

Hydroxylation of Phenol Catalyzed by Iron Metal-Organic Framework (Fe-BTC) with Hydrogen Peroxide

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Abstract

Liquid phase catalytic hydroxylation of phenol by Fe-containing metal-organic framework, Fe-BTC (BTC = 1,3,5-benzenetricarboxylate) using 30% H₂O₂ as an oxidant and H₂O as solvent showed good activity and stability under mild reaction conditions. Phenol reacts with hydrogen peroxide over Fe-BTC to produce two main products, *viz.*, catechol and hydroquinone. The effect of temperature, time, substrate/hydrogen peroxide mole ratio and amount of catalyst on catalytic performance were studied. The catalyst could be reused four times without losing significant loss of catalytic performance. The crystallinity and structure of catalyst were unchanged during the catalysis reaction, as confirmed by comparison of XRD and SEM of the fresh and reused catalyst. A reaction mechanism is proposed based on the experimental results.

Keywords

Metal-Organic Frameworks, Fe-BTC, Phenol Hydroxylation, Hydrogen Peroxide

1. Introduction

The hydroxylation of phenol to dihydroxybenzenes is an important organic intermediate for the synthesis of perfumes, dyes, medicines, pesticides, rubbers and other fine chemicals [1] [2] [3]. However, phenol is also known as highly toxic, carcinogenic and poorly biodegradable waste from most chemical industries wastewater [4] [5]. From the point of environmental view, the conversion of phenol to value added products is highly desired. The products, catechol (CAT) and hydroquinone (HQ) are synthesized by various soluble oxidizing

agents [6], which require toxic solvents, high temperature reaction and also generate large quantities of wastes [7]. In recent years, much attention has been dedicated on the development of selective, reusable and stable heterogeneous catalysts for the direct one-step selective hydroxylation of phenol to corresponding catechol (CAT) and hydroquinone (HQ) using hydrogen peroxide as an oxidant due to cheap and environmentally benign reagent which produces only water and molecular oxygen as by-product during catalysis reaction [8]-[13].

Metal-organic frameworks (MOFs), as a new class of crystalline porous materials have lots of potential applications in catalysis [14] [15] [16] [17] due to large surface area, ordered crystalline structure, ability to tune pore size, structural diversity and chemical stability. Fe-containing MOFs, iron metal-organic frameworks of 1,3,5-benzenetricarboxylate (BTC), Fe-BTC have been appeared to be an active catalyst for a large variety of organic synthesis [18] [19] [20] [21] [22]. This MOF, commercialized as Basolite F300, has a semiamorphous structure with specific surface area of 1300 - 1600 m²/g and large pore size. The framework of Fe-BTC is composed of trimers of iron octahedral sharing a common vertex μ_3 -O connected by the bridging organic linker (BTC), which exhibits two types of mesoporous cages of free apertures of 25 and 29 Å, accessible through two types of microporous windows of 5.5 and 8.6 Å [18] [21] [23] [24]. In particular, another crystalline Fe-based MOF, MIL-100(Fe) is iso-structural to Fe-BTC, having the same building units with two types of cages in the range of mesopores [25]. The catalytic behavior of both MOFs has been systematically compared in various catalysis reactions to find out the relation between structure and activity [26] [27] [28] [29]. Wang *et al.* reported the catalytic activity of two Fe-based MOFs, MIL-100(Fe) and MIL-68(Fe), for the photo-catalytic benzene hydroxylation to phenol using 30% H₂O₂ in acetonitrile that showed high selectivity [30]. Recently, we have reported the synthesis of new Fe-containing MOF, Fe-MOF-74, having identical framework structure for previously reported for MOF-74, which showed higher product yield (CAT + HQ) as well as a shorter induction period than other iron based catalysts such as Fe-MCM-41 or FeO_x/MCM-41 for phenol hydroxylation using hydrogen peroxide in water [7]. As a consequence, very recently, we have also reported that iron-based MOF, Fe-BTC shows high selectivity and stability in the hydroxylation of benzene and toluene using 30% H₂O₂ [31]. These results encouraged us to test the catalytic performance of Fe-containing commercially available MOF as catalyst for hydroxylation of arenes using H₂O₂, since H₂O₂ is cheap and environmentally friendly reagent as well as easy catalyst recovery from reaction mixture from ecological point of view. In the present study, we describe the catalytic efficacy of commercially available iron-containing MOF, Fe-BTC, as selective, reusable and stable catalyst for hydroxylation of phenol for the preparation of commercially important diphenols using H₂O₂. The effect of various reaction parameters, such as, temperature, time, substrate-oxidant mole ratio and catalyst amount on catalytic performance were investigated. This work describes in more detail, the sta-

