## Mesoporous chitosan-immobilized iron tetrakis(4carboxyphenyl)porphyrin as a model of cytochrome P-450 enzyme for oxidation of ethylbenzene

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Natural Science Foundation of Guangxi Province, Grant/Award Number: 2014GXNSFDA118009; Experimental Innovation Project Foundation of Guangxi University, PR China, Grant/Award Number: 201510593308; Scientific and Technological Project of Guangxi Province, Grant/Award Number: 12118008-12-3; National Natural Science Foundation of China, Grant/Award Number: 51363001 Mesoporous chitosan-grafted iron tetra (4-carboxyphenyl) porphyrin catalyst (Fe TCPP/mesp-CTS) was prepared and investigated as a practical model for the nano-cavity and coordinate regulation-catalysis(CRC) function in cytochrome P-450 enzyme. Fe TCPP/mesp-CTS was characterized by X-ray Diffraction(XRD), Thermogravimetry(TG), Ultraviolet–visible spectroscopy(UV-Vis), Ultraviolet–visible–Diffuse reflectance spectroscopy(UV-DRS), Scanning electron microscope (SEM), Fourier transform infrared spectroscopy(FT-IR), and X-ray photoelectron spectroscopy(XPS) techniques. The catalytic activity of Fe TCPP/mesp-CTS for ethylbenzene oxidation was investigated and it was proved to be a better catalyst than Fe TCPP/macp-CTS based on the ethylbenzene conversion, turnover numbers(TON), and the reusability. These results are attributed to the mesocavity and CRC of amino group in Fe TCPP/mesp-CTS. The highest ethylbenzene conversion and yields of ketone and alcohol were 24.4% and 18.2%, respectively.

#### **KEYWORDS**

catalysis, ethylbenzene oxidation, iron porphyrin, mesoporous chitosan, oxygen

## **1** | INTRODUCTION

The selective oxidation of ethylbenzene to valuable products is an important reaction for chemical industry.<sup>[1,2]</sup> Many types of metalloporphyrins have been widely used as cytochrome P-450 enzyme models for catalytic oxidation of various hydrocarbons into oxygenic compounds.<sup>[3,4]</sup> However, homogeneous metalloporphyrin catalysts are not practical in large-scale process owing to the drawbacks of deactivation and low reusability.<sup>[5]</sup> Immobilization of metalloporphyrin onto various supports has been found to be an effective way to increase the stability of metalloporphyrin and the substrates conversion. The supported metalloporphyrin catalyst is easier to be recovered. Therefore, many kinds

of supports have been used to improve the catalytic activity of metalloporphyrin, such as zinc oxide,<sup>[6]</sup> multi-wall carbon nanotubes,<sup>[7]</sup> boehmite,<sup>[8]</sup> merrifield resin,<sup>[9]</sup> cyclodextrin polymers,<sup>[10]</sup> and so on.

Natural organic polymers such as chitosan (CTS) are promising supports for catalytic application due to the high surface area, low cost, biodegradability, biocompatibility, nontoxicity and renewability.<sup>[11,12]</sup> Chitosan has been used as the support for Fe<sub>3</sub>O<sub>4</sub>,<sup>[13]</sup> chiral bifunctional thioureas,<sup>[12]</sup> imidazole Schiff,<sup>[14]</sup> and peroxotungstate<sup>[15]</sup> in many studies. It has been found that chitosan was also a great support for Co(II) TPP, M TPPs, Mn TPP, (TPPFe<sup>III</sup>)<sub>2</sub>O, [Fe<sup>III</sup> (TPP)]Cl, and M TCPP.<sup>[16–23]</sup> The N atoms in the amino groups of CTS coordinate to the metal ions of metalloporphyrins, resulting in the enhanced catalytic activity of the CTS supported metalloporphyrin. However, the traditional CTS has very small surface area, and the metalloporphyrins could not be well dispersed on it for efficient catalysis of hydrocarbons oxidation reaction. Therefore, new methods need to be employed to modify the CTS to make it being a better support for metalloporphyrins. Mesoporous materials with the advantages of large surface area, well-defined pore size, high mechanical and thermal stability, have been used as support in many studies, and these materials present good catalytic performance and stability.<sup>[24-27]</sup> Based on these facts, the porous chitosan was used as the support for metalloporphyrins and the resulted M TCPP/p-CTS showed great catalytic activity for aerobic oxidation of cyclohexane due to the porosity and specific surface area of chitosan.<sup>[23]</sup> Even more promisingly, mesoporous chitosan, with larger specific surface area, more mesoporous cavity and coordination function, would be a more hopeful mimic of the nano-cavity and coordinate regulation-catalysis(CRC) function in cytochrome P-450 enzyme. With these knowledge, mesoporous CTS will be used as a promising support for metalloporphyrin to achieve higher catalytic activity.

