Anchoring of Fe(III)salicylamide onto MCM-41 for Catalytic Hydroxylation of Phenol in Aqueous Medium Using Hydrogen Peroxide as Oxidant

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Abstract Fe(III)salicylamide immobilized on MCM-41 has been developed for hydroxylation of phenol in water medium using hydrogen peroxide as the oxidant. In the first step, the amine group containing 3-aminopropyltrimethoxy silane has been immobilized on the surface of MCM-41 via co-condensation. The amine group upon condensed with methyl salicylate afford a bidentate ligand in the mesoporous matrix for anchoring Fe(III) ions in the second step. Small angle XRD, N₂ adsorption-desorption isotherms, ¹³C and ²⁹Si cross-polarization magic angle spinning NMR spectroscopy, Fourier transform infrared spectroscopy (FT-IR) and diffuse reflectance UV-vis spectra were employed for the characterization of the catalysts. The heterogeneous iron salicylamide complex shows excellent catalytic activity in phenol hydroxylation using hydrogen peroxide as the oxidant and water as the solvent. Notably, phenol shows high conversion (64.6%) with very high selectivity for dihydroxybenzene compounds. The heterogeneous catalyst shows a successive slight decrease in catalytic activity when reused for three more times.

Keywords Mesoporous silica · Salicylamide complex · Immobilization · Phenol hydroxylation

1 Introduction

Environment benign technology is one of the major goals of the present research in chemistry. There is an urgent

K. M. Parida (⊠) · S. Singha · P. C. Sahoo Colloids and Materials Chemistry Department, Institute of Minerals & Materials Technology, Bhubaneswar 751013, Orissa, India e-mail: paridakulamani@yahoo.com need for finding clean oxidants for oxidation of organic compounds. Hydrogen peroxide is used as a clean oxidant because the oxidation affords only water as byproduct. Catalytic hydroxylation of phenol to catechol and hydroquinone is an important industrial reaction [1]. It is most desirable that the dihydroxybenzenes could be produced by direct hydroxylation of phenol with environmentally benign oxidants like hydrogen peroxide. Mineral acids, simple metal ions and metal complexes are traditional catalyst used for this reaction. Homogeneous processes for production of dihydroxybenzenes are the Rhone-Poulenc process [2], where the oxidation of phenol is carried out by strong mineral acids or the Hamilton process [3] where Fenton reagent is used as a catalyst. But these homogeneous catalysts are difficult to separate and recover from the reaction mixture, which prevents their practical utilization in phenol hydroxylation. The heterogenizations of homogeneous catalyst have gained considerable interest over the last few decades, because one of the most attractive advantages is the easy separation of the products from the catalyst without tedious experimental work-up [4–6]. The first commercial application of TS-1 for phenol hydroxylation was by Enichem in 1986 in Italy. An increasing impetus of studies on various metalosilicates such as TS-2, Ti- β , TAPO-5, TAPO-11, Ti-ZSM, VS-2 and Cu-AIPO4-5 has been shown by many publications [7, 8]. Although some of these transition metal framework substituted zeolites have exhibited attractive catalytic conversion, selectivity and stability in phenol hydroxylation, their complicated synthesis, high cost, and low reaction rate limit their commercial application.

On the other hand, metal-modified mesoporous silica (MCM-41, SBA-15, MCM-48) and complex immobilized mesoporous silica have become target catalysts aimed at accelerating the reaction rate of phenol hydroxylation

[9, 10]. Mesoporous silica, especially MCM-41 is a good choice because of its high surface area, high thermal and chemical stability and easy preparation method. The silica based hybrid materials, which offer pore sizes in the range 20–100 Å are suitable for liquid phase reactions, because they allow easy diffusion of reactant to the active sites [11, 12]. Their surface silanol groups can also be functionalized by different organoalkoxy groups, hence allowing subsequent attachment of the catalytic active species. Wu and coworker [13] reported that immobilization of [Fe(II)phen]²⁺ onto MCM-41 induces enhancement of hydroxylation activity by about two times (27.5–53.1%).

Here in, we report the satisfactory heterogenization of Fe(III) onto organically modified MCM-41 by a two-step process. The prepared catalyst is robust enough to achieve high catalytic performance for liquid phase hydroxylation of phenol using hydrogen peroxide as oxidant and water as solvent. Moreover, the anchored catalyst can be recycled three times without significant loss in catalytic activity. The effect of reaction temperature, time, solvents and phenol to oxidant ratio on conversion and product selectivity were also examined for the optimization of the process parameters.

2 Experimental Methods

2.1 Materials

(3-Aminopropyl) trimethoxysilane (APTMS), tetraethyl orthosilicate $Si(OC_2H_4)_4$ (TEOS), cetyl trimethyl-ammoniumbromide (CTAB) (Aldrich), methylsalicylate

Scheme 1 Preparation of heterogeneous catalyst Fe(III)salicylamide–MCM-41 (II). Conditions: (a) Condensation in ethanol. (b) FeCl₃·6H₂O in ethanol



Amine modified MCM-41

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(CDH), $FeCl_3 \cdot 6H_2O$ (Merck), phenol (Aldrich), catechol, hydroquinone, 1, 4-benzoquinone and acetic acid (Merck) were used without further purification.

2.2 Synthesis Procedures

2.2.1 Preparation of Hybrid Mesoporous Material: Salicylamide Functionalized MCM-41 (I)

MCM-41 was prepared by a standard procedure [14]. Organic amine modified mesoporous silica (Scheme 1) was prepared according to literature [15] using C₁₆H₃₃N(CH₃)₃ Br (CTAB) as template, tetraethylorthosilicate (TEOS) as silica precursor and 3-aminopropyltrimethoxysilane (3-APTMS) as organoalkoxysilane precursor. The mixture contained CTAB/ TEOS/APTMS/NaOH/H2O in the molar ratio 1.0:8.16: 1.05:2.55:4857. The mixture of CTAB (2.0 g, 5.49 mmol), 2.0 M of NaOH (aq) (7.0 mL, 14.0 mmol) and H₂O (480 g, 26.67 mol) was heated at 80 °C for 30 min to reach pH 12.3. To this clear solution, TEOS (9.34 g, 44.8 mmol) and APTMS (1.03 g, 5.75 mmol) were added sequentially and rapidly via injection. Following the injection, a white precipitation was observed after 3 min of stirring. The reaction temperature was maintained at 80 °C for 2 h. The product was isolated by hot filtration, washed with copious amount of water and ethanol and dried under vacuum. To this dried product, an acid extraction process was performed in a methanol (100 mL) mixture of concentrated hydrochloric acid (1.0 mL) at 60 °C for 6 h. with continuous stirring. The resulting surfactant free product was filtered and washed with water and ethanol and then dried under vacuum. The solid was then refluxed with methyl salicylate (5.75 mmol) in ethanol for 3 h at 60 °C. The



resulting product was dried in a desiccator and denoted as MCM-41-salicylamide.

2.2.2 Preparation of Fe(III)salicylamide-MCM-41 (II)

The metal complex (II) (Scheme 1) was prepared by taking $FeCl_3 \cdot 6H_2O$ (0.045 g, 0.17 mmol) in 10 mL of ethanol along with 0.1 g of the hybrid organoalkoxy silane functionalised MCM-41 and stirring the suspension for 12 h at room temperature. Atomic absorption spectrometric analyses showed an iron content of the sample is ca. 0.37%.

2.2.3 Preparation of Fe(III)salicylamide

An equimolar amount of APTMS (5.75 mmol) in dichloromethane (10 mL) was added to a stirred solution of methyl salicylate (5.75 mmol) in dichloromethane (10 mL). The resulting solution was stirred for 4 h at room temperature. Removal of solvent under vacuum yields a bright white solid. To this FeCl₃·6H₂O (0.17 mmol) was added in 20 mL of ethanol and stirred for 24 h. The resulting solid was filtered, washed with copious amounts of ethanol and dried under vacuum. From the AAS analysis the iron content was found to be 0.43%.

2.3 Physico-Chemical Characterizations

Powder X-ray diffraction (XRD) patterns of the samples were obtained on Rigaku D Max III VC diffractometer with Cu K α radiation at 40 kV and 40 mA in the range of $2\theta = 0-10^{\circ}$. The scanning rate was 2° min⁻¹. Nitrogen adsorption–desorption isotherms were measured at liquid nitrogen temperature using ASAP 2020 (Micromeritics). Samples were out gassed at 100 °C for 3 h to evacuate the physically adsorbed moisture before the measurement. Specific surface area was calculated using the BET method. Solid-state ¹³C and ²⁹Si cross-polarization magic-angle spinning NMR spectra were recorded at 100.58 and 79.46 MHz, respectively using a Bruker Avance 400 MHz spectrometer. The FTIR spectra of the samples were recorded using Varian 800-FTIR in KBr matrix in the range of 4000–400 cm⁻¹. The co-ordination environments of the samples were examined by diffuse reflectance UV–vis spectroscopy. The spectra were recorded on a Varian-100 spectrophotometer in the wavelength range of 200–800 nm in BaSO₄ phase. The Fe loading and leaching of the reaction solution were determined by atomic absorption spectroscopy (AAS) with a Perkin-Elmer Analysis 300 using acetylene (C_2H_2) flame.

2.4 Catalytic Reaction

Catalytic tests of the prepared heterogeneous catalysts (Scheme 2) were carried out in a 100 mL two necked round bottom flask fitted with a reflux condenser. About 0.47 g (5 mmol) of phenol was dissolved in 10 mL of deionized water and 0.05 g of the catalyst was added to it. To this mixture 0.16 mL (5 mmol) of aqueous H_2O_2 (30%) was added through the septum using syringe pump over 10 min at the beginning of the reaction. Reaction was carried out for 2 h at 80 °C. The reaction products were analyzed by off-line gas chromatography (Shimadzu GC-17A) equipped with a capillary column (ZB-1, 30 m length, 0.53 mm I.D. and 3.0 µm film thickness) using flame ionization detector (FID). The self-decomposition of H₂O₂ was measured by the amount of O₂ released under reaction conditions in controlled experiments. The conversion and selectivity were calculated as follows.

Conversion (%) =
$$\frac{\text{Moles of the phenol reacted}}{\text{Total moles of the phenol}} \times 100$$

Selectivity (%) = $\frac{\text{Moles of the product formed}}{\text{Moles of the phenol reacted}} \times 100$

3 Results and Discussion

3.1 Characterizations

3.1.1 XRD Studies

The small angle X-ray diffraction patterns of MCM-41, MCM-41–salicylamide and Fe(III)salicylamide–MCM-41 are shown in Fig. 1. In the low angle region ($2\theta \approx$





Fig. 1 XRD spectra of (*a*) Fe(III)salicylamide–MCM-41, (*b*) MCM-41–salicylamide, (*c*) MCM-41

1.5–5°), three characteristic Bragg's reflections were observed in all these materials. The diffraction lines can be indexed by assuming a hexagonal symmetry of these materials. The pronounced d_{100} reflection and less intense

 d_{110} and d_{200} reflections correspond well to the hexagonal arranged pore structure of MCM-41. But XRD pattern of Fe(III)salicylamide–MCM-41 shows slightly broadening of (110) and (200) reflections compared to parent MCM-41 but are well resolved, indicates that immobilization of the salicylamide complex has little effect on the long range ordering of the parent support. The broadening of the reflections may be mainly due to contrast matching between the silicate framework and organic moieties, which are located inside the framework of MCM-41 [16, 17]. All the peaks are well resolved, indicative of the good quality of the material.

3.1.2 N₂ Sorption Studies

 N_2 adsorption–desorption isotherms of MCM-41 and Fe(III)salicylamide–MCM-41 are given in Fig. 2. These samples exhibit type IV isotherms (defined by IUPAC) with small hysteresis, which is characteristics for mesoporous materials. A sharp increase in the adsorption of N_2 between the relative pressure of 0.3 and 0.4 can be assigned to the capillary condensation [18]. The nitrogen sorption study showed that the BET surface area of MCM-41 is



1350 m² g⁻¹ and the mesopore volume is 1.26 cm³ g⁻¹. The average pore diameter is calculated to be 21.9 Å using the BJH method. All calculated values are in agreement with those reported for good quality mesoporous silica. Fe(III)salicylamide–MCM-41 shows less N₂ uptake (BET surface area 880 m² g⁻¹⁾ and pore volume 0.78 cm³ g⁻¹. It was reported that organic groups incorporated in MCM-41 are mainly located on internal surfaces close to the pore windows. The decrease in pore volumes and size is also possible proof that metal complex are successfully introduced into the framework [19].

3.1.3 ¹³C CP-MAS NMR Studies

The ¹³C CP-MAS NMR spectrum of MCM-41–salicylamide is shown in Fig. 3a. The sharp peak at 10.4 ppm is ascribed to the carbon atom bonded to silicon. The signal at 21.7 ppm corresponds to methylene carbon and the peak at 43 ppm can be attributed to the carbon atom attached to the nitrogen atom. The existence of a peak at 164.7 ppm is due to the carbon atom of the amide group. Resonance in the range 120–148.6 ppm is evidence for the presence of aromatic ring.

3.1.4 ²⁹Si CP-MAS NMR Studies

Figure 3b shows the ²⁹Si CP-MAS NMR spectra of MCM-41-salicylamide. Three resonance peaks due to the Si environments of Q⁴ [siloxane, (SiO)₄Si] ($\delta = -110$ ppm), O^3 [single silanol(SiO)₃Si(OH)] ($\delta = -102$ ppm), and O^2 [geminal silanol, $(SiO)_2Si(OH)_2$] ($\delta = -92$ ppm) can be seen. In addition to these three peaks, the sample displays two more resonance peaks at $\delta = -66$ ppm, assigned to T³ $[C-Si(OSi)_3]$, and at -57 ppm, attributed to T² $[C-Si(O-Si)_3]$ $Si_2(OH)$]. The existence of T³ confirms the modification of MCM-41 by organic moieties [20, 21]. The appearance of the Q^3 signal indicates the presence of some residual noncondensed OH groups attached to the silicon atom. The ²⁹Si CP-MAS NMR provides direct evidence that the hybrid MCM-41-salicylamide sample consists of a highly condensed siloxane network with organic fragments covalently bonded to the silica frame work. Figure 3c shows the CP-MAS ²⁹Si NMR spectral deconvolution plot for T type silicon species of MCM-41-salicylamide. The relative integral intensities of T type silicon species allow the quantitative assessment of the degree of incorporation of the organic moieties.

3.1.5 IR Studies

Figure 4 displays the IR spectra of MCM-41(4(a)), MCM-41–salicylamide (4(b)) and Fe(III)salicylamide–MCM-41(4(c)) in the range 400–4000 cm⁻¹. The stretching



Fig. 3 13 C CP-MAS NMR spectrum of **a** MCM-41–salicylamide, 29 Si CP-MAS NMR spectrum of **b** MCM-41–salicylamide, **c** spectral deconvolution curve of T typed silicon species of MCM-41–salicylamide

vibrations of Si–O–Si bond in parent MCM-41 as well as in all modified samples appear around 1050 cm^{-1} indicate that silica framework was not affected after modification, which is in accordance with the XRD results. A characteristic peak around 3400 cm⁻¹ (stretching) for [Fe(III)salicylamide–MCM-41] indicates some free Si–OH groups along with some unreacted phenolic –OH groups are still present after formation of the complex. The peak at 3100 cm⁻¹ is assigned to N–H stretching vibration and



Fig. 4 FT-IR spectra of (*a*) MCM-41, (*b*) MCM-41–salicylamide, (*c*) Fe(III)salicylamide–MCM-41

2970 cm⁻¹ is due to asymmetric stretching vibration of $-CH_2$ units. But in the case of metal complex immobilized MCM-41 all peaks are slightly shifted to a lower frequency due to coordination with iron. Sharp absorption peak around 1600 cm⁻¹ may be attributed to the presence of amide group [22].

3.1.6 UV-Vis Spectral Studies

The immobilization of Fe(III) complex on MCM-41 is further confirmed by diffuse reflectance UV–vis spectra. The spectra of Fe(III)salicylamide (a), Fe(III)salicylamide– MCM-41 (b) and MCM-41–salicylamide (c) are shown in Fig. 5. A series of characteristic bands at 220, 260 and 380 nm appear due to intra ligand electronic transition of the phenyl ring and lone pair present in nitrogen of MCM-41–salicylamide. A similar type of results are also found in



Fig. 5 UV–vis spectra of (*a*) Fe(III)salicylamide, (*b*) Fe(III)salicyl-amide–MCM-41, (*c*) MCM-41–salicylamide

Fe(III)salicylamide–MCM-41 and Fe(III)salicylamide but with slightly less intense, which could be attributed to attachment of metal to nitrogen and oxygen. The broad band around 580 nm in Fe(III)salicylamide–MCM-41 may be assigned to the d-d transition in metal as reported in the literature [23–26].

3.2 Phenol Hydroxylation

3.2.1 Catalytic Activity

The results on catalytic activities for hydroxylation of phenol over various catalysts are listed in Table 1. Hydroxylation over pure MCM-41 is negligible indicating that the host is inactive even in the presence of H_2O_2 Fe(III)salicylamide-MCM-41 showed a very high activity and resulted in a phenol conversion 64.6%. This shows that the complex immobilized MCM-41 has an enormous effect on the catalytic performance. The coordination environment around iron in Fe(III)salicylamide-MCM-41 is less crowded in comparison to the bulkier metal-porphyrins or metal-phthalocyanines anchored on MCM-41 matrix [27]. Probably, hydrogen peroxide has enough space to bind iron in the intermediate stage of the catalytic reaction and thereby facilitating the hydroxylation reaction. We have also carried out the reaction using the corresponding homogeneous analogue Fe(III)salicylamide under identical reaction conditions, but conversion is only 32%. This may be due to the formation of catalytically inactive μ -oxobridge dimer by the homogeneous complex which has been speculated as the cause of catalytic deactivation. Among other heterogeneous catalysts, titanium silicates (TS-1) which is a titanium containing zeolite gives only 36% conversion, when the reaction was carried out at 70 °C taking acetonitrile as solvent [8]. J. S. Choi and co worker reported phenol hydroxylation by using Fe-MCM-41 as catalyst, which showed 60% conversion [28]. In comparison to the above two cases our catalyst is found to be more efficient in terms of conversion using water as the solvent. Further, it is worth mentioning here that the selectivity of thermodynamically more stable product, i.e. catechol is high compared to hydroquinone [29]. Ray et al. have reported immobilization of salicyladimine complex onto amorphous silica and MCM-41 for evaluation of their efficacies towards hydroxylation of phenols. They found MCM-41 supported catalyst showed a higher phenol conversion than the amorphous silica, which is due to higher surface area of MCM-41 [30].

The mechanism of phenol hydroxylation is known to proceed via a redox mechanism involving a Fe(III)/Fe(II) redox pair which is illustrated in Scheme 3. The electrophilic attack of the hydroxyl radical is proposed to be the reaction pathway for dihydroxybenzene over this catalyst.

Samples	Phenol conv. (%)	Product selectivity (%)		CAT/HQ	Hydrogen peroxide		TOF ^e		
		CAT	HQ	BQ	(mol/mol)	SD ^b (%)	Conv. ^c (%)	SE ^d (%)	
MCM-41	-	-	_	-	-				
Fe(III)salicylamide-MCM-41	64.6	67.4	30.2	2.4	2.23	37	64	68	494
Fe(III)salicylamide	32	63.4	31	5.6	2.04	63	68	33	149

Table 1 Hydroxylation of phenol by H₂O₂ under the same reaction conditions^a

CAT catachol, HQ hydroquinone, BQ 1,4-benzoquinone

^a Reaction temperature 80 °C, reaction time 2 h, phenol/ H_2O_2 (molar ratio) = 1, amount of catalyst 0.05 g, water as solvent

^b Self-decomposition (SD) of H_2O_2 = volume of oxygen released in the reaction

^c Conversion of H_2O_2 = consumption of H_2O_2 (including self-decomposition)/initial amount of H_2O_2

^d Selectivity (SE) of $H_2O_2 = H_2O_2$ consumption for product formed/total consumption of H_2O_2

^e TOF = Moles of product formed per mole of Fe in the catalyst per hour

Scheme 3 Mechanistic pathway for phenol hydroxylation



As OH radical is an electrophile, which behaves different from that OH⁻. So OH radical tends to have an attack preferably at ortho and para position of the phenol molecule to produce catechol and hydroquinone. The selfdecomposition of H_2O_2 is obvious in the reaction system; this may hinder the effective utilization of H_2O_2 (Table 1), thus the formation of dihydroxybenzene derivatives. Generally, the catalytic activity and product selectivity in phenol hydroxylation in presence of hydrogen peroxide are highly influenced by the reaction time, temperature, types of solvents, phenol to hydrogen peroxide ratio, which are investigated systematically and described as follows.

3.2.2 Effect of Time

Time dependence of activity in phenol hydroxylation is summarized in Table 2. The phenol conversion and selectivity for hydroxylation products are enhanced with increase in time and the reaction acquires a steady state after 2 h. It is also found that 1, 4-benzoquinone dominates the reaction products at early stage of the reaction. But the selectivity for 1, 4-benzoquinone decreases whereas those for catechol and hydroquinone increases with increase in reaction time. Similar types of results were found on TS-1 [8] and metal complex oxides [31]. It may presumably due

 Table 2 Effect of reaction time on phenol hydroxylation

Reaction time (h)	Phenol conversion (%)	Product selectivity (%)			
		CAT	HQ	BQ	
0.5	7	53.0	20.7	26.3	
1	28	53.3	25.8	20.9	
1.5	46	62.3	26.4	11.3	
2	64.6	67.4	30.2	2.4	

Reaction temperature 80 °C, phenol/H₂O₂ (molar ratio) = 1, amount of catalyst 0.05 g, water as solvent

to the fast oxidation of phenol in the reaction medium by a large concentration of H_2O_2 , which could cause the formation of 1, 4-benzoquinone in relatively large amount. The subsequent disappearance of 1, 4-benzoquinone can be explained due to its deeper oxidation by H_2O_2 with the formation of hydroquinone [32].

3.2.3 Effect of Temperature

Effect of temperature on phenol hydroxylation is depicted in Table 3. It is observed that phenol conversion increases as the temperature increases from 40 to 80 °C. At 40 °C, phenol conversion is only 22.4%. But the 1, 4-benzoqouinone selectivity is comparatively high (10.8%). Conversion goes on increasing up to 80 °C, above which a sudden minimal yield of dihydroxybenzene products was obtained, which is due to enhanced H_2O_2 decomposition. Similar observation was reported earlier for Fe containing catalyst [28].

3.2.4 Effect of Solvent

Solvent plays an important role in phenol hydroxylation. It has a profound effect on phenol conversion, hydrogen peroxide decomposition and the ratio of catechol to hydroquinone formation. We have performed the reaction in water, acetonitrile, ethanol and dichloromethane. The conversion and product selectivity are illustrated in Table 4. A change from organic solvent to water leads to a

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Reaction medium	Phenol conversion (%)	Product selectivity (%)		vity (%)
		CAT	HQ	BQ
Water	64.6	67.4	30.2	2.4
Acetonirtile	29.6	43.3	39.9	16.8
Ethanol	8.6	46.4	29.7	23.9
Dichloromethane	3.8	56.4	30.1	13.5

Reaction temperature 80 °C, reaction time 2 h, phenol/H₂O₂ (molar ratio) = 1, amount of catalyst 0.05 g

significant increase in phenol conversion. This may be attributed that, both phenol and H_2O_2 dissolve easily in water to form active hydroxyl radicals. The generation of radical is more stable in polar solvents and polarity order is water > acetonitrile > alcohol > dichloromethane. Ethanol is a well-known scavenger for hydroxyl radical; hence negligible conversion takes place [33].

3.2.5 Effect of the Molar Ratio of Phenol to H_2O_2

The molar ratio of phenol to H_2O_2 has significant effect on phenol hydroxylation activity. Reactions were performed varying the amount of H_2O_2 to a fixed amount of phenol in 1:1 to 1:0.33 (phenol: H_2O_2) ratio. At the standard reaction conditions (in 1:1 ratio) 64.6% conversion was obtained. As the H_2O_2 amount reduced to 1/3 (phenol: H_2O_2 ratio 1:0.33), conversion decrease to 37%.

3.2.6 Catalytic Stability and Reusability

Fe(III)salicylamide–MCM-41 catalyst was recovered from reaction mixture by filtration after each reaction and washed thoroughly with ethanol and dichloromethane. It was reused successively three times under the same reaction conditions. The recovered catalyst is found to exhibit almost the same catalytic activity (slightly less in second and third run) for phenol hydroxylation (shown in Table 5). To test if iron is leaching out of the catalyst, the hot reaction mixture was filtered after the reaction is over and

 Table 3 Effect of temperature on phenol hydroxylation

Temperature (°C)	Conversion	Product distri	CAT/HQ		
	of phenol (%)	CAT	HQ	BQ	(mol/mol)
40	22.4	62.3	26.9	10.8	2.31
50	36.9	65.7	27.1	7.2	2.42
60	50.3	65.8	29.5	4.7	2.23
70	61.3	67.3	29.5	3.2	2.28
80	64.6	67.4	30.2	2.4	2.23

Reaction time 2 h, phenol/ H_2O_2 (molar ratio) = 1, amount of catalyst 0.05 g, water as solvent

Table 5 Catalytic reusability test for hydroxylation of phenol

Run	Phenol conversion (%)	Selectiv	vity (%)	wt% of iron	
		CAT	HQ	BQ	from AAS
1	64.3	67.3	30.2	2.5	0.36
2	62.5	67.2	29.9	2.9	0.35
3	61.8	67.3	30.0	2.7	0.33

Reaction temperature 80 °C, reaction time 2 h, phenol/ H_2O_2 (molar ratio) = 1, amount of catalyst 0.05 g, water as solvent

the filtrate was subjected to atomic absorption spectroscopic analysis. The analysis showed iron was absent in the filtrate. Besides, filtrate mixture also did not show any catalytic activity towards phenol hydroxylation reaction. These results indicated that the catalyst was regenerable and reusable.

4 Conclusions

Fe(III)salicylamide complex was successfully anchored to a mesoporous silica matrix via a covalent bond. XRD and N_2 adsorption–desorption confirm that the mesoporosity is retained even after complexation. The ¹³C CP MAS NMR spectra show all possible peaks corresponding to both the aliphatic and aromatic carbon atoms. Solid-state ²⁹Si CP MAS NMR shows that the organic group is successfully bonded to mesoporous silica. FT-IR and diffuse reflectance UV–vis spectra confirm formation of the complex. The catalysts exhibit excellent catalytic performance and stability in phenol hydroxylation reaction for the formation of dihydroxybenzene derivatives using H₂O₂. One of the most interesting thing for water as solvent is that it is safe, cheap, environmental friendly and meets the needs of sustainable development in chemical industries.

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