bility of Fe-BTC using various spectroscopic and microscopic techniques.

2. Experimental

2.1. Materials

Phenol ACS reagent (99%), hydrogen peroxide (30%) and MOF (Fe-BTC, Basolite®F300) were obtained from Sigma-Aldrich and used without further treatment.

2.2. Characterization of Fe-BTC

Powder X-ray diffraction pattern was recorded on a RigakuUltimaIVdiffractometer with Cu-K α ($\lambda = 1.54 \text{ \AA}$) at 0.2 min^{-1} . FTIR spectra were measured as KBr discs on aIRPrestige (Shimadzu) spectrometer. SEM micrographs were taken on a JEOL (JSM-6490LA) instrument.

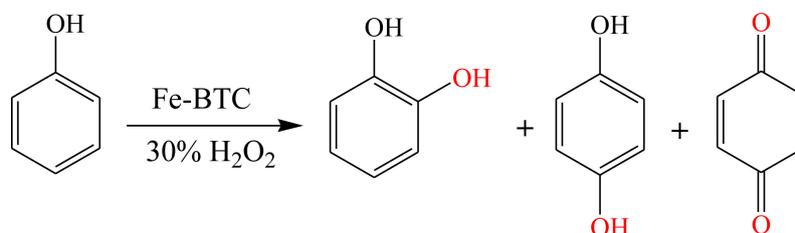
2.3. Catalysis Reaction

The hydroxylation of phenol was performed in a two-necked round bottom flask fitted with a water-cooled condenser. Typically, phenol (470 mg), water (15 cm^3) and catalyst (20 mg) were introduced to a round bottom flask and the mixture stirred at 50°C . Required amount of hydrogen peroxide (30%) was added into the reaction mixture through a syringe with constant stirring. The conversion and products were analyzed by GC (Perkin-Elmer, Clarus 500) fitted with a DB-Wax coated capillary column (30 m, 0.32 mm, $0.25 \mu\text{m}$) and an FID. The products were identified by comparison with that of the authentic compounds. The concentration of phenol was determined from the average three runs.

3. Results and Discussion

The hydroxylation of phenol was studied in water medium using 30% H_2O_2 over Fe-BTC by varying the various reaction parameters, such as temperature, time, substrate/ H_2O_2 mole ratio and amount of catalyst. Phenol was converted to two main products, such as, catechol (CA) and hydroquinone (HQ). The reaction is shown in **Scheme 1**.

The influence of temperature on the catalytic performance of phenol hydroxylation is shown in **Figure 1**. Phenol conversion increases from 8.8% to 16.9% with gradually increasing the reaction temperature from 35°C to 70°C using



Scheme 1. Phenol hydroxylation reaction catalyzed over Fe-BTC.

