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Notes

Hydroxylation of benzene and toluene by heterogeneous iron metal-organic framework (Fe-BTC)

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Liquid phase catalytic hydroxylation of benzene and toluene by Fe-containing metal-organic framework (Fe-BTC; BTC = 1,3,5-benzenetricarboxylate) using 30% hydrogen peroxide as an oxidant exhibits good activity and high product selectivity under mild reaction conditions. The effects of temperature, time, substrate/ hydrogen peroxide mole ratio and solvent on catalytic performance are investigated. The catalyst can be reused four times without significant loss of catalytic performance. The hot filtration experiments suggest that hydroxylation reaction occurs on the Fe sites in the MOF matrix. The crystallinity and structure of Fe-BTC remain unchanged during the catalysis reaction, as confirmed by comparison of XRD, FTIR and SEM of the fresh and reused catalyst.

Keywords: Catalysis, Liquid phase catalysis, Metal organic frameworks, Hydroxylation, Fe-BTC, Benzene, Toluene

The selective hydroxylation of benzene and toluene to phenol or cresols is an important industrial technology. Phenol from direct benzene hydroxylation is a useful intermediate for the manufacture of agrochemicals, petrochemicals and plastics[1]. The hydroxylation products of toluene, such as cresols, are important intermediates for the preparation of a wide range of products, including phenolic resins, antioxidants, pharmaceuticals, agrochemicals and dyes[2,3]. The products are synthesized commercially by multi-step processes, which require hazardous materials and also generate large quantities of by-products[4-6]. In recent years, much attention has been focused on the development of selective, reusable and stable catalysts for the one-step selective hydroxylation of benzene and toluene using various oxidants such as N_2O, air and H_2O_2[7-16]. Among these oxidants, H_2O_2 is the most attractive due to it being a cheap and environmentally benign reagent with only water produced as the by-product[17,18]. Direct hydroxylation of benzene derivatives with H_2O_2 has been extensively investigated with a variety of heterogeneous catalysts over recent decades, such as Fe/activated carbon[9,19], molecular sieves[20], $VOPO_4$ encapsulated graphene oxide[12], Fe complexes immobilized on amine-functionalized activated carbon and hexagonal mesoporous silica[13], Cu complexes immobilized on mesoporous silica alumina[14], molybdovanadophosphoric anion ionic-liquid[21], Fe complexes incorporating periodic mesoporous organosilica[22], $H_5PMo_{10}V_2O_{40}$ immobilization on protonated graphitic carbon[23] and Cu-Ag nanoparticles onto graphitic carbon nitride[24]. Among these catalysts, iron-based heterogeneous catalysts have attracted considerable attention in the recent years due to their high efficiency[13,22]. However, selective hydroxylation of benzene derivatives are still a big challenge. Further efforts to improve catalytic systems for the hydroxylation of benzene derivatives with improved product selectivity are highly desired.

Metal-organic frameworks (MOFs), as a class of crystalline porous materials have many potential applications as catalysts[25-28]. Their large surface area, ordered crystalline structure, structural diversity, chemical stability as well as the ability to tune their pore size makes them highly adaptable. Recently, Zhang *et al.*[29] reported the catalytic activity of Cu-based MOF for the hydroxylation of benzene to phenol using H_2O_2 under visible light with high conversion (29%) and selectivity (95%). We have reported the synthesis of a new Fe-containing MOF, Fe-MOF-74, which has an identical framework structure to MOF-74[30]. It exhibited excellent activity and selectivity for phenol hydroxylation using hydrogen peroxide in water at as low as 10 °C or as high as 50 °C[30]. Among the Fe-containing MOFs, iron metal-organic frameworks of 1,3,5-benzenetricarboxylate (BTC) (Fe-BTC) has been found to be an active catalyst for a large variety of organic synthesis[31-35]. This MOF, commercialized as Basolite F300, has a semiamorphous structure with specific surface area of 1300–1600 m^2/g and large pore size. The framework of Fe-BTC is composed of trimers of iron octahedral sharing a common μ_3-O vertex connected by the bridging organic linker (BTC). BTC exhibits two types of mesoporous cages with free apertures of 25 and 29 Å, accessible through two types of microporous windows[32,34] of 5.5 and 8.6 Å. In particular, another crystalline Fe-based MOF, MIL-100(Fe) is iso-structural with Fe-BTC, having the same building units with two types of cages in the range of mesopores[36]. The catalytic behavior of both MOFs has been systematically compared in various catalytic reactions to find out the relationship between structure and activity[37-40]. Recently, Wang *et al.*[18] reported the activity of two Fe-based MOFs, MIL-100(Fe) and MIL-68(Fe), for photo-catalytic hydroxylation of benzene to phenol using 30% H_2O_2 in acetonitrile. Both catalysts exhibited high phenol selectivity[18].

