

Direct synthesis, characterization of Cu-SBA-15 and its high catalytic activity in hydroxylation of phenol by H₂O₂

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Received 12 October 2004; received in revised form 20 December 2004; accepted 21 December 2004

Available online 26 January 2005

Abstract

Transition metal copper substituted mesoporous silica (Cu-SBA-15) was synthesized using triblock copolymers surfactant as template agent under acidic condition. The result Cu-SBA-15 was characterized with XRD, ICP-AES, FT-IR and N₂ adsorption–desorption measurements, which prove that Cu(II) was mainly incorporated into the framework of Cu-SBA-15. Its catalytic activity was studied for phenol hydroxylation using H₂O₂ (30%). The substituting element (Cu²⁺) is incorporated into the framework position forming a new type of active site which raises the phenol conversion to 62.4% and the diphenol (the mixture of catechol (CAT) and hydroquinone (HQ)) selectivity to 97%. The Cu-SBA-15 has very high selectivity for catechol (about 71% selectivity), which is completely different from that of the microporous titanium silicalite zeolites (47.1% phenol conversion and about 50% selectivity to CAT under same reaction conditions). The results obtained indicate that the selective oxidation of phenol with H₂O₂ by a radical substitution mechanism.

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Keywords: Cu-SBA-15; Cu-substituted mesoporous silicas; Phenol hydroxylation; Catalytic oxidation; Oxidant catalyst

1. Introduction

The incorporation of transition metal ions into the framework sites of the molecular sieve has attracted considerable attentions as the preparation of novel catalysts, owing to which possess the advantages of both homogeneous catalysis as the metal ion in the solution and heterogeneous catalysis as the molecular sieve in the polyphase system. Several successful examples of transition metal incorporated molecular sieves had been demonstrated for examples, Al, Ti, Ga, Mn, Cr and Fe [1–5]. Especially, Ti-substituted molecular sieves, such as TS-1, Ti-beta and Ti-MCM41 have displayed the excellent redox catalytic activities, and the TS-1 as catalyst has been used in industrial production of diphenols [5–10]. These successful efforts show that incorporation of transition metal ions into the framework of the porous materials is an efficient method for the designable prepara-

tion of the novel catalysts on the molecular and atomic level.

Mesoporous molecular sieve possess a large surface area and uniform mesoporous channels, these are advantageous characteristics of a catalytic support. In recent years, to design transition metal active centers on molecular sieves have attracted increasing attentions. SBA-15 is a new type of mesoporous silica molecular sieves with uniform hexagonal channels ranging from 5 to 30 nm, thick walls (3.1–6.4 nm), and with higher hydrothermal stability than those of MCM-41 [11,12]. The SBA-15 has been extensively applied in many fields [13–19]. Copper ion and the complexes containing copper ion have long been found to be effective catalysts and be used in a wide range of organic synthesis [20–25]. Cu(II) substituted molecular sieves were found to be efficient catalysts in liquid phase oxidation of aromatic compounds, and the copper site in the framework of molecular sieves is active centre in phenol hydroxylation [26,27]. So it can be envisioned that the mesoporous molecular sieve SBA-15 containing copper in the framework may be a highly promis-

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ing catalytic materials. However, it has not been reported by far.

Many efforts have been devoted to the propinquity investigations. Incorporation of transition metals, such as Al, V, Ti, and Fe into the framework of SBA-15 has been reported [28–31], and the synthesis of Cu-Zeolite [32] and Cu-MCM-41 [33] in basic media has been investigated. However, these methods of preparation for them are not satisfactory for the incorporation of Cu into the framework of SBA-15 (Cu-SBA-15) under acidic condition. In the present work, we reported a simple and efficient approach to the direct synthesis of Cu-SBA-15 material using H_3PO_4 as acid source and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as concomitant salt. The experimental results show that Cu-SBA-15 material has a high catalytic activity for the hydroxylation of phenol with 30% aqueous H_2O_2 as oxidant in aqueous solution, and very high selectivity for catechol.

2. Experimental

2.1. Catalyst preparation

The copper-containing SBA-15 (Cu-SBA-15) mesoporous material was prepared according to the following procedure: an amount of 12 ml of the ethanol solution containing 0.5 g triblock poly(ethylene oxide)₂₀-poly(propylene oxide)₇₀-poly(ethylene oxide)₂₀ (EO₂₀PO₇₀EO₂₀ Aldrich) was added dropwise to the aqueous solution under vigorous stirring, which was prepared by dissolving $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, 0.5 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 4 ml H_3PO_4 (85%) in 30 ml distilled water and then stirring for at least 3 h, and the mixture was stirred for 12 h at 60 °C. Then TEOS (1.1 g) was added as silica source. After the mixture was stirred for at least 20 h and aged for 48 h at 90 °C, the solid obtained was filtered off, dried in the air, and calcined at 550 °C for 6 h to produce the mesoporous material containing Cu(II) ion.

2.2. Characterization of the catalyst

The X-ray power diffraction (XRD) patterns of siliceous SBA-15, as-synthesized and calcined Cu-SBA-15 samples were measured at room temperature on the Bruker D8-

ADVANCE equipment with an X-ray source of Cu $\text{K}\alpha$ radiation at $\lambda = 1.5418 \text{ \AA}$. N_2 adsorption–desorption of the calcined Cu-SBA-15 samples were measured using Quantachrome Autosorb 3-B adsorption apparatus. Surface area was obtained basing on the BET method using the amount of N_2 adsorption at 77 K. The pore size distribution and pore diameter of the sample was obtained by the calculation of the B.J.H. method. The sample was evacuated at 473 K for 12 h before the adsorption–desorption measurement. IR spectrum was recorded on Nicolet Nexus 670 spectrometer, using KBr pellets. ICP-AES results were determined using Thermo Jarrell Asch IRIS Advange 1000.

2.3. Phenol hydroxylation and analytical procedure

The investigation of their catalytic activity was carried out by the procedure as follows: the reaction was performed in a 100 ml three-necked round-bottom flask, equipped with a magnetic stirrer, a reflux condenser and a temperature controllable water-bath. In a typical run, 0.94 g of phenol, 0.05 g catalyst and 10.8 g of water were added to the reactor. When the mixture was heated to the reaction temperature under vigorous stirring, 2.28 g of a 30% aqueous H_2O_2 was added to the reactor. The reaction products were analyzed by high performance liquid chromatography (HPLC) (Dikma C184.6 mm i.d. \times 250 mm column), using UV detectors at 254 nm. The H_2O_2 conversion was determined by the methods:

- (1) The efficiency conversion of H_2O_2 was calculated as follows: H_2O_2 eff. conv. = $100 \times \text{H}_2\text{O}_2(\text{mol})$ consumed in formation of diphenols and benzoquinone/ H_2O_2 (mol) converted.
- (2) The H_2O_2 conversion was determined by the iodometry method.

3. Results and discussion

3.1. Characterization of Cu-SBA-15

3.1.1. Synthesis and X-ray diffraction

Cu-SBA-15 was synthesized using H_3PO_4 as acid source and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as concomitant salt. It is noteworthy that the P and Al elements in the final products prepared (Cu-SBA-15) have not been detected by ICP analysis, and the molar

Table 1
XRD parameters of Cu-substituted SBA-15; d -value of reflection, constants of unit cell and pore volume^a

SBA-15	$d\{hkl\}$ (Å)			a_0^b (Å)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)
	{100}	{110}	{200}		
Si as-syn.	96.8	55.5	48.8	111.8	0.76
Si calc.	94.5	54.5	47.2	109.1	
Cu as-syn.	99.3	58.7	50.7	114.7	0.81
Cu calc.	98.9	57.2	49.5	114.2	

^a Si/Cu = 36 in all samples.

^b $a_0 = (2/\sqrt{3}) \cdot d_{100}$.

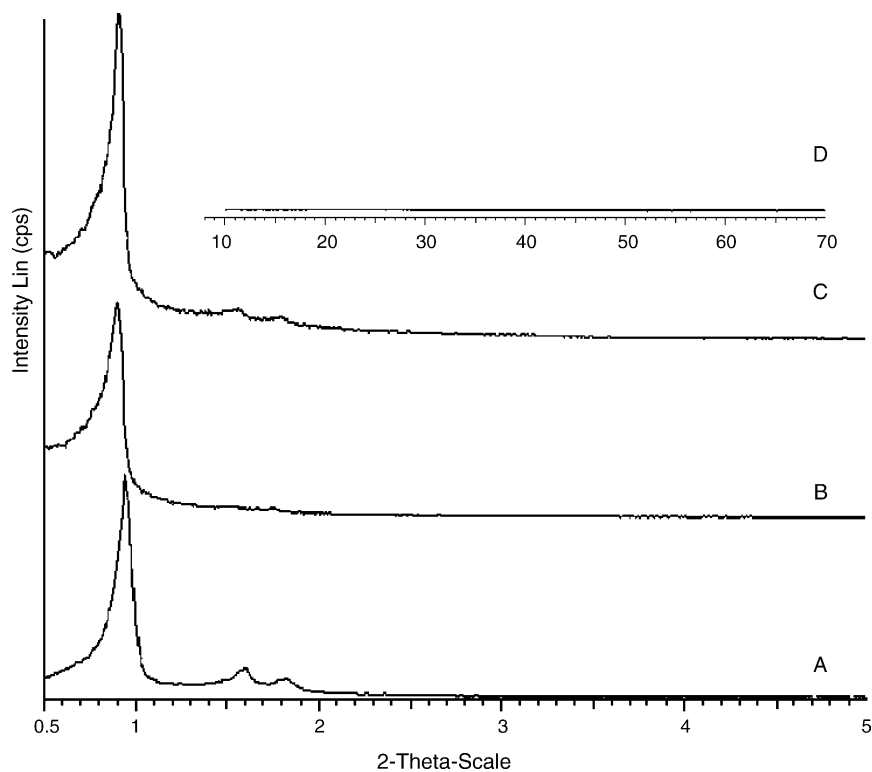


Fig. 1. XRD patterns of (A) SBA-15, (B) as-synthesized Cu-SBA-15, (C) calcined Cu-SBA-15, (D) calcined Cu-SBA-15 in higher angle.

ratio of Si/Cu determined by ICP is 36. However, the Cu-SBA-15 cannot be obtained if without $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and H_3PO_4 in the reactants, this phenomenon may be attributed to that the PO_4^{3-} can act as buffer reagent to prevent the tempestuous change of pH and level of the reactive conditions in the reactive system, and that $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ may act as a mineralizing agent [34].

The XRD patterns of mesoporous copper-containing SBA-15 is shown in Fig. 1. The d_{100} spacing, pore volumes and unit cell parameters of Cu-SBA-15 and SBA-15 before and after calcination are given in Table 1. The low angle XRD patterns show a prominent peak corresponding to (100) reflections and much weaker, whereas observable peaks corresponding to (110) and (200) reflections, which is the typical character of the SBA-15 molecular sieve reported [12]. The unit cell dimension ($a_0 = 2d_{100}/\sqrt{3}$) of calcined Cu-SBA-15 (Cu calc.) is 114.2 Å. In comparison with each other it is found the a_0 of as-synthesized Cu-SBA-15 (Cu-as-syn.) is 2.5 Å greater than that of Si-as-syn. Such expansion of unit cell parameter may hint the successful incorporation of copper into the framework, although the accuracy of the XRD measurement was not sufficient to differentiate the metal-modified and the pure silica form material. Furthermore, the higher-angle XRD pattern shows that there has no formation of copper oxide particles (aggregation) in or outside the pores of Cu-SBA-15, which sustain that the product Cu-SBA-15 is in a pure crystal phase, and the Cu may be incorporated into the framework of mesoporous material Cu-SBA-15 (Fig. 1).

3.1.2. IR results

The framework IR spectrum of calcined Cu-SBA-15 is shown in Fig. 2. An adsorption band at ca. 960 cm^{-1} is observed, and a very similar band is also observed in titanium

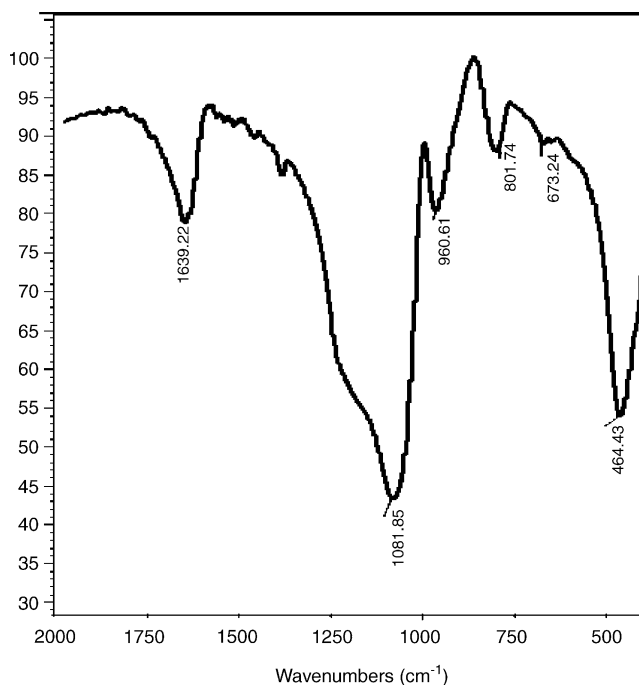


Fig. 2. FT-IR spectra of calcined Cu-SBA-15 mesoporous materials.

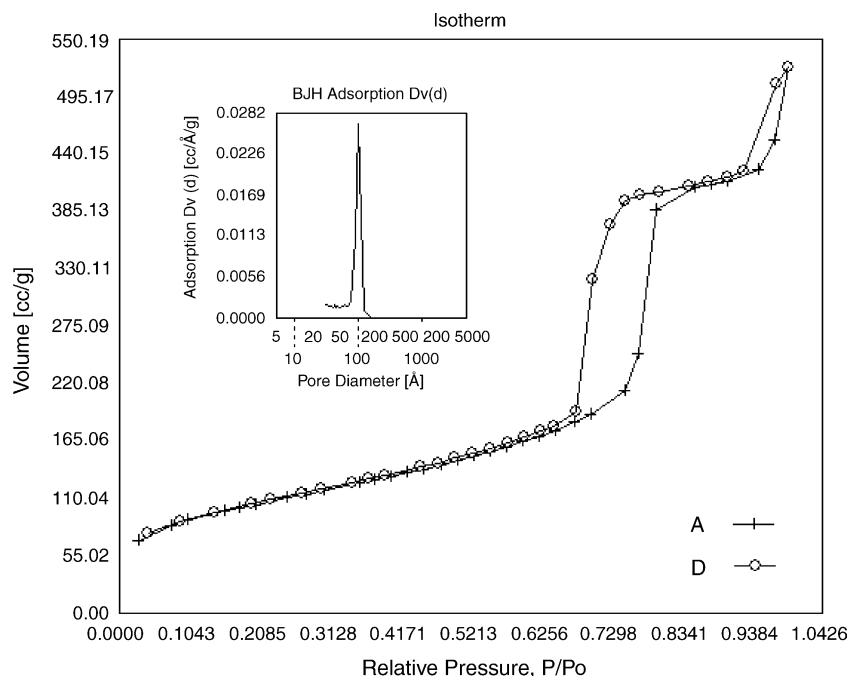


Fig. 3. N_2 adsorption–desorption isotherms of Cu-SBA-15 at 77 K.

siloxane polymers [35], mixed oxides [36] or TiO_2 -grafted on silica [37], which is attributed to a modification of SiO_4 units indirectly relating to the presence of heterometals. Therefore, the IR band at 960 cm^{-1} could be assigned to Si–O–T (T=Cu) vibration in the Cu-containing SBA-15 framework structure. IR spectrum of sample also shows no presence of CuO due to the lack of a Cu–O stretch vibration band at 536 cm^{-1} [38]. The results of the XRD, IR and ICP testify completely that the Cu was incorporated into the framework sites of the SBA-15.

3.1.3. N_2 adsorption–desorption

The N_2 adsorption–desorption isotherm (Fig. 3) is of Type IV in nature and exhibited a clear H1-type hysteresis loop at high relative pressure, suggesting that Cu-SBA-15 have very regular mesoporous channels. The average pore size calculated from the BJH method is at about 8.2 nm with the unit cell dimension $a_0 = 11.42\text{ nm}$ and the wall thickness can be calculated as 3.2 nm, which is similar to the mesoporous molecular sieve prepared with neutral block co-polymer templates [12]. The BET surface area of the calcined Cu-SBA-15 is $728\text{ m}^2\text{ g}^{-1}$, and the pore volumes of Cu-SBA-15 and SBA-15 samples are $0.81\text{ m}^3\text{ g}^{-1}$ and $0.76\text{ m}^3\text{ g}^{-1}$, respectively, which is in accordance with XRD results and confirms the expansion of the mesopores on the introduction of the Cu(II) in the Si framework.

3.2. Catalytic phenol hydroxylation

3.2.1. Catalytic activity

The results of the catalytic activities using different catalysts at 60°C were listed in Table 2. No products are detected

using SBA-15 as catalyst, whereas the Cu-SBA-15 shows a very high catalytic activity for hydroxylation of phenol and resulted in a phenol conversion of 59.4%, and this result indicates that the Cu as framework species has the tempestuous effect on the catalytic performance of Cu-SBA-15. By comparing the catalytic performance of Cu-SBA-15 with TS-1, the phenol conversion on Cu-SBA-15 is 12.3% higher than that on TS-1, and Cu-SBA-15 also shows higher catalytic activity than Cu-HMS catalyst (see Table 2) indicating that Cu-SBA-15 is an excellent catalyst and Cu is a highly efficient centre of catalyst for the phenol hydroxylation. Moreover, the catalytic performance of Cu-SBA-15 is obviously superior to that of Cu/SBA-15 prepared by immersion method, and the conversion of phenol over Cu-SBA-15 is 17.5% higher

Table 2

Catalytic activities and selectivity in phenol hydroxylation by H_2O_2 over various catalysts^a

Catalyst	Phenol conv. (%)	Product selectivity (%) ^b		
		CAT	HQ	BQ
SBA-15	0.0	0.0	0.0	0.0
Cu-HMS	32.7	65.5	30.6	3.9
Cu/SBA-15 ^c	41.9	65.0	31.0	4.0
Cu-SBA-15	59.4	71.0	26.2	2.8
TS-1 ^d	47.1	53.3	45.7	1.0

^a Reaction conditions: water as a solvent, reaction temperature 60°C , $\text{pH} = 7.0$, $H_2O_2/\text{phenol} = 2$ (molar ratio), reaction time 4 h, catalyst/phenol = 5% (weight ratio).

^b CAT = catechol, HQ = hydroquinone, and BQ = benzoquinone. The product of tar is not included, and the product selectivity is $\text{CAT (or HQ or BQ)}/(\text{CAT} + \text{HQ} + \text{BQ})$.

^c Prepared by immersion method.

^d $m(\text{TAPOH})/m(\text{SiO}_2) = 0.2$.

than that on Cu/SBA-15. This observation indicates that the catalytic activity of the framework Cu(II) in Cu-SBA-15 is higher than the extraframework Cu(II) supported on SBA-15. This may be due to that the electric and geometric arrangement of tetrahedrally coordinated framework Cu(II) can lead to the changing of the electric field environment in the inner channels of SBA-15, and then favorably promote catalytic activity for phenol hydroxylation. Furthermore, it is worth mentioning that the selectivity of CAT in this reaction is very high (CAT/HQ = 3) on the Cu-SBA-15, this high CAT selectivity is in good agreement with previous results over Cu/MCM-41 and Cu-HMS catalysts [26,27], but completely different from that of the microporous titanium silicalite zeolites TS-1. A possible reason accounting for such a difference is that hexagonal structure of Cu-SBA-15 is completely different from the three-dimensional microstructure of TS-1.