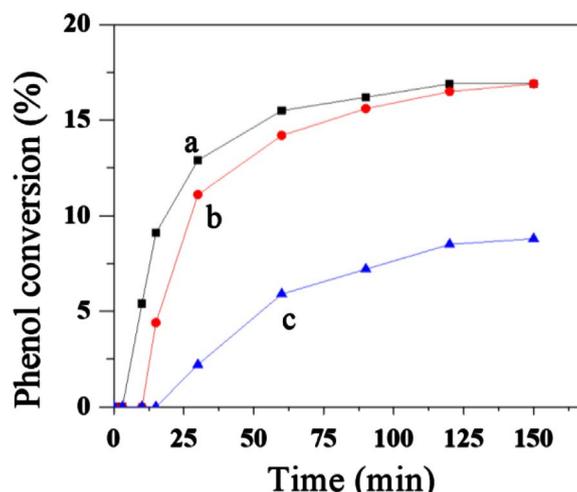


Figure 1. Effect of reaction temperature on the catalytic activity over Fe-BTC for phenol hydroxylation of phenol with phenol: H_2O_2 ratio of 1:1: (a) 70°C, (b) 50°C and (c) 35°C.

phenol to hydrogen peroxide mole ratio of 1:1, however, the induction period became shorter with an increase of temperature (Table 1). On the other hand, BQ selectivity increases from 2.3% to 8.2% with increase of temperature due to further oxidation of HQ to BQ [7].

Figure 2 shows the conversion of phenol as a function of hydrogen peroxide concentration with varying the amount of H_2O_2 from 1:0.5 to 1:2 in phenol to H_2O_2 mole ratio at 50°C. Phenol conversion increased from 9.1% to 16.9% with an increase in the concentration of H_2O_2 from 1:0.5 to 1:1 in phenol to H_2O_2 mole ratio and then leveled off to 16.9%.

To examine the effect of catalyst amount on the catalytic activity the phenol hydroxylation reaction was carried out with varying the amount of catalyst from 0.010 g to 0.030 g using phenol to H_2O_2 mole ratio of 1:1 at 50°C. As shown in Table 1, the phenol conversion was not effected by increasing the catalyst amount and only the induction period became shorter with increasing the amount of Fe-BTC.

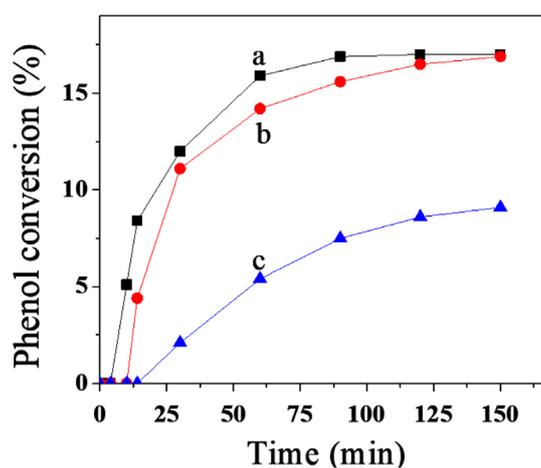
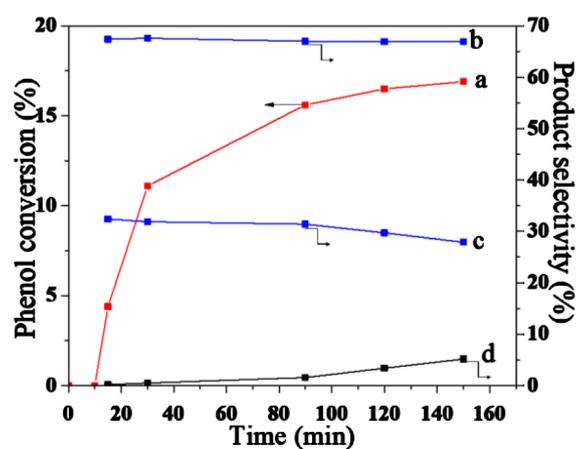
Figure 3 shows the reaction profile as a function of reaction time. The reaction was carried out using phenol to H_2O_2 mole ratio of 1:1 at 50°C. The results showed that the conversion increased progressively with time, while the selectivity of CA remained fairly constant at ca. 66.9%, but, the selectivity of HQ was largely affected with a drop from 32.4% to 27.9%. During this period, BQ selectivity increased from 0.2% to 5.2%. This may be due to further oxidation of HQ to BQ in the presence of excess H_2O_2 [7].