The present study describes the catalytic efficacy of the commercially available iron-containing MOF, Fe-BTC, as a selective, reusable and stable catalyst for hydroxylation of benzene and toluene to produce commercially important phenol and cresols. The effect of various reaction parameters, such as temperature, time, substrate/oxidant mole ratio and solvent on catalytic performance were investigated. This work also describes in detail the investigations on the stability of Fe-BTC using various spectroscopic and microscopic techniques.

Experimental

Benzene ACS reagent (99.0%), toluene (99.9%), hydrogen peroxide (30%), MOF (Fe-BTC, Basolite®F300), iron(III) acetylacetonate (99.9%), acetonitrile (HPLC), methanol (HPLC) and acetone (HPLC) were obtained from Sigma-Aldrich and used without further treatment. Powder X-ray diffraction pattern was recorded on a Rigaku UltimaIV diffractometer with Cu-Kα (λ = 1.54 Å) at 0.2 min^{-1}. FTIR spectra were measured as KBr discs on a IRPrestige (Shimadzu) spectrometer. SEM micrographs were taken on a JEOL (JSM-6490LA) instrument. Fe content in the filtrate was measured by atomic absorption spectroscopy using Perkin-Elmer AAS AAnalyst 200.

The hydroxylation of benzene and toluene was carried out in a two-necked round bottom flask (50 mL) fitted with a water-cooled condenser. Typically, benzene (395 mg), acetonitrile (10 mL) and catalyst (20 mg) were introduced into a round bottom flask and the mixture stirred at 65 °C. Hydrogen peroxide (30 wt%, 1134 mg) was then added to the reaction mixture using a syringe with constant stirring, maintaining the desired reaction temperature. Hydroxylation of benzene under solvent-free conditions was also carried out in a round bottom flask equipped with a cooling condenser. The catalyst (40 mg) and benzene (3900 mg) were added to the flask. After the mixture was heated at 65 °C, the oxidant (30% hydrogen peroxide, 2268 mg) was added with a syringe to the reactant mixture and stirred for 4 h. Aliquots were withdrawn at different time intervals and analyzed by GC with toluene as the internal standard.

A hot filtering experiment of benzene was carried out by quickly separating the catalyst from the reaction mixture after 90 min of reaction. The filtrate mixture was further stirred at 65 °C for an additional period of upto 2 h. The conversion and products were analyzed by GC (Clarus 500, Perkin-Elmer), fitted with a high performance HP-1 capillary column and FID. Each measurement was made in triplicate. After completion of the reaction, the crude products were analyzed using GC-MS/MS (Shimadzu GCMS-TQ8040), fitted with an Rxi-5ms fused silica capillary column.

Results and discussion

Fe-BTC was evaluated for the hydroxylation of benzene using 30% H_2O_2 as the oxidant by varying the various reaction parameters, such as temperature, time, substrate/H_2O_2 mole ratio and solvent. The results are summarized in Table 1. Benzene reacts with hydrogen peroxide over Fe-BTC to give two products in liquid phase, viz., phenol and benzoquinone. The reaction products were identified by comparison with the corresponding pure compounds using GC co-injection. To confirm the purity of the products, the reaction mixture was characterized by GC-MS/MS. The GC-MS/MS data showed the peak at *m/z* 94, confirming the presence of phenol as the main product (Supplementary data, Fig. S1). However, benzoquinone could not be detected by GC-MS/MS.

The influence of temperature on the catalytic performance of benzene hydroxylation is shown in Fig. 1. Benzene conversion increases from 3.4% to 7.4% with a gradual increase in the reaction temperature from 40 °C to 65 °C in acetonitrile using benzene-to-H_2O_2 mole ratio of 1:2. A further increase in the temperature to 75 °C resulted in a slight decrease in the conversion to 7.0%. It has been reported that competitive decomposition of H_2O_2 to H_2O and O_2 occurs at high temperature leading to a lower conversion[41]. The selectivity to phenol was observed to gradually decrease from 97.2% to 85.9%

Table 1 — Effect of temperature, benzene/H_2O_2 mole ratio, solvent and recycle runs of benzene hydroxylation over Fe-BTC[a]

Temp. (°C)	Benzene:H_2O_2	Solvent	Benzene conv.[b] (%)	Product selectivity (%)	
				Phenol[c]	BQ[d]
40	1:2	Acetonitrile	3.4	97.2	2.8
50	1:2	Acetonitrile	5.2	97.0	3.0
65	1:1	Acetonitrile	4.8	95.6	4.4
65	1:2	Acetonitrile	7.4	92.7	7.3
65	1:3	Acetonitrile	8.2	86.7	13.3
65	1:2[e]	Acetonitrile	7.3	92.6	7.4
65	1:2[f]	Acetonitrile	7.2	92.7	7.3
65	1:2	Acetone	1.3	-	-
65	1:2	Methanol	2.5	-	-
75	1:2	Acetonitrile	7.0	85.9	14.1

[a] React. cond.: benzene (5 mmol), solvent (10 mL), catalyst (20 mg), 30% H_2O_2 and 4 h.
[b] Benzene conv. = (moles of benzene reacted/initial moles of benzene)×100.
[c] Phenol selectivity = (moles of phenol produced/moles benzene reacted)×100.
[d] 1,4-Benzoquinone. [e] Second run. [f] Fourth run.

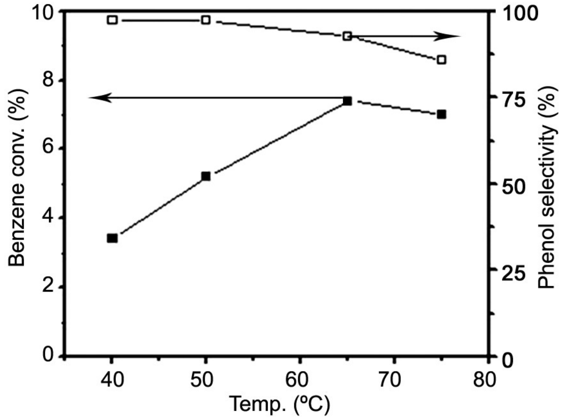

Fig. 1 — Effect of reaction temperature on the catalytic activity over Fe-BTC for benzene hydroxylation. [React. cond.: 5 mmol benzene; 10 mmol 30% H_2O_2; 20 mg catalyst; 10 mL acetonitrile).

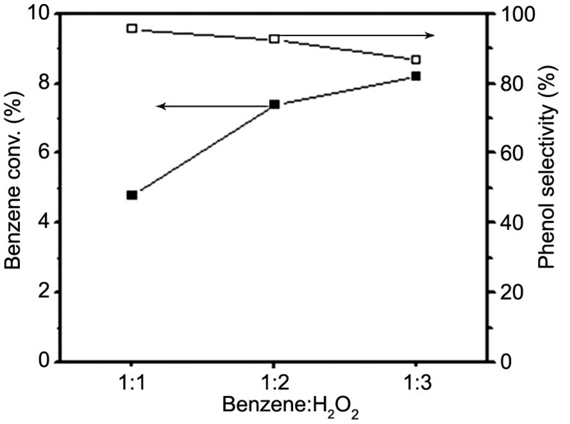

Fig. 2 — Effect of H_2O_2 concentration on the catalytic activity over Fe-BTC for benzene hydroxylation. [React. cond.: 5 mmol benzene; 20 mg catalyst; 10 mL acetonitrile; react. temp. 65 °C; time 4 h].

with an increase of temperature from 40 °C to 75 °C. This may be due to the further oxidation of phenol at the elevated temperature. Identical results have also been reported earlier for other catalysts[19,41]. Based on the present experimental results, subsequent hydroxylation reactions were carried out at 65 °C. A blank test reaction showed that there was no catalytic activity in the absence of Fe-BTC at 65 °C using benzene-to-H_2O_2 mole ratio of 1:2.

Figure 2 shows the benzene conversion and phenol selectivity as a function of H_2O_2 concentration. The reaction was carried out at 65 °C with fixed amount of benzene. Benzene conversion increased from 4.8% to 8.2% with an increase in the concentration of H_2O_2 from 1:1 to 1:3 in benzene-to-H_2O_2 mole ratio. However, phenol selectivity was observed to reduce from 95.6% to 86.7%. This is most likely due to further oxidation of phenol in the presence of excess H_2O_2. The results indicated that benzene-to-H_2O_2 mole ratio of 1:2 is the optimum, giving the maximum of both conversion and phenol selectivity.

To examine the influence of reaction time on the catalytic activity, the benzene hydroxylation reaction was performed at 65 °C using benzene to H_2O_2 mole ratio of 1:2. Figure 3 shows the reaction profile as a function of time. Benzene conversion reached 7.4% with 92.7% phenol selectivity after 4 h. After 5 h, phenol selectivity dropped to 89.0% with benzene conversion levelling off at 7.5%, indicating that phenol was further converted to other by-products at longer reaction time[19].

