (OCH_3), nitro (NO_2), and chloro (Cl^-) groups on either *ortho*, *para* or *meta* position of the aromatic ring have been investigated under optimized conditions. Benzaldehyde substituted with an electron-withdrawing group tends to be oxidized with more difficulty than unsubstituted benzaldehyde and those with an electron-donating group. The oxidative esterification reaction is amenable to both electron-rich and electron-poor aromatic aldehydes Benzaldehyde bearing electron-donating groups such as methoxy at the *ortho*-position can also be employed as facile substrates that provide the corresponding ester in a high yield. The lower selectivity is probably due to the decline of electrophilic properties since the electron-donating groups on the benzaldehyde can reduce the electrophilicity of the carbonyl group, thus benzaldehyde is hindered to form the ester. However, the one with electron-withdrawing groups at the same position such as chloride performs poorly in conversion.

The reactions have been extended to other alcohols using benzaldehyde as the standard aldehyde such as ethanol, n-propanol, ^{i}PrOH, n-butanol, and ^{t}BuOH (Table 5). In case of straight-chain alcohols, the % benzaldehyde conversion varies slightly: methanol ~ ethanol (79 %) < n-propanol (80 %) < n-butanol (81 %). The selectivity towards corresponding ester formation decreases. Benzaldehyde conversion and corresponding ester selectivity have been found to decrease in the case of branched alcohols due to an increase in the steric hindrance that would have significantly affected the activity of the reaction.

The error range in the case of experimental data of oxidative bromination and esterification related to the variation of catalyst concentration is displayed in Figures 8A and 8B.

The catalytic activity of PS-Cu(II)PBMZL has been compared with Cu(II)PBMZLH under optimized conditions. The unbound Cu(II)PBMZLH exhibits 56 % benzaldehyde conversion with 54 % methyl benzoate selectivity.

Mechanism

Both oxidative bromination and esterification have been found to occur through a non-free radical mechanism which was confirmed by carrying out the reactions in the presence of radical abstractor like BHT. The reaction between H_2O_2 and complex bound to the polymer matrix is expected to lead to the formation of hydroperoxo intermediates **(A)**which may further react with the coordinated substrate to give oxidized products by homolytic cleavage of O-O bond of H_2O_2 resulting in OH radicals or by heterolytic cleavage (Schemes 3 and 4). For further confirmation for the type of mechanism in the probe reactions and to check for homolytic versus heterolytic scission of the peroxide O-O bond, the oxidative bromination, and esterification under the optimized reaction conditions have been carried out using methyl-1-phenyl-2-propyl hydroperoxide (MPPH) as a mechanistic probe.It is known that, if the reaction proceeds via heterolytic cleavage of the O-O

Table 5 — Oxidative esterification using different alcohols

Alcohol used	Ester formed	Ester selectivity	% Benzaldehyde conversion
Methanol	methyl benzoate	82	79
Ethanol	ethyl benzoate	49	79
n-propanol	propyl benzoate	45	80
iso-propanol	isopropyl benzoate	40	56
n-butanol	butyl benzoate	40	81
tert-butanol	tertiary butyl benzoate	21	14

Reaction conditions: [benzaldehyde] = 30 mmole; 90 mmole of H_2O_2; 30 mmole of K_2CO_3; 10 mL of alcohol; 50 mg of catalyst at 60 °C for 3 h

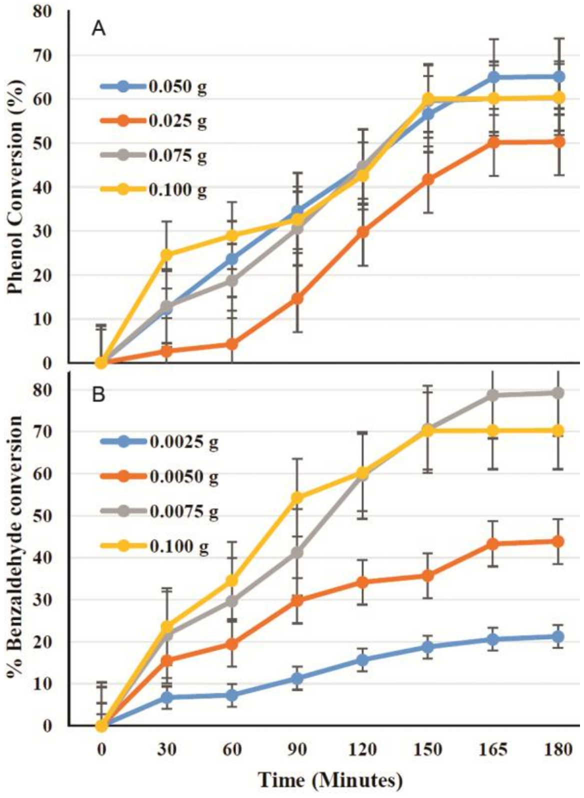


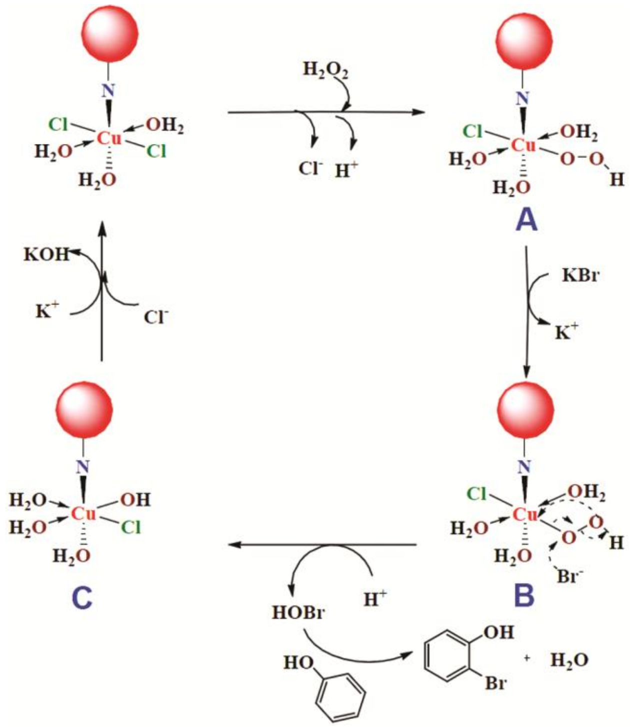
Fig. 8 —(A) Error bars represent standard deviations on the basis of variation in concentration of catalyst a) oxidative bromination of phenol and, (B) oxidative esterification of benzaldehyde.

bond, 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[37,38].[40]. The reactions are carried out using MPPH (1.4 g) under respective optimized conditions and the reaction products are analyzed by GC which reveals the presence of 2-methyl-1-phenyl-2-propanol in case of oxidative bromination and esterification indicating heterolytic cleavage of the O-O bond. In the case of oxidative bromination, intermediate (B) will later react with Br^- ion to liberate HOBr that will later attack the substrate by an electrophilic attack (Br^+) to give bromo-product whereas, in case of oxidative esterification, a coordinated hemiacetal intermediate (F)is expected that further undergo rearrangement to give ester[39,40](Schemes 3 and 4).

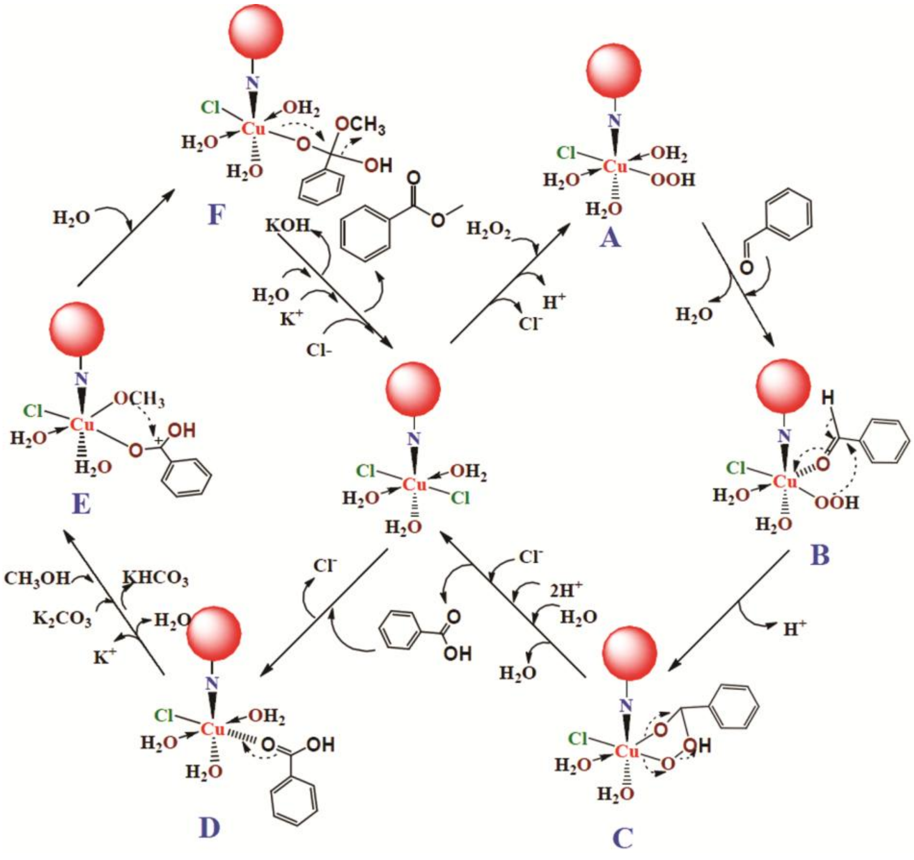
^{1}H NMR spectral data of bromination and esterification products

1. 4-Bromo aniline

^{1}H NMR (400 MHz, $CDCl_3$): *δ 3.69 (br, s, 2H), 6.60 (d, J = 7.63 Hz, 2 H), 7.27 (d, J = 7.93 Hz, 2H).*



Scheme 3─Proposed mechanism for oxidative bromination using PS-Cu(II)PBMZL



Scheme 4 — Proposed mechanism for oxidative esterification using PS-Cu(II)PBMZL

2. 4-Bromophenol

^1H NMR (400 MHz, $CDCl_3$): δ 4.83 (br, s. 2H), 7.34 (d, J = 8.34 Hz, 2H), 7.84 (d, J = 8.34 Hz, 2H)

3. 4-Bromoanisole

^1H NMR (400 MHz, $CDCl_3$): δ 3.82 (s, 3H), 6.79-6.84 (m, 2H). 7.39-7.44 (m, 2H)

4. 4-Bromotoluene

^1H NMR (400 MHz, $CDCl_3$): δ 2.32 (s, 3H) 7.06 (d, J = 8.4 Hz, 2H) 7.38 (d, J = 8.4 Hz, 2H).

5. 4-Amino-2-bromophenol

^1H NMR (400 MHz, $CDCl_3$): δ 4.83 (br, s, 2H), 7.28 (s, 1H), 7.34 (s, 1H), 7.84 (m, J=8.34 Hz, 2H).

6. Bromobenzene

^1H NMR (400 MHz, $CDCl_3$): δ 7.21-7.41 (m, 3H), 7.51-7.62 (m, 2H).

7. 3-Bromonitrobenzene

^1H NMR (400 MHz, $CDCl_3$): δ 7.48-7.54 (m, 1H), 7.64 (d. J=7.58 Hz,1H), 8.15 (d, J = 8.08 Hz, 1H), 9.21 (s, 1H).

8. Methylbenzoate

^1H NMR (400 MHz, $CDCl_3$): δ 3.91 (s, 3H) 7.38-7.47 (m, 2H), 7.50-7.59 (m, 1H), 8.04 (d, J = 8.08 Hz, 2H).

9. Ethylbenzoate

^1H NMR (400 MHz, $CDCl_3$): δ 1.38 (t, J=7.20Hz, 3H), 4.36 (q, J = 7.16 Hz, 2H), 7.39-7.45 (m, 2H), 7.50-7.56 (m, 1H), 8.03 (dd, J=8.34, Hz, 2H)

10. Propyl benzoate

^1H NMR (400 MHz, $CDCl_3$): δ 1.00-1.04 (t, 3H), 1.72-1.83(m, 2H), 4.27 (t, J=6.65 Hz, 2h), 7.34-7.46 (m, 2H), 7.47-7.60 (m. 1H), 8.00-8.08 (m, 2H)

11. n-Butylbenzoate

^1H NMR (400 MHz, $CDCl_3$): δ 0.90-0.95 (m, 3H), 1.41-1.52 (m, 2H), 1.69-1.79(m, 2H), 4.31 (t, j=6.63 Hz, 2H).

12. iso-Propyl benzoate

^1H NMR (400 MHz, $CDCl_3$): δ 1.37 (d, J=6.26 Hz, 6H), 7.38-7.44 (m, 2H), 7.49-7.55 (m, 1H), 8.04 (dd, J=8.36, 1.32 Hz, 2H).

13. Tert-butyl benzoate

^1H NMR (400 MHz, $CDCl_3$): δ 1.60 (s, 9H), 7.47-7.50 (m, 2H), 7.60-7.64 (m, 1H), 8.12-8.16 (m, 2H).

14. Methyl-2-chloro-benzoate

^1H NMR (400 MHz, $CDCl_3$): δ 3.91 (s, 3H), 7.38-7.46 (m, 2H), 7.51-7.57 (m, 1 H), 8.04 (d, J=8.08 Hz, 1H) 7.79 (J=8.38, 1.26 Hz, 1H).

15. Methyl-3-chloro-benzoate

^1H NMR (400 MHz, $CDCl_3$): δ 3.90 (s, 3H), 7.30-7.37 (m, 1H), 7.49 (d, J=9.10 Hz, 1H), 7.89 (d, J=7.87 Hz, 1H), 7.98 (s, 1H).

16. Methyl-4-chloro-benzoate

^1H NMR (400 MHz, $CDCl_3$): δ 3.90 (s, 3H), 7.39 (d, J=8.71 Hz, 2H), 7.95 (d, J=8.75 Hz, 2H)

17. Methyl-4-hydroxy-benzoate

^1H NMR (400 MHz, $CDCl_3$): δ 2.08 (s, 3H), 6.34-6.42 (m, 2H), 6.94 (br, s, 1H), 7.90 (d, J=8.85 Hz, 2H).

18. Methyl-4-methoxy-benzoate

^1H NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 3h), 3.87 (s, 3H), 6.83-7.06 (m, 2H), 7.80-7.85 (m, 2H).

19. Methyl-2-hydroxy-benzoate

^1H NMR (400 MHz, $CDCl_3$): δ 1.39 (s, 3H), 6.84 (t, J=7.02 Hz, 1H), 6.96 (d, J=7.58 Hz, 1H), 7.41 (t, J=6.94 Hz, 1H), 7.82 (d, J=7.92 Hz, 1H), 10.86 (s, 1H).

Recyclability of catalyst

For a heterogeneous catalyst, it is important to examine its ease of separation, recoverability, and reusability. The recycling ability of the PS-Cu(II)PBMZL has been investigated by separating the catalyst from the reaction mixture after the reaction. It is then washed with water, followed by ethanol, dried at 120 ºC and reused for oxidative bromination and oxidative esterification under respective optimized conditions. The results show that catalyst is stable up to four runs (Figure 9 A-B).

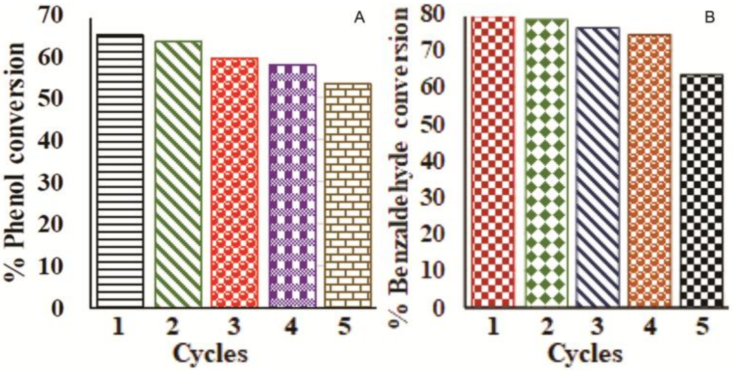


Fig. 9 ─(A)Recycling test of PS-Cu(II)PBMZL for oxidative bromination and(B)Recycling test of PS-Cu(II)PBMZL for oxidative esterification

Thus, the anchoring of the complex on the polymer support has been found to increase the life of the catalyst as the active sites are well dispersed thus reducing dimerization in turn leading to the retention of catalytic activity. To test the metal leaching from PS-Cu(II)PBMZL, the reactionhas been carried out under optimized conditions for 90 min. Later the catalyst is removed from the reaction mixture and the reaction is further continued until 180 min. It has been observed that there is a negligible conversion in the absence of catalyst indicating that metal has not leached out from the catalyst.

Conclusion

Cu(II) complex of 2-phenylbenzimidazole is successfully immobilized on the polymer matrix and characterized by physicochemical techniques. The FT-IR, UV-Vis/DRS spectra and TG analysis confirm the complexation on the polymer matrix. The coordination environments around the Cu center in PS-Cu(II)PBMZL was found to be distorted octahedral through UV-Vis DRS and ESR spectral studies. PS-Cu(II)PBMZL has been used as catalysts in oxidative bromination and oxidative esterification of organic compounds. In case of oxidative bromination, PS-Cu(II)PBMZLH displayed 65% phenol conversion with 61% 2-bromophenol selectivity. The % benzaldehyde conversion and methyl benzoate selectivity in case of oxidative esterification using PS-Cu(II)PBMZL has been found to be 79 and 82. In both the probe reactions, the % conversion and product selectivity are higher in the case of polymer bound complexes compared to their unbound complexes.

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