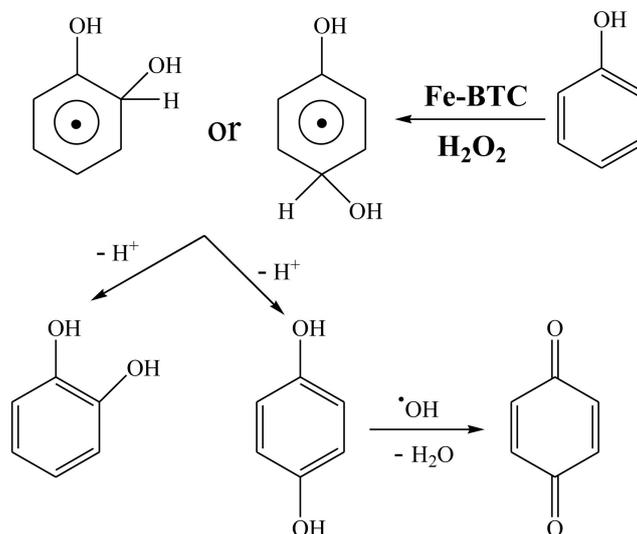
Based on experimental data, a proposed reaction mechanism is shown in Scheme 2. The reaction proceeds through the formation of hydroxyl radical via $\text{Fe}^{2+}/\text{Fe}^{3+}$ in the presence of H_2O_2 and catalyst, and finally the attack of hydroxyl radicals at ortho or para positions of phenol to generate CAT and HQ [7] [32]. Hydroquinone can be further oxidized to benzoquinone (BQ).

Table 1. Influence of reaction temperature, phenol/H₂O₂ mole ratio and amount of catalyst on the hydroxylation of phenol over Fe-BTC.

Temp. (°C)	Phenol:H ₂ O ₂	Catalyst amount (g)	Induction period (min)	Phenol conv. (%)	Product selectivity (%)		
					CAT	HQ	BQ
35	1:1	0.020	15	8.8	66.6	31.1	2.3
50	1:0.50	0.020	14	9.1	66.6	31.3	2.1
	1:1	0.020	10	16.9	66.9	27.9	5.2
	1:2	0.020	4	17.0	66.4	25.9	7.7
	1:1	0.010	16	16.0	66.6	28.0	5.4
	1:1 ^a	0.020	10	16.9	66.9	27.9	5.2
	1:1	0.030	3	16.9	66.5	28.0	5.5
	1:1 ^b	0.020	10	16.9	66.9	27.9	5.2
	1:1 ^c	0.020	10	16.9	66.9	27.9	5.2
70	1:1	0.020	3	16.9	66.4	25.4	8.2

^aFirst run. ^bSecond run. ^cFourth run.

**Figure 2.** Effect of phenol to H₂O₂ ratio for phenol hydroxylation at 50 °C: (a) 1:2, (b) 1:1 and (c) 1:0.5.**Figure 3.** Effect of reaction time on the activity over Fe-BTC for phenol hydroxylation with phenol:H₂O₂ ratio of 1:1 at 50 °C: (a) phenol conversion, (b) CAT selectivity, (c) HQ selectivity and (d) BQ selectivity.



Scheme 2. Reaction path for phenol hydroxylation reaction catalyzed over Fe-BTC.