In the present study, the Fe TCPP/mesoporous-CTS (Fe TCPP/mesp-CTS) and Fe TCPP/macroporous CTS (Fe TCPP/macp-CTS) were prepared via an acylation reaction of Fe TCPP with mesp-CTS. XRD, TG, UV–Vis, UV-DRS, FT-IR, SEM and XPS techniques were used to characterize the inner structure, morphology, thermal and photo electronic properties of the prepared catalysts. The catalytic activity for catalytic oxidation of ethylbenzene to ketone and alcohol was investigated. In addition, the effects of oxygen pressure, reaction temperature, amount of Fe TCPP, reaction time as well as the reuse of catalysts for ethylbenzene oxidation were revealed.

### 2 | EXPERIMENTAL

### 2.1 | Materials

The chemical reagents used were of analytical grade and were employed without further purification. Chitosan ( $M_w \sim 3.9 \times 10^4$  Da, degree of deacetylation was 93%) was purchased from Zhejiang Jinke Biochemistry Co., Ltd., Nanning, China.

## 2.2 | Preparation of Fe TCPP catalysts

6.25 g of 4-carboxybenzaldehyde and 180 ml of propionic acid were mixed with stirring. Upon complete dissolution

of 4-carboxybenzaldehyde, the solution was heated to 180 °C. 3.0 mL of pyrrole was slowly dropped into the solution, and then refluxed for another 2 h. The solution was cooled to room temperature and kept overnight. The reaction mixture was then filtered, and the resulted filter cake was vacuum dried at 120 °C for 6 h after washing with deionized water. The purified TCPP was obtained by recrystallization.

0.53 g of TCPP was add into 120 ml of N,N-dimethyl formamide with stirring at a speed of 100 rpm. Upon complete dissolution of TCPP, the solution was heated to 151 °C, and 1.54 g of  $FeCl_2 \cdot 4H_2O$  was added to the mixture and refluxed for 1 h. 100 ml of deionized water was added to the solution after the reaction mixture cooled down to room temperature and the resulted mixture was kept at room temperature overnight. The mixture was filtered and the obtained cake was washed with deionized water, and Fe TCPP was obtained by vacuum drying at 65 °C for 4 h.

# 2.3 | Preparation of mesp-CTS and macp-CTS

18.75 g of CTS was dissolved in 1000 ml of 0.7 mol $\cdot$ L<sup>-1</sup> diluted acetic acid with stirring at ambient temperature for 20 min. The resulting colloidal solution was added dropwise to a 5 mol $\cdot$ L<sup>-1</sup> NaOH solution, forming microparticles of CTS. The microparticles were obtained by filtering and washing with deionized water until the filtrate became neutral. The microparticles were added to 2.5% (m/m) of glutaraldehyde solution in a ratio of 1 g CTS particles to 1.5 ml glutaraldehyde, and immerged for 24 h. Hereafter, the resulting microparticles were washed with deionized water until no glutaraldehyde remained. A part of microparticles was dried in a freeze dryer, then mesoporous microparticles(mesp-CTS) were obtained. Besides, the other part of microparticles was dried via vacuum drying at 55 °C to obtain macroporous microparticles (macp-CTS).