The properties of a solvent in a hydroxylation reaction play an important factor to maintain both the conversion and product selectivity[42,43]. To study the

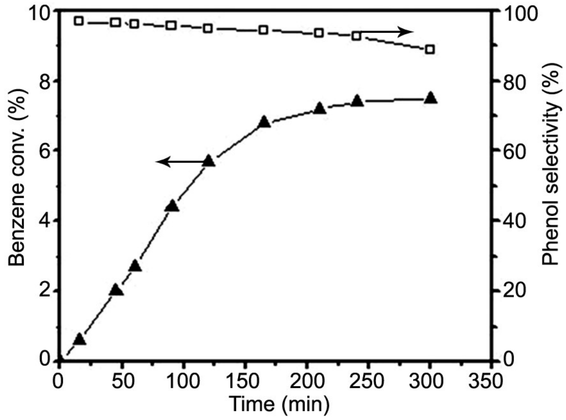

Fig. 3 — Effect of reaction time on the activity over Fe-BTC for benzene hydroxylation at 65 °C.

influence of the solvent, the catalytic reaction of benzene (with H_2O_2 as oxidant, mole ratio: 1:2) was carried out separately in acetonitrile, methanol and acetone at 65 °C. Acetonitrile exhibited much higher conversion to phenol (7.4%) than methanol (2.5%) or acetone (1.3%) (Table 1). Stöckmann *et al.*[44] mentioned that acetonitrile does not act as an inert solvent, and reacts with hydrogen peroxide giving a reactive intermediate. A similar trend in solvent dependent activity was reported in phenol hydroxylation reactions using Fe-containing MOF, Fe-MOF-74[30]. The high benzene conversion in acetonitrile may be associated with the generation of a peroxycarboximidic acid intermediate[30, 44].

The hydroxylation of benzene under solvent-free condition was also carried out using 30% H_2O_2 as an oxidant at 65 °C. The benzene conversion and selectivity to phenol were lower (4.5% conversion and 86.4% phenol selectivity) than in the presence of acetonitrile at benzene-to-H_2O_2 mole ratio of 1:2 after 4 h.

To check whether the observed catalytic reaction is occurring on Fe sites in the MOF matrix or with the leached active metal in homogeneous phase, the catalytic reaction was performed in acetonitrile using benzene-to-H_2O_2 mole ratio of 1:2 at 65 °C and the catalyst was quickly separated from the mixture after 90 min reaction time. The filtrate was heated with constant stirring at 65 °C for another 2 h (Fig. 4). No significant increase in activity was observed after removal of Fe-BTC, suggesting that the benzene hydroxylation reaction occurred at the framework Fe sites in the MOF matrix. Further confirmation of the heterogeneity of the catalyst was obtained from the catalyst recycling tests under the same reaction conditions as described for the hot filtering experiments. In the recycling test, the catalyst was recovered by a simple filtration technique, washed with solvent, dried at 120 °C under vacuum for 4 h and reused. The conversion and phenol selectivity were almost identical (Table 1). The metal content in the filtrate mixture after the third cycle was determined by atomic absorption spectroscopy and no Fe was observed in the filtrate after the catalytic reaction. To further check the structural stability of the catalyst, XRD and FTIR analysis of reused catalyst were carried out. The XRD patterns and FT-IR spectra (Supplementary data, Figs S2 and S3 respectively) before and after reaction were almost identical, indicating that no structural deterioration took place during hydroxylation reaction. The reused catalyst was also studied by scanning electron microscopy (SEM). The SEM images confirmed that the morphology was retained during the reaction (Supplementary data, Fig. S4).

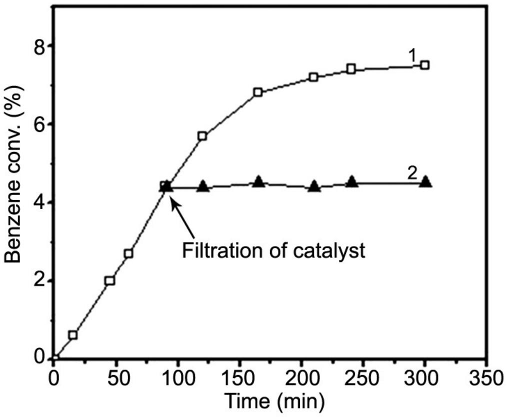

Fig. 4 — Benzene hydroxylation with and without catalyst. [30% H_2O_2 at 65 °C, 20 mg catalyst in acetonitrile. (1) with Fe-BTC catalyst, and, (2) filtrate (catalyst separated out after 90 min)].

The hydroxylation of benzene (with H_2O_2 mole ratio of 1:2) was also investigated using free iron(III) acetylacetonate at 65 °C under identical reaction conditions as described above. $Fe(acac)_3$ (0.08 mmol) exhibited much higher conversion (23.4%) and comparable selectivity of phenol (91.2%) than Fe-BTC. Comparison of the catalytic activity in the hydroxylation of benzene with Fe-containing heterogeneous catalysts using H_2O_2 as oxidant and acetonitrile as solvent showed that the Fe-BTC exhibited much higher conversion and selectivity of phenol than those previously reported for activated carbon supported Fe or other carbon-free support-based iron catalysts such as Fe/γ-Al_2O_3, Fe/MCM-41 and Fe/HY[19]. Fe-BTC also showed comparable

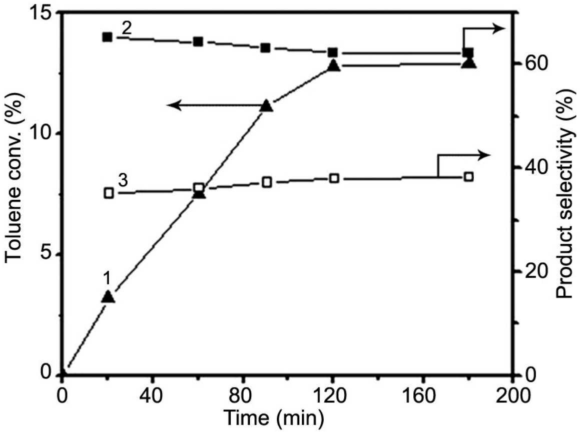

Fig. 5 — Effect of reaction time on the activity over Fe-BTC for toluene hydroxylation. [React. cond.: 5 mmol toluene; 10 mmol 30% H_2O_2; 20 mg catalyst; 10 mL acetonitrile; react. temp. 65 °C. (1) toluene conversion, (2) *o*-cresol selectivity, (3) *p*-cresol selectivity].

selectivity of phenol with that reported for the well-known Fe-based MOFs, MIL-100(Fe) and MIL-68(Fe)[18]. A high phenol selectivity but lower benzene conversion was observed for Fe-BTC when compared with the recently reported results for iron(III) compounds incorporated into periodic mesoporous organosilica catalyst[22].

The catalytic activity of Fe-BTC was also studied in the liquid phase hydroxylation of toluene in acetonitrile medium using the substrate-to-H_2O_2 mole ratio of 1:2 at 65 °C. Toluene was converted to two main products, *o*-cresol and *p*-cresol. The reaction products were identified by comparison with the corresponding pure compounds using GC co-injection and GC-MS/MS. (Supplementary data, Figs S5 and S6). No other side products were detected in the reaction mixture.

Figure 5 shows the reaction profile as a function of reaction time. The results show that the conversion increased progressively with time and reached 12.8% after 120 min. Selectivity to *o*-cresol is affected slightly with a drop from 65.2% to 62.3%, while with *p*-cresol, the selectivity increased marginally from 34.8% to 37.7%. This may be due to further oxidation of the primary products at longer reaction time.

The reusability of the catalyst in toluene hydroxylation was examined by consecutive reuse of Fe-BTC under the same reaction conditions. The conversion and products selectivity remained virtually constant. To further check the heterogeneity of the catalyst, hot filtering experiment was performed under the same reaction conditions as described for recycling test. In the hot-filtering experiment, the catalyst was quickly removed from the reaction mixture after 60 min and then the filtrate mixture was heated at constant stirring for further 1 h (Supplementary data, Fig. S7). No significant increase in conversion was observed after removal of the catalyst, indicating that the hydroxylation reaction took place at the framework Fe sites within the MOF matrix.

In summary, Fe-BTC showed high selectivity (>90%) in the hydroxylation of benzene using the environmentally benign 30% hydrogen peroxide in acetonitrile at 65 °C. Fe-BTC was also found to be an efficient catalyst for the hydroxylation of toluene to useful products (*o*-cresol and *p*-cresol) using 30% hydrogen peroxide as an oxidant under mild reaction conditions. The nature of solvent was found to have a significant role in the catalytic activity of the hydroxylation reaction. The catalyst can be reused four times without significant loss of catalytic performance. In addition, high selectivity and retention of crystallinity of catalyst during catalysis reaction in hydroxylation of benzene and toluene make this catalytic system attractive for industrial applications.

Supplementary data

Supplementary data associated with this article are available in the electronic form at http://www. niscair. res.in/jinfo/ijca/IJCA_57A(06)778-783_SupplData.pdf.

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