It is important to check the stability of the catalyst under the same reaction conditions, since active metal leached from the catalyst could be responsible for the experimental catalytic performance [33] [34]. The stability of catalyst in phenol hydroxylation was examined by performing consecutive reuses of Fe-BTC using phenol-to- H_2O_2 mole ratio of 1:1 at 50°C . At the end of each reaction cycle, Fe-BTC was recovered by simple filtration and washed with water and ethanol, and dried at 120°C under vacuum for 4 h and reused. The catalyst was reusable for four times with little loss of activity and selectivity (Table 1). XRD of reused catalyst indicated that the structure of catalyst was retained after recycle run (Figure 4). The reused catalyst was also examined by scanning electron microscope (SEM). The SEM images confirmed that the morphology was retained during the reaction (Figure 5). These observations support that the phenol hydroxylation reaction took place at the framework Fe sites within the MOF matrix.

4. Conclusion

The commercially available MOF, Fe-BTC showed an efficient heterogeneous catalyst for hydroxylation of phenol to useful products such as catechol (CAT) and hydroquinone (HQ) using environmentally benign 30% hydrogen peroxide in water medium under mild reaction conditions. The material could be recycled without significant loss of catalytic activity and product selectivity. In addition, commercially available, eco-friendly route and high stability of Fe-BTC catalyst during catalysis reaction in hydroxylation of phenol make this catalytic system attractive for industrial application for diphenol production. The formation of hydroxyl radical through redox path over the Fe-BTC catalyst and the attack of hydroxyl radical at ortho or para position of phenol was proposed as the mechanism for hydroxylation of phenol.

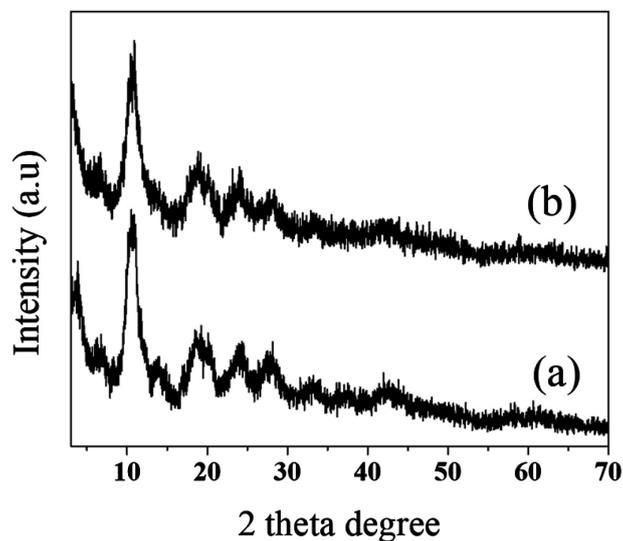


Figure 4. X-ray powder diffraction patterns of (a) Fe-BTC and (b) reused Fe-BTC catalyst after fourth run.

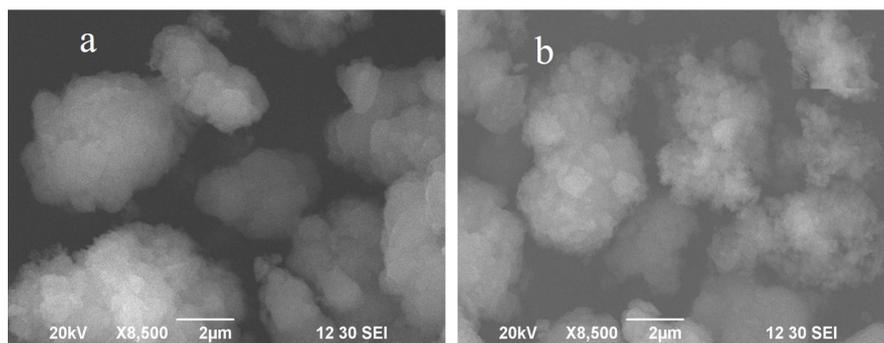


Figure 5. Scanning electron microscope of (a) fresh Fe-BTC and (b) reused Fe-BTC catalyst after fourth run. 20 kV accelerating voltage, the X8500 current magnification and 2 µm scale bar were applied in this scanning.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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