## 2.4 | Preparation of Fe TCPP/mesp-CTS and Fe TCPP/macp-CTS

In order to mimic the nano-cavity and CRC function in cytochrome P-450 enzyme, mesp-CTS and macp-CTS grafted Fe TCPP were prepared. 0.025 g of Fe TCPP dissolved in 130 ml of dichloromethane and 2 ml of N, N-dimethyl formamide (DMF) were mixed under nitrogen atmosphere, and 1 ml of thionyl chloride was added dropwise into the mixture, and then it was refluxed at 53 °C for 3 h. 25 g of mesp-CTS and 120 ml of

dichloromethane were added and continuously refluxed for another 1 h. The mixture was cooled down to room temperature and filtered, the resulting filter-cake was washed with dichloromethane. The mesp-CTS grafted Fe TCPP (Fe TCPP/mesp-CTS) was obtained via vacuum drying at 55 °C for 2 h. The macp-CTS grafted Fe TCPP (Fe TCPP/macp-CTS) was obtained in the same way. The amount of Fe TCPP grafted on per gram of mesp-CTS and macp-CTS was 1.00 mg and 0.87 mg, respectively, as determined by UV–Vis spectrophotometry<sup>[28]</sup> and also by ICP-AES.<sup>[23]</sup>

## 2.5 | Characterization of supported catalyst materials

XRD patterns of mesp-CTS and Fe TCPP/mesp-CTS were obtained using a D/MAX-2600/PC X-ray powder diffraction instrument, equipped with a Cu Ka radiation source. Thermo analytical TG for the catalyst materials was recorded on a STA 409 PC/PG Luxx thermoanalyser, the measurements were carried out using 5 mg samples in air over the temperature range of 0-550 °C, with a heating rate of 10 °C min<sup>-1</sup>. UV-vis spectra of the immobilized catalyst in DMF suspension and the unsupported catalyst in DMF solutions were recorded using a TU-1810SPC spectrometer. UV-vis diffuse reflectance spectra (UV-DRS) were recorded on a Perkin-Elmer L-17 spectrometer. Amounts of metalloporphyrins-grafted on mesp- and macp-CTS were measured via inductively coupled plasma atomic emission spectroscopy (ICP-AES, Spectroflame model FVMØ3). FT-IR spectra were recorded on a Nexus470 IR spectrophotometer in the range of 4000-400 cm<sup>-1</sup> at a resolution of 2 cm<sup>-1</sup>, using KBr pellets. SEM images were recorded in a S-3400 scanning electron microscope. The specific Brunauer-Emmet-Teller surface areas (S<sub>BET</sub>), N<sub>2</sub> adsorption/desorption isotherms and Barrett-Joyner-Halenda (BJH) pore-size distribution curves at 77 K by using ultra-high-purity grade N<sub>2</sub> (99.999%) for the grafted metalloporphyrin materials were measured in liquid nitrogen bath with a TriStar II 3020 instrument. X-ray photoelectron spectroscopy (XPS) was performed with an XPS spectrometer(Kratos Ultra Axis DLD), which was equipped with an Al Karadia-tion source at 150 W with pass energy of 40 eV.

## 2.6 | Oxidation of ethylbenzene over the grafted catalyst materials

Fe TCPP/mesp-CTS, Fe TCPP/macp-CTS and Fe TCPP were tested as catalysts for ethylbenzene oxidation reaction. The oxidation reactions were carried out in a WDF-05 autoclave reactor equipped with a magnetic stirrer. A WILEY-Organometallic 3 of 11 Chemistry

mixture of 200 ml of ethylbenzene, and certain amount of catalyst was stirred and heated at 135–165 °C. Air was then continuously pumped into the reaction system, and the air pressure was maintained at 0.6–0.9 MPa. The flow rate of air was measured with a rotameter. Samples of the oxidation mixture were quantified on a GC-7900 chromatograph, using p-dichlorobenzene as the internal standard. After the oxidation was stopped, the grafted catalyst was recovered by simple filtration from reaction mixture. It was washed with ethanol and was dried in air before use in subsequent ethylbenzene oxidation reaction.