Generally, the catalytic activity and product selectivity in phenol hydroxylation by hydrogen peroxide are strongly influenced by surface area of the catalyst, solvents, reaction time, and reaction temperature, which are investigated systematically as follows.

3.2.2. Influence of reaction media

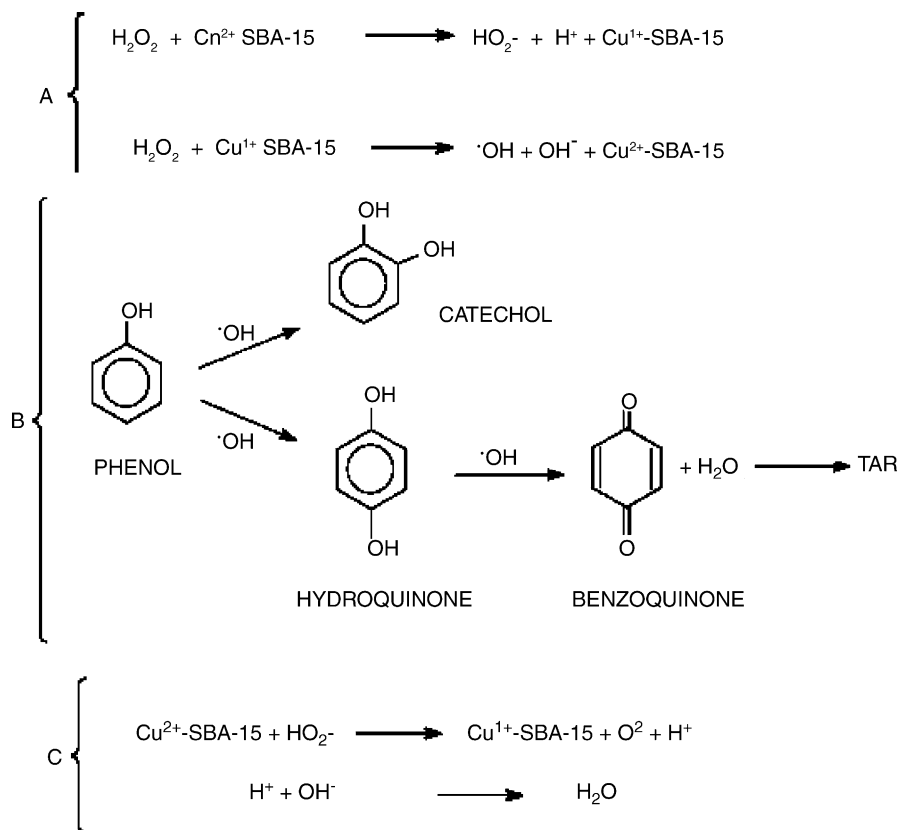
It has been reported the solvents in this reaction have a great influence on the phenol conversion and the selectivity

Table 3
Effect of reaction medium of phenol hydroxylation catalyzed by Cu-SBA-15^a

Reaction medium	Phenol Conv (%)	Product selectivity (% mol)		
		CAT	HQ	BQ
Water	59.4	71.0	26.2	2.8
Acetonitrile	0.0	–	–	–
Acetone	0.0	–	–	–
Methanol	0.0	–	–	–

^a Other reaction conditions are the same as those in Table 1.

of products over microporous titanosilicalites. Table 3 presents a summary of solvent influence in phenol hydroxylation over Cu-SBA-15 catalyst. While acetone, acetonitrile and methanol were used as solvents, phenol hydroxylation reaction did not occur. A change from organic solvents to water led to a significant increase in phenol conversion, and which indicates that water was the best solvent for phenol hydroxylation using Cu-SBA-15 as catalyst. This may be attributed to that phenol and H₂O₂ reach the active sites and the species dispersed more easily in water than in the organic solvents. The other reason is the active species, such as OH· produced in organic solvents may react with them rather than the phenol. One of the most interesting is water as media, which is safe, cheap, and environmentally friendly solvent,



Scheme 1. Reaction path for the hydroxylation of phenol.

Table 4
Catalytic activities and selectivity in phenol hydroxylation by H₂O₂ over Cu-SBA-15 catalyst with various reaction time^a

Time (h)	Phenol conv. (mol%)	H ₂ O ₂ eff conv. (%)	H ₂ O ₂ conv. (%)	Product selectivity		
				CAT	HQ	BQ
0.25	5.3	25.6	12.5	45.1	36.8	20.1
0.5	12.8	39.1	18.9	44.3	41.9	14.8
0.75	17.2	42.1	22.8	45.6	43.2	11.2
1	20.7	42.3	26.7	46.2	44.5	9.3
2	24.1	43.0	30.5	47.7	43.7	8.6
4	59.4	46.7	65.3	71.0	26.2	2.8
6	62.4	40.8	78.5	70.9	26.4	2.7
8	62.6	36.6	87.2	71.2	27.0	1.8
10	62.7	34.9	91.3	70.8	27.6	1.6

^a Other reaction conditions are the same as those in Table 1.

and meets the needs of sustainable development in chemical industries.

3.2.3. Reaction mechanism

The reaction mechanism for the oxidation of aromatic compounds employing transition metals has been previously studied [28]. The reaction path proposed for the present study involves following steps shown in Scheme 1. In step A, the interaction of Cu-SBA-15 catalysts and hydrogen peroxide yields HO• and HO₂• species, via a redox mechanism. In step B, hydroquinone and catechol are subsequently obtained in parallel processes, by the attack of HO• radicals to the aromatic ring, benzoquinone can be formed by the consecutive oxidation of hydroquinone. In addition, a little tar was formed during the procedure of phenol hydroxylation due to over-oxidation of BQ. In step C, oxygen and water are formed in side reactions by the decomposition of H₂O₂.

3.2.4. Influence of reaction time

Table 4 presents the dependence of phenol conversion and selectivity with reaction time in water using Cu-SBA-15 as catalyst. From the results in Table 4, it was found that H₂O₂, phenol conversion and selectivity of CAT increase with increasing reaction time. In contrast, the selectivity of BQ decreased with reaction time increase, whereas the selectivity of hydroquinone, firstly increased, and then decreased with reaction time increase. A relatively short reaction time resulted in incomplete conversion of phenol as well as undesirable product selectivity. In the region from 0 to 6 h, the change of them is the more notable. When the reaction time was 0.25 h,

phenol conversion was 5.3%, CAT selectivity is 45.1% and H₂O₂ conversion is 12.5%. When the reaction time was 6 h, the corresponding phenol and H₂O₂ conversion, and CAT selectivity are 62.4, 65.3, and 70.9% (see Table 4), which attained the maximal yield of hydroxylation products under present conditions, when the reaction time was further prolonged, the phenol conversion and the selectivity of CAT have almost no change, but the conversion of H₂O₂ still increase. This result illustrates that H₂O₂ take part in other chemical reaction expect the phenol hydroxylation. It is a noteworthy that the selectivity of HQ decreased remarkably (from 44.5% at 1 h to 27.0% at 8 h) when the CAT selectivity increase with reaction time. A possible reason may account for such a result is that hydroquinone is consumed in the formation of BQ products, whereas CAT, the thermodynamically favored isomer, was not further oxidized [27]. And the higher selectivity of BQ in early stage of the reaction and the variation of the selectivity for HQ with reaction time (see Table 4) maybe arise from two factors: firstly, a fast over oxidation of HQ by the higher concentration of H₂O₂ could cause the formation of BQ in the more amount in the initial action, and which gradually decreased with the concentration of H₂O₂ decrease; secondly, the side reaction of BQ oxidation to tar could take place in the reaction procedure, but its reaction rate is the lower and which lead to the little amount of tar observed in the end of reaction.

3.2.5. Influence of reaction temperature

Phenol conversion and product selectivities in the temperature range of 40–90 °C for phenol hydroxylation over

Table 5
Catalytic activities and selectivity in phenol hydroxylation by H₂O₂ over Cu-SBA-15 catalyst with various reaction temperature^a

Temperature (°C)	Phenol conv. (mol%)	H ₂ O ₂ eff conv. (%)	H ₂ O ₂ conv. (%)	Product selectivity		
				CAT	HQ	BQ
40	34.9	34.9	53.2	63.7	30.0	6.3
60	59.4	46.7	65.3	71.0	26.2	2.8
80	64.1	41.8	78.5	78.9	18.8	2.3
90	65.5	40.5	82.4	76.8	21.3	1.9

^a Other reaction conditions are the same as those in Table 1.

Table 6
Catalytic activities and selectivity in phenol hydroxylation by H₂O₂ over Cu-SBA-15 catalyst with regeneration of the catalyst^a

Run	Phenol conv. (%)	Product selectivity (%)		
		CAT	HQ	BQ
First run	59.4	71.0	26.2	2.8
Second run (used sample from run 1)	19.3	64.9	17.0	18.1
Third run (regeneration by calcinations at 550 °C for run 3)	57.6	71.4	26.4	2.2

^a Other reaction conditions are the same as those in Table 1.

Cu-SBA-15 catalyst are listed in Table 5. It is observed that phenol conversion increases with temperature increase from 34.9% at 40 °C to 65.5% at 90 °C. Meanwhile, H₂O₂ efficiency also increases with temperature from 34.9% at 60 °C to 46.7% at 60 °C. However, when the temperature is raised to 90 °C, the H₂O₂ efficiency reduces to 40.5%. In addition, BQ selectivity decreased with temperature increasing in the range of 40–90 °C. At 40 °C BQ selectivity was 6.3%, and it decreased to 1.9% at 90 °C. To explain the decrease of BQ selectivity at higher temperature, it is proposed that BQ was further oxidized to tar, and similar phenomena have been observed in the literature [39].

3.2.6. Regeneration of the catalyst

The catalytic activity of Cu-SBA-15 catalyst was monitored over three runs of the reaction, and the results are presented in Table 6. After the first run of phenol hydroxylation, the activity of Cu-SBA-15 catalyst reduced a lot from 59.4% (first run) to 19.3% (second run). A reasonable explanation may be that Cu-SBA-15 with larger channels has little effects of the channel constraints on the formation of the brown tar species inside the channels of Cu-SBA-15. The tar species gradually poisons the Cu²⁺ active sites, and finally, leads to the loss of activity of the catalyst. Therefore, in order to recover the catalytic activity, the used catalyst is necessary to be regenerated by the calcination to remove the contamination matters. TG analysis on the used catalyst in oxygen atmosphere exhibited a weight loss of about 20% in the range of 500–650 °C. Moreover, after calcination at 550 °C for 2 h, the initial level of catalytic activity of Cu-SBA-15 was recovered (see Table 6). These results indicated that the catalyst was regenerable and reusable by calcination.

4. Conclusion

The copper-containing ordered mesoporous material Cu-SBA-15 was synthesized using triblock copolymers surfactant as template under acidic condition, and was characterized systematically. The results demonstrated that some Cu²⁺ ions have been successfully incorporated into the framework of SBA-15 and then cause the expansion of the unit cell. The active centers of Cu²⁺ in the framework are favorable for phenol hydroxylation and have good selectivity for catechol. The preparation of this material may offer a very good redox catalyst for the industry of fine chemicals.

Acknowledgements

This work was granted financial support from the Natural Science Foundation of China (NSFC Grant Nos. 20273021 and 20173017).

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