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Oxidation of phenol and toluene over polymer supported Co(II) and Fe(III) catalysts

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Polymer supported iron and cobalt complexes of 2,6-bis(benzimidazolyl)pyridine (BBP) abbreviated as Fe(PS-BBP)Cl_3 and Co(PS-BBP)Cl_2 exhibited catalytic activity towards oxidation of phenol and toluene to give catechol and benzaldehyde as major products respectively using TBHP as an oxidant. The influence of temperature, reaction time, solvents, concentration of catalyst, substrate to oxidant ratio and oxidants on the oxidation reactions have been studied. Under optimized conditions, Fe(PS-BBP)Cl_3 gave 92.3% conversion of phenol and 88.2% toluene whereas, Co(PS-BBP)Cl_2 gave 97.5 and 86.3% conversion of phenol and toluene respectively. Catalysts have been recyclable without loss in their activity and possible mechanisms of these reactions have been also worked out.

Keywords: Co(PS-BBP)Cl_2, Fe(PS-BBP)Cl_3, Tert-butyl hydroperoxide (TBHP), Toluene, Phenol

Heterogeneous catalysis in oxidation reactions are important technology for the conversion of aromatic compounds into industrially important oxygenated compounds[1]. Polymer supported transition metal complexes are gaining importance as efficient heterogeneous catalysts in a variety of organic transformations as they are nontoxic, non-volatile and easily recyclable[2]. The various supports have been used to immobilize metal complexes, but polymer supports showed better catalytic activities as compared to inorganic supports[3-5]. However, to overcome the issues of catalyst recovery from the reaction products, low catalytic activity and stability associated with homogeneous catalysts, more efficient and environment friendly heterogeneous catalysts have been developed for phenol and toluene oxidation.

Phenols are poorly biodegradable toxins found in wastewaters from coal processing, pharmaceutical industry, petroleum refineries, and resins and plastics processing plants. The removal of these from wastewater by oxidation is economically attractive due to the less consumption of chemicals, and the intermediate products are less toxic and degradable[6]. Oxidation of phenols using oxidants like hydrogen peroxide, permanganate, molecular oxygen and ozone, are widely studied[7,8]. Oxidants work either alone or with a catalyst. Heterogeneous catalysts involving metal oxides[9] and supported metal oxides[10] with oxidant were also used for oxidation of phenol. Unsupported Schiff base complexes of metal ions also catalyzed phenol oxidation in presence of H_2O_2 as oxidant[11], but in the presence of polymer-supported transition metal complexes, the phenol gave good conversions and selectivities[12-16].

Selective oxidation of sp^3 hybridized carbon of inactive hydrocarbons to industrially important intermediates remains a challenge[17,18]. The oxidation of toluene to benzaldehyde (BZ), benzoic acid (BA) is an important conversion in chemical industry because benzaldehyde and benzoic acid are widely used to synthesize pharmaceuticals, food preservatives, dyes, perfume, solvents and resins[19,20]. Some catalysts including g-C_3N_4 (graphene sheet of carbon nitride)nanocomposite [21,22], copper-based oxides[23] and Mn(salen) complex [Mn(salen) = {(R,R)-N,N-bis (3,5-di-tert-butylsalicylidenato)-1,2-cyclohexanediamine (2-)}chloromanganese(III)][24] have been reported as effective catalysts for the selective oxidation of toluene with different oxidants. However, the major problem associated with these technologies is that toluene conversion gave a poor selectivity of benzaldehyde and benzyl alcohol[21–26]. Pd and Au nanoparticles supported on hydroxyapatite, bis-(l-tyrosinato)copper(II) immersed in a magnetite-infused silica matrix were also used in toluene oxidation but the conversion and selectivity was low[27,28].

In the current work, catalytic activity of polymer anchored Fe(III) and Co(II) complexes were investigated towards phenol and toluene oxidation using tert-butyl hydroperoxide (TBHP) as oxidant. The effect of various reaction conditions on the activity and selectivity of catalysts were studied. Polymer supported cobalt complex showed high efficiency in oxidation of phenol and toluene in presence of TBHP as compared to polymer supported Fe(III) complex, which indicated that the activities of anchored metal complexes is also influenced by the type of metal and coordination geometry. The recyclability and heterogeneity of the polymer anchored catalysts were also evaluated.

Materials and Methods

Chloromethylated polystyrene divinyl benzene (PS) was obtained as a gift from THERMAX Ltd. India. TBHP (70%), phenol and toluene were purchased from Merck A. R. grade and used without further purification. Solvents were freshly distilled by standard methods[29]. The products were analyzed by using a Shimadzu 14B gas chromatograph equipped with FID detector and BP-5 capillary column. Known chemical standards can be injected in the GC to determine the corresponding retention time, which allows the identification of the compounds from experimental samples To identify the reaction products, the retention time of the standard was used and peak areas were used to calculate the amount of the reaction products in the mixture.

Preparation of polymer supported cobalt and iron complexes [VO(PS-BBMA)]SO_4

Chloromethylated polystyrene (1.0 g, Cl content 6 mmol) was swelled in DMF for 2 h, and then a solution of BBP (0.31 g, 1 mmol) in DMF (10 mL) was added, followed by triethylamine (4 mL) and ethyl acetate (30 mL). The mixture was heated at 100 °C for 48 h. After cooling, it was filtered, Soxhlet extracted with ethanol, and dried. 1.0 g of functionalized polymer (PS-BBP) was added to THF (10 mL) and kept for 1 h. A solution of $CoCl_2.6H_2O$ (0.23 g; 1 mmol) in THF (10 mL) was added to it and the mixture was stirred at 60 °C for 48 h. The resultant greenish blue colored beads were filtered off and washed by Soxhlet extraction and dried at 100 °C (Scheme 1).

Similarly Fe(PS-BBP)Cl_3 (Scheme 1) was synthesized by reacting PS-BBP (1 g) with $FeCl_3$ (0.17 g; 1 mmol) in methanol (20 mL) and stirred at 60 °C for 48 h. The resultant red colored beads were filtered off and washed by Soxhlet extraction using methanol and dried at 100 °C (Scheme 1). The complexes were characterized by various physico-chemical techniques and it is reported elsewhere[30,31].

General procedure for oxidation of phenol and toluene catalyzed by Co(PS-BBP)Cl_2 and Fe(PS-BBP)Cl_3

In a typical reaction, aqueous 70% TBHP (20 mmol) was added to the phenol/toluene taken in 5 mL of acetonitrile. Co(PS-BBP)Cl_2/Fe(PS-BBP)Cl_3 catalysts (30 mg) were added to it and the reaction mixture was stirred at desired temperature. The reaction progress was monitored by withdrawing 0.1 mL of reactant mixture at regular intervals and analyzed by gas chromatography (GC).

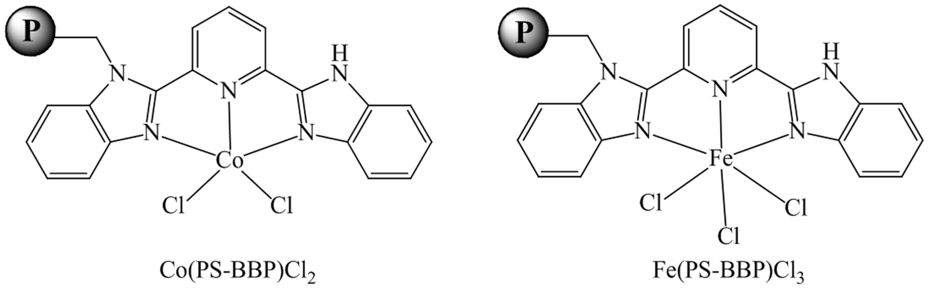
Results and Discussion

To determine suitable reaction conditions for maximum conversion of phenol and toluene, the effects of solvents, catalyst concentration, oxidants, temperature, reaction time and substrate: TBHP ratio were investigated using Co(PS-BBP)Cl_2 and Fe(PS-BBP)Cl_3 catalysts.

Phenol oxidation

Effect of solvents

In order to probe the role of different solvents, 5 mL of acetonitrile, ethanol and water were used for oxidation of phenol in the presence of 30 mg



Co(PS-BBP)Cl_2

Fe(PS-BBP)Cl_3

Structure of catalysts

Scheme 1

Co(PS-BBP)Cl_2, 1:2 phenol to TBHP ratio at 50 °C for 6 h. In water and ethanol medium only 24.6 (78.4% catechol selectivity) and 30.8% (85.5% catechol selectivity) phenol conversion took place respectively. The highest conversion of 97.5% was obtained using 5 mL acetonitrile as solvent in 6 h (Table 1, entry 3; Supplementary Data, Fig. S1). For 60 mg of Fe(PS-BBP)Cl_3 at 70 °C in 6 h, among the solvents used, acetonitrile showed maximum conversion (Table 2, entry 3; Fig. S1). The conversion followed the order: acetonitrile > water > ethanol (Table 1 and 2, entry 3). Hence acetonitrile was chosen as solvent for further reactions.

Effect of catalysts concentration

With variation of different amounts of Co(PS-BBP)Cl_2 catalyst (10, 20, 30 and 40 mg) using 1:2 phenol to TBHP ratio at 50 °C in 6 h, 30 mg of catalyst (0.0175 mmol, Table 1, entry 3) showed better conversion (97.5%) and selectivity towards catechol (90.8%) whereas, at lower concentration (10 mg; 0.0051 mmol, Table 1, entry 4), phenol conversion was found to be 47.6% with 84.7% selectivity towards catechol. Further increase in its concentration to 40 mg (0.0221 mmol, Table 1, entry 6; Supplementary Data, Fig. S2), the conversion and selectivity remained constant.

For Fe(PS-BBP)Cl_3 catalyst (40, 50, 60 and 70 mg) maintaining other conditions constant (60 mg of Fe(PS-BBP)Cl_3; 5 mL CH_3CN; 1:2 phenol: TBHP ratio, 70 °C; 6 h), phenol conversion was found to be in the order; 60 mg; 0.0204 mmol (92.3%) > 70 mg; 0.0241 (92.1%) > 50 mg; 0.0170 mmol (62.3%) > 40 mg; 0.0136 mmol (51.2%) (Table 2, entries 3, 6, 5 and 4).

Table 1 — Influence of solvents, Co(PS-BBP)Cl_2 concentration, temperature, oxidants and phenol: TBHP ratio on phenol oxidation

Entry No.	Solvent	Catalyst conc. (mg)	Oxidants	T (°C)	Phenol: TBHP	Phenol conversion (%)	Product selectivity (%)	
							CAT	HQ
1	H_2O	30	TBHP	50	1:2	24.6	78.4	21.5
2	EtOH	30	TBHP	50	1:2	30.8	85.5	14.4
3	**CH_3CN**	**30**	**TBHP**	**50**	**1:2**	**97.5**	**90.8**	**9.2**
4	CH_3CN	10	TBHP	50	1:2	47.6	84.7	15.2
5	CH_3CN	20	TBHP	50	1:2	78.9	87.9	12.1
6	CH_3CN	40	TBHP	50	1:2	97.5	90.8	9.2
7	CH_3CN	30	O_2	50	1:2	11.6	65.5	34.5
8	CH_3CN	30	H_2O_2	50	1:2	53.2	79.5	20.5
9	CH_3CN	30	TBHP	30	1:2	46.3	57.4	42.6
10	CH_3CN	30	TBHP	40	1:2	63.0	65.5	34.5
11	CH_3CN	30	TBHP	60	1:2	55.6	76.1	23.8
12	CH_3CN	30	TBHP	50	1:1	46.3	72.5	27.5
13	CH_3CN	30	TBHP	50	1:3	89.8	88.3	11.6

T: Temperature; CAT: catechol; HQ: hydroquinone

Table 2 — Influence of solvents, Fe(PS-BBP)Cl_3 concentration, temperature, oxidants and phenol: TBHP ratio on phenol oxidation

Entry No.	Solvent	Catalyst conc. (mg)	Oxidants	T (°C)	Phenol: TBHP	Phenol conversion (%)	Product selectivity (%)	
							CAT	HQ
1	H_2O	60	TBHP	70	1:2	45.3	80.1	19.9
2	EtOH	60	TBHP	70	1:2	42.3	73.8	26.2
3	**CH_3CN**	**60**	**TBHP**	**70**	**1:2**	**92.3**	**91.2**	**8.8**
4	CH_3CN	40	TBHP	70	1:2	51.2	76.6	23.4
5	CH_3CN	50	TBHP	70	1:2	62.3	67.9	32.1
6	CH_3CN	70	TBHP	70	1:2	92.1	91.3	8.7
7	CH_3CN	60	O_2	70	1:2	33.2	72.6	27.4
8	CH_3CN	60	H_2O_2	70	1:2	70.1	79.1	20.9
9	CH_3CN	60	TBHP	50	1:2	36.6	60.3	39.7
10	CH_3CN	60	TBHP	60	1:2	81.3	80.3	19.7
11	CH_3CN	60	TBHP	80	1:2	79.3	74.4	25.6
12	CH_3CN	60	TBHP	70	1:1	45.6	72.8	27.2
13	CH_3CN	60	TBHP	70	1:3	92.1	90.7	9.3

T: Temperature; CAT: catechol; HQ: hydroquinone

Effect of oxidants

To determine a suitable oxidant, phenol oxidation was carried out using TBHP, H_2O_2, and O_2 with Co(PS-BBP)Cl_2 and Fe(PS-BBP)Cl_3. The phenol conversion over Co(PS-BBP)Cl_2 followed the order: TBHP (97.5%, Table 1, entry 3) > H_2O_2 (53.2%, Table 1, entry 8) > O_2 (11.6%, Table 1, entry 7) and for Fe(PS-BBP)Cl_3, TBHP gave 92.3% phenol conversion with 91.2 and 8.8% selectivity towards catechol and hydroquinone respectively (Table 2, entry 3). Using H_2O_2 and O_2, phenol conversion was 70.1 and 33.2% respectively (Table 2, entries 8 and 7). Hence TBHP was chosen as oxidant for phenol oxidation.

Effect of temperature

With increase in reaction temperature from 30 to 50 °C with Co(PS-BBP)Cl_2 catalyst, phenol conversion increased from 46.3 to 97.5% in 6 h, while the selectivity towards catechol increased from 57.4 to 90.8% but it decreased to 76.1% at 60 °C (Table 1, entry 11; Supplementary Data, Fig. S3).

The phenol oxidation was carried out by varying the temperature in the range 50-80 ºC in the presence of Fe(PS-BBP)Cl_3 catalyst in 6 h. Phenol conversion increased from 36.6% at 50 °C (Table 2, entry 9) to 92.3% at 70 °C (Table 2, entry 3), further increase in temperature to 80 °C, resulted detrimental to the phenol conversion (79.3%) and catechol selectivity (74.4%) (Table 2, entry 11). Hence for Co catalyst, 50 °C was the optimum temperature while for Fe catalyst 70 °C in 6 h.

Effect of phenol: TBHP ratio

The catalytic efficiency of the Co(PS-BBP)Cl_2 and Fe(PS-BBP)Cl_3 complexes in the oxidation of phenol was evaluated at different phenol/TBHP molar ratios viz. 1:1, 1:2 and 1:3. Percentage phenol conversion was found to be in the order 1:2 (97.5%) > 1:3 (89.8%) > 1:1 (46.3%) (Table 1, entry 3, 13 and 12; Supplementary Data, Fig. S4) and 1:2 (92.3%) > 1:3 (92.1%) > 1:1 (45.6%) (Table 2, entry 3, 13 and 12) for Co(PS-BBP)Cl_2 and Fe(PS-BBP)Cl_3 respectively.

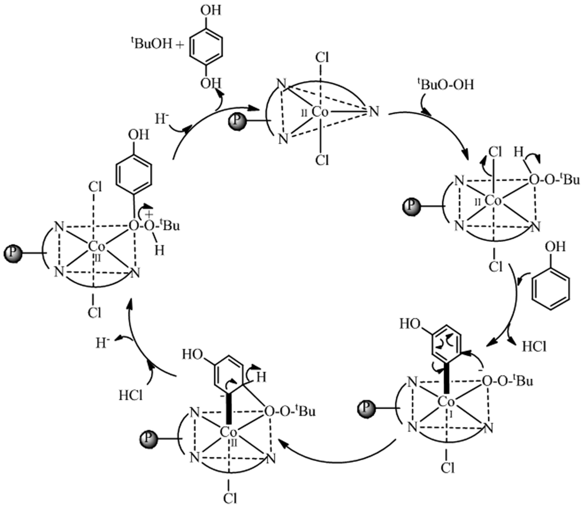
Plausible reaction mechanism

In order to prove whether the oxidation reactions of phenol and toluene occurred via radical pathway or ionic mechanism, the reactions were performed in the presence of radical scavenger, butylated hydroxytoulene (BHT), wherein the oxidation of substrates was not affected indicating that the reaction followed ionic mechanism. A plausible mechanism for the oxidation of phenol is presented for Co(PS-BBP)Cl_2 and Fe(PS-BBP)Cl_3 in Schemes 2 and 3 respectively.

Toluene oxidation

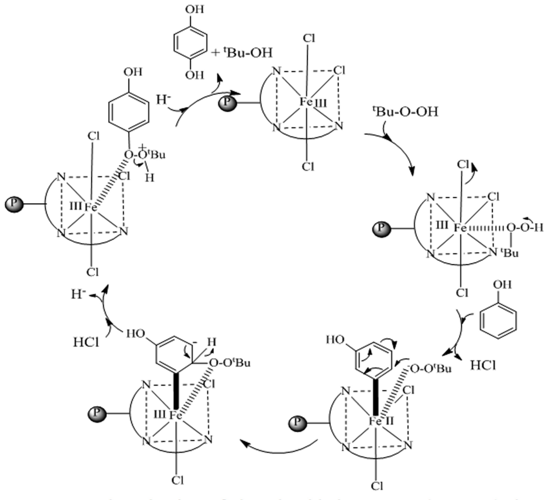
Effect of solvents

The influence of solvents on the toluene conversion was investigated using acetonitrile, ethanol and water, 20 mg of Co(PS-BBP)Cl_2 at 60 °C in 5 h where acetonitrile showed maximum conversion of 86.3% (Table 3, entry 3; Supplementary Data, Fig. S5), while least conversion (30.8%) was encountered in ethanol (Table 3, entry 2). Whereas for Fe(PS-BBP)Cl_2, for 80 mg at 60 °C in 5 h maximum toluene conversion was 88.2% with selectivity towards benzaldehyde was 93.3% shown by acetonitrile (Table 4, entry 3). Hence CH_3CN was chosen as solvent for toluene oxidation.



Proposed mechanism of phenol oxidation over Co(PS-BBP)Cl_2

Scheme 2



Proposed mechanism of phenol oxidation over Fe(PS-BBP)Cl_3

Scheme 3

Table 3 — Influence of solvents, Co(PS-BBP)Cl_2 concentration, temperature, oxidants and toluene: TBHP on toluene oxidation

Entry No.	Solvent	Catalyst conc. (mg)	Oxidants	T (°C)	Toluene: TBHP	Toluene conversion (%)	Product selectivity (%)	
							BD	BA
1	H_2O	20	TBHP	60	1:2	32.6	67.7	32.3
2	EtOH	20	TBHP	60	1:2	30.8	62.6	37.4
3	**CH_3CN**	**20**	**TBHP**	**60**	**1:2**	**86.3**	**91.9**	**8.1**
4	CH_3CN	10	TBHP	60	1:2	42.3	78.7	21.3
5	CH_3CN	30	TBHP	60	1:2	86.2	90.3	9.7
6	CH_3CN	20	O_2	60	1:2	12.9	75.9	24.1
7	CH_3CN	20	H_2O_2	60	1:2	56.3	90.8	9.2
8	CH_3CN	20	TBHP	40	1:2	47.6	76.0	24.0
9	CH_3CN	20	TBHP	50	1:2	74.6	83.5	16.5
10	CH_3CN	20	TBHP	70	1:2	86.3	91.9	8.1
11	CH_3CN	20	TBHP	60	1:1	43.1	91.9	8.1
12	CH_3CN	20	TBHP	60	1:3	86.3	80.6	19.4

T: Temperature; BD: Benzaldehyde; BA: Benzoic acid

Table 4 — Influence of solvents, Fe(PS-BBP)Cl_3 concentration, temperature, oxidants and toluene:TBHP on toluene oxidation

Entry No.	Solvent	Catalyst conc. (mg)	Oxidants	T (°C)	Toluene: TBHP	Toluene conversion (%)	Product selectivity (%)	
							BD	BA
1	H_2O	80	TBHP	60	1:2	32.0	89.3	10.7
2	EtOH	80	TBHP	60	1:2	39.3	79.3	20.7
3	**CH_3CN**	**80**	**TBHP**	**60**	**1:2**	**88.2**	**93.3**	**6.7**
4	CH_3CN	60	TBHP	60	1:2	45.3	86.3	13.7
5	CH_3CN	70	TBHP	60	1:2	68.3	80.9	19.1
6	CH_3CN	90	TBHP	60	1:2	88.2	93.3	6.7
7	CH_3CN	80	O_2	60	1:2	No reaction		
8	CH_3CN	80	H_2O_2	60	1:2	69.3	88.3	11.7
9	CH_3CN	80	TBHP	40	1:2	31.1	82.3	17.7
10	CH_3CN	80	TBHP	50	1:2	49.3	40.3	19.7
11	CH_3CN	80	TBHP	70	1:2	64.3	88.1	11.9
12	CH_3CN	80	TBHP	60	1:1	43.5	76.3	23.7
13	CH_3CN	80	TBHP	60	1:3	88.1	93.1	6.9

T: Temperature; BD: Benzaldehyde; BA: Benzoic acid

Effect of catalysts concentration

Toluene oxidation was carried out with three different amounts of Co(PS-BBP)Cl_2 (10, 20, 30 mg) in CH_3CN at 60 °C using 1:2 toluene to TBHP ratio. The results indicated that increasing the concentration of catalyst Co(PS-BBP)Cl_2 from 10 (0.0051 mmol) to 20 mg (0.0102) increased the conversion from 42.3 to 86.3% at 6 h (Table 3, entries 4 and 3; Supplementary Data, Fig. S6). Further increase in catalyst amount to 30 mg (0.0175 mmol), does not result in conversion and selectivity (Table 3, entry 5).

When four different amounts (60, 70, 80 and 90 mg) of Fe(PS-BBP)Cl_3 catalyst was used, 60 mg (0.0204 mmol) gave 45.3% conversion (Table 4, entry 4), while 80 (0.0273 mmol) of catalyst showed a maximum conversion of 88.2% (Table 4, entry 3), further increase in concentration to 90 mg (0.0301 mmol) the conversion and selectivity remain constant. Hence, 80 mg catalyst was considered as optimum concentration to carry out the reaction.

Effect of oxidants

Effect of oxidants on toluene conversion was investigated using 1:2 molar ratio of toluene to oxidant, 20 mg of Co(PS-BBP)Cl_2 in 5 mL CH_3CN at 60 ^{o}C for 5 h. TBHP gave 86.3% toluene conversion with 91.9 and 8.1% selectivity towards benzaldehyde and benzoic acid (Table 3, entry 3), while H_2O_2 and oxygen gave 56.3 (Table 3, entry 7) and 12.9% toluene conversion respectively (Table 3, entry 6). With 50 mmol of toluene, 80 mg Fe(PS-BBP)Cl_3 in 5 mL CH_3CN at 60 °C for 6 h, the conversion of toluene with TBHP (100 mmol) was 88.2% with 93.3 and 6.7% selectivity towards benzaldehyde and benzoic acid respectively (Table 4, entry 3), while toluene conversion was 69.3% (Table 4, entry 8) with

H_2O_2 (100 mmol) and no conversion in O_2 (1 atm). Hence TBHP was chosen as oxidant for toluene oxidation.

Effect of temperature

The performance of Co(PS-BBP)Cl_2 and Fe(PS-BBP)Cl_3 catalysts towards toluene oxidation was investigated at four different temperatures, viz. 40, 50, 60 and 70 °C whilst keeping all the other parameters constant. As the temperature was increased from 40 to 60 °C, the toluene conversion increased from 47.6 to 86.3% (Table 3, Supplementary Data, Fig. S7) and 31.1 to 88.2% (Table 4) in Co(PS-BBP)Cl_2 and Fe(PS-BBP)Cl_3 catalysts respectively. By increasing the temperature to 70 °C no appreciable increase in toluene conversion was observed. Hence, 60 °C was optimized for the reaction.

Effect of toluene: TBHP ratio

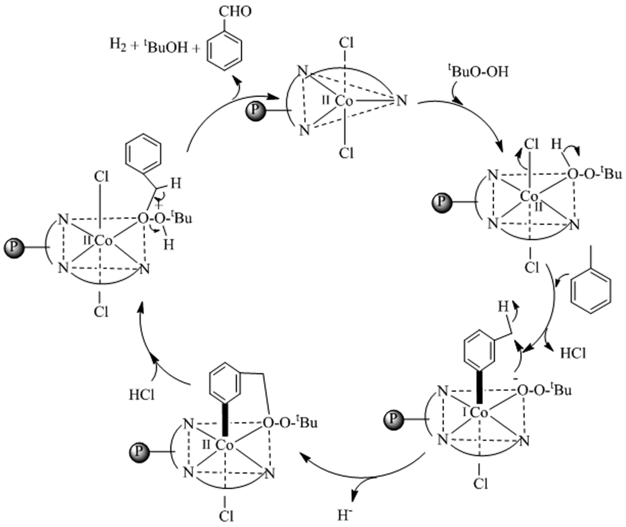
In order to determine the effect of toluene/TBHP molar ratio, the reactions were carried out with three different molar ratios (1: 1, 1: 2 and 1: 3), whilst keeping a fixed amount of toluene (50 mmol) and Co(PS-BBP)Cl_2 (20 mg) / Fe(PS-BBP)Cl_3 (80 mg) in 5 mL of CH_3CN at 60 °C. When the ratio was increased to 1:2, conversions increased to 86.3 and 88.2% using Co(PS-BBP)Cl_2 and Fe(PS-BBP)Cl_3 (Table 3, entry 3, Supplementary Data, Fig. S8) respectively. Hence, 1:2 (tolune:TBHP) molar ratio was considered as optimum for toluene oxidation.

Plausible reaction mechanism

The possible reaction mechanism for the oxidation of toluene is depicted for Co(PS-BBP)Cl_2 and Fe(PS-BBP)Cl_3 in Scheme 4 and 5.

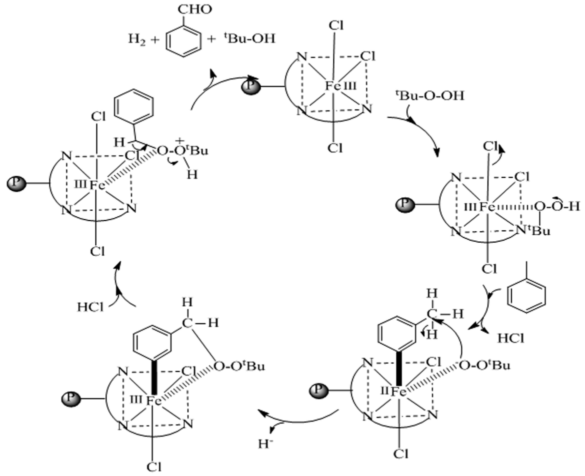
Recycling ability and Heterogeneity test

The recycling ability of the Co(PS-BBP)Cl_2 and Fe(PS-BBP)Cl_3 catalysts was investigated by separating the catalysts from the reaction mixture after the completion of the reaction and were washed with CH_3CN, dried at 100 ºC and reused for oxidation reactions under optimized reaction conditions. As a consequence, catalysts were stable up to six runs with slight decrease (5.6%) in phenol and toluene conversion thereafter (Fig. 1). To test the heterogeneous nature of the reactions in presence of catalysts, reactions were carried out under optimized conditions for 3 h. Later the catalyst was separated from the reaction mixture and the reaction was continued for 3 more hours. It was observed that there was no rise in yield of substrates in absence of catalysts. The solution was tested for metal content by AAS. The absence of Co and Fe in the reaction



Proposed mechanism of toluene oxidation over Co(PS-BBP)Cl_2

Scheme 4



Proposed mechanism of toluene oxidation over Fe(PS-BBP)Cl_3

Scheme 5

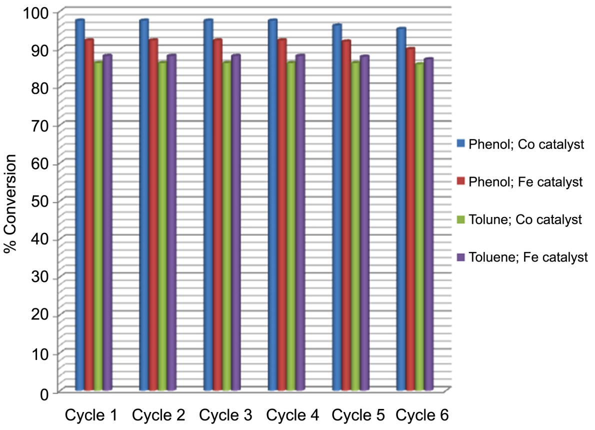


Fig. 1 — Recycling studies of Co(PS-BBP)Cl_2 and Fe(PS-BBP)Cl_3.

Table 5 — Optimized reaction conditions for phenol and toluene oxidation

Conditions	$Co(PS\text{-}BBP)Cl_2$		$Fe(PS\text{-}BBP)Cl_3$	
	Phenol	Toluene	Phenol	Toluene
Temperature (°C)	50	60	70	80
Time (h)	6	5	6	6
Substrate concentration (mmol)	50	50	50	50
Substrate:Oxidant	1:2	1:2	1:2	1:2
Oxidant	TBHP	TBHP	TBHP	TBHP
Solvent (5 mL)	CH_3CN	CH_3CN	CH_3CN	CH_3CN
Catalyst concentration (mmol)	0.0175	0.0102	0.0204	0.0204
Conversion (%)	97.5	86.3	92.3	88.2
Selectivity (%)	90.8 (CAT)	91.9 (BD)	91.2 (CAT)	93.3 (BD)
TON (h^{-1})	464	423	377	360

TON = Turnover number

mixture indicated that the metal has not leached out from the catalysts and they were heterogeneous in nature. The recycled catalysts were tested for metal content and were found identical to the fresh catalyst (Table 5, and discussed in the Conclusion below).

Conclusions

Polymer-supported iron and cobalt complexes of 2,6-bis(benzimidazolyl)pyridine were investigated towards oxidation of phenol and toluene as shown in Table 5. In case of phenol oxidation catechol is the major product with a maximum conversion of 97. 5% with 90.8% selectivity in the presence of $Co(PS\text{-}BBP)Cl_2$, whilst 92.3% conversion and 91.2% selectivity using $Fe(PS\text{-}BBP)Cl_3$. Toluene oxidation gave 86.3 and 88.2% conversion in the presence of polymer supported Co and Fe catalysts respectively. The supported catalyst showed a good conversion in comparison with the unsupported catalysts, and this clearly suggested that the polymer support was able to improve the catalytic activity. The polymer supported cobalt complex showed higher turnover number than the corresponding iron complex. However, slow deactivation of the catalyst was accompanied by a gradual change in colour of the catalyst surface. Cobalt and iron content in recycled catalysts (after sixth cycle) was determined by ICP-OES and the metal content was found to be slightly decreased (2.9% of Co and 1.5% of iron). The catalysts were found to be recyclable without loss in activity up to six runs, suggesting that this approach could find promising applications in organic synthesis. All these catalysts are recyclable and heterogeneous in nature.

Supplementary Data

Supplementary data associated with this article are available in the electronic form at http:// www.niscair.res.in/jinfo/ijca/IJCA_58A(09) 964-971_SupplData.pdf.

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