### **3** | **RESULTS AND DISCUSSION**

## 3.1 | Characterization for grafted catalyst materials

XRD analysis was applied to the cross-linked mesoporous chitosan and Fe TCPP/mesp-CTS. As shown in Figure 1 (left), after cross-linking of glutaraldehyde with partial amino of chitosan, there was one characteristic peak of the cross-linked chitosan at about  $2\theta = 20^{\circ}$  [29]. The XRD patterns of Fe TCPP/mesp-CTS showed one broad peak at about  $2\theta = 20^{\circ}$ , which was similar to that of chitosan, indicating that the amorphous structure of chitosan was unchanged after grafting with Fe TCPP. However, the characteristic peak of Fe TCPP/mesp-CTS was more intense and wider than that of chitosan. This is probably due to the carboxyl groups of Fe TCPP reacted with thionyl chloride(SOCl<sub>2</sub>) to form acyl chloride, which further acylated amino group(NH<sub>2</sub>-) of chitosan, and reduced the amount of amino group(NH<sub>2</sub>-) on chitosan. This reaction could increase the crystallinity of chitosan. These results also indicated that Fe TCPP was grafted on mesp-CTS.

Figure 1(right) displays TG and DTA curves of Fe TCPP/mesp-CTS. It showed that, Fe TCPP/mesp-CTS lost about 1.9% of its moisture, H<sub>2</sub>O, which was hydrogenbonded with amino and hydroxyl groups in mesp-CTS, from 60 °C to 200 °C, and lost about 4.1% of inter water in mesp-CTS after 200 °C, further carbonizing. The above results demonstrated that Fe TCPP/mesp-CTS was stable at 200 °C, which was quite fit to our oxidation conditions between 130 °C and 165 °C.

Figure 2 (left) is UV–vis spectra of Fe TCPP and Fe TCPP/mesp-CTS (Fe TCPP/macp-CTS). A large Soret peak of Fe TCPP was observed at 418 nm. After Fe TCPP was grafted on CTS, two obvious peaks appeared at 413 nm and 429 nm. The saddle-shaped Soret peak may be explained by the coordination between iron porphyrin complex and amino group in CTS, and the acylation reaction between Fe TCPP and CTS. The intensity of



**FIGURE 1** XRD patterns of mesp-CTS (left) and Fe TCPP/mesp-CTS, and TG and DTA curves of FeTCPP/mesp-CTS (right)

Soret peaks of Fe TCPP/CTS was much lower than that of Fe TCPP, which can be ascribed to the small amount of Fe TCPP grafted on CTS. The results indicated that Fe TCPP was immobilized on mesp- and macp-CTS via coordination and acylation. The UV-DRS spectra for Fe TCPP/mesp- and macp-CTS were different from those of Fe TCPP and mesp- and macp-CTS (Figure 2 right), indicating that Fe TCPP was grafted onto mesp- and macp-CTS. This is caused by the reaction of the carboxyl groups in Fe TCPP and the amino groups in mesp- and macp-CTS.

Figure 3 shows the IR spectra of CTS, cross-linked CTS(CL-CTS), Fe TCPP, and Fe TCPP/mesp-CTS (Fe TCPP/macp-CTS). The bands at about 3370 cm<sup>-1</sup> and 3445 cm<sup>-1</sup> in the IR spectra of CTS were assigned to the amino groups and hydroxyl groups of CTS.<sup>[16]</sup> Bands at about 1654 cm<sup>-1</sup> and 1596 cm<sup>-1</sup> were assigned to the O = C and NH<sub>2</sub> of the O = C-NH- and amino groups,



**FIGURE 2** UV-vis spectra at room temperature: (a) solution of Fe TCPP, (b) DMF suspension of Fe TCPP/mesp-CTS (Fe TCPP/macp-CTS) (left). UV-DRS spectra for Fe TCPP/mesp-CTS and mesp-CTS (right)

respectively.<sup>[30]</sup> Bands at 2870 cm<sup>-1</sup> and 2928 cm<sup>-1</sup> were assigned to the stretching vibrations of CH and CH<sub>2</sub> groups, and bands at 1321 cm<sup>-1</sup> was due to the N-acetyl groups.<sup>[31]</sup> After forming the cross-linked CTS, the original broad band at 3370 cm<sup>-1</sup> changed to relatively narrow band at 3445 cm<sup>-1</sup>, which was due to the decrease of amount of amino groups and the relative increase of amount of hydroxyl groups. The bands at about 1654 cm<sup>-1</sup> and 1596 cm<sup>-1</sup> disappeared and a new band appeared at 1606 cm<sup>-1</sup> due to cross-linking of chitosan with glutaraldehyde. The bands at about 3445 cm<sup>-1</sup> and 1698 cm<sup>-1</sup> in the IR spectra of Fe TCPP were attributed to hydroxyl and carbonyl groups in the carboxyl groups of Fe TCPP, respectively. And the band at about



**FIGURE 3** FT-IR spectra of CTS, cross-linked-CTS (CL-CTS), Fe TCPP and Fe TCPP/mesp-CTS (Fe TCPP/macp-CTS) in the range of 4000~400 cm<sup>-1</sup>

999 cm<sup>-1</sup> was believed to be the characteristic peak of Fe–N bond in Fe TCPP.<sup>[32]</sup> When Fe TCPP was grafted on mesp-CTS to form Fe TCPP/mesp-CTS, the original band at 1606 cm<sup>-1</sup> for the amino groups of mesp-CTS, and band at 1698 cm<sup>-1</sup> for the carbonyl groups of Fe TCPP, both disappeared. Instead, a peak at about 1635 cm<sup>-1</sup> for the carbonyl groups (O = C–NH–) in Fe TCPP/mesp-CTS appeared, indicating the acylation of CTS by Fe TCPP. Besides, another new peak at 560 cm<sup>-1</sup> for Fe TCPP/mesp-CTS was observed, which may be caused by the coordination of N atoms in amino groups of CTS to the

iron ions of Fe TCPP.<sup>[23]</sup> These results confirmed that Fe TCPP was immobilized on mesp-CTS.

The morphology of mesp-CTS, macp-CTS and corresponding grafted Fe TCPP were investigated as shown in Figure 4. The SEM images of chitosan-grafted catalyst material showed that Fe TCPP/mesp-CTS provided a mesocavity for mimicking the nano-cavity in cytochrome P-450 enzyme: mesp-CTS and Fe TCPP/mesp-CTS (Figure 4a and b) exhibited mesoporous structure, with a pore diameter (BJH adsorption average pore diameter) of about 47 nm (Figure 4e), and the type of pore were mostly present in the grafted catalyst. The specific surface area of Fe TCPP/mesp-CTS and mesp-CTS, were found to be about 58  $m^2/g$  for both of them. However, macp-CTS and Fe TCPP/macp-CTS showed macroporous structure, the BJH adsorption average pore diameter was about 55.0 nm, and the type of pore were mostly present in the grafted catalyst (Figure 4f). The specific surface area of Fe TCPP/macp-CTS and macp-CTS, both were found to be about 1.4 m<sup>2</sup>/g. Therefore, Fe TCPP/mesp-CTS present the characteristics of mesostructured catalyst material, which would bettering the catalytic activity of Fe TCPP.

The acylation and coordination of Fe TCPP on mesp-CTS(or macp-CTS) changed electron cloud density of all elements, especially the Fe and elements(Cl, N) around it in Fe TCPP. These changes were seen and assigned in Figure 5 and in Table 1.<sup>[33–35]</sup> When the amino groups of mesp-CTS were acylated by Fe TCPP, and the coordination of amino groups in mesp-CTS to Fe TCPP occured, these reactions could cause the following Binding Energy(BE) changes: First, the BEs of nitrogen element in the NH<sub>1 or 2</sub>- $C_{sp}^{3}$  unit of CTS increased about 1.6 eV. This was because the nitrogen atom of amino group donated its electron lone pair to the iron ion in Fe TCPP, and on another hand, the carbonyl group of Fe TCPP attracted the electron lone pair, resulting the increased 1.5 eV of the BEs for the carbon element in the C-C-NH1 or 2 unit. Second, the coordination of the electron lone pair of N in amino group of CTS to the iron ion in Fe TCPP, not only decreased the BEs of Fe ion in the Fe-N unit about 13.7 (5.9) eV, but also caused the decrement of 0.9(0.5) eV for the BEs of chlorine element in the Cl-Fe unit. Third, the BEs of nitrogen elements in the N-Fe unit have increased about 2.3 eV, which indicated that the four-nitrogen-atom-combined iron in Fe TCPP was more stable after immobilization. The immobilzation also resulted the other changes of BEs for other elements shown in Table 1. The coordination of amino groups in mesp-CTS to Fe TCPP will improve the catalytic activity and stability of Fe TCPP, and the acylation of Fe TCPP to mesp-CTS would benefit to the coordination and graft-immobilization of Fe TCPP on mesp-CTS.



## 3.2 | Catalysis of Fe TCPP/mesp-CTS for ethylbenzene oxidation with $O_2$

The effect of reaction temperature on ethylbenzene oxidation reaction was shown on Figure 6a. When the temperature was below 150 °C, the selectivity of ketone and alcohol increased with increasing temperature. However, when the temperature was higher than 150 °C, the selectivity of ketone and alcohol decreased from 72.2% to 68.3%. The selectivity of ketone and alcohol at 145 °C was lower than that at 150 °C, but the ethylbenzene conversion (24.2%), TON ( $3.02 \times 10^5$ ), and yields of ketone and alcohol (16.8%) were the highest than those at other temperatures. The decrease in ethylbenzene conversion at 155 °C could be due to the destruction of the part catalyst at higher temperatures, and the reduction in selectivity at higher temperatures may be attributed to further oxidation of the ketone and alcohol into by-products.<sup>[36]</sup> Therefore, the optimal reaction temperature was 145 °C.

Pressure has an effect on the catalytic activity of Fe TCPP/mesp-CTS, the reaction pressure from 0.7 MPa to 0.9 MPa was investigated at 145 °C, and the results were shown in Figure 6b. Ethylbenzene conversion and TON

**FIGURE 4** SEM images and pore diameter distribution of mesp-CTS (a and e), Fe TCPP/mesp-CTS (b and e), Fe TCPP/macp-CTS (c and f) and macp-CTS(d and f)

slowly increased with increasing pressure from 0.7 MPa to 0.9 MPa, and the biggest ethylbenzene conversion and TON were 24.9% and  $3.12 \times 10^5$  at 0.9 MPa, respectively. However, the selectivity of ketone and alcohol (69.2%) and yields (16.7%) were the highest at 0.8 MPa. Higher oxygen pressure means higher initial oxygen concentration in the oxidation reaction mixture, which accounts for the increasing ethylbenzene conversion with the increasing of pressure. However, after a certain oxygen concentration was reached (0.8 MPa), the ethylbenzene conversion only increased 0.6% with further increasing oxygen pressure to 0.9 MPa. The decrease of selectivity (ketone and alcohol) at 0.9 MPa was because high oxygen concentration overly oxidized ketone and alcohol into byproducts. Furthermore, the high oxygen concentration destroyed a small amount of the metalloporphyrin on the catalyst surface, resulting in its catalysis decrease.<sup>[37]</sup> Based on the above results, the optimal oxygen pressure for the oxidation was 0.8 MPa.

Figure 6c shows the effect of amount of Fe TCPP used in Fe TCPP/mesp-CTS form on its catalytic activity. As the Fe TCPP amount was 0.75 mg, the selectivity to ketone and alcohol (74.3%), and yields (18.2%) were the



**FIGURE 5** X-ray photoelectron spectra and main spectral bands based on the binding energy (BE) of the key elements (Fe, cl, N and C) for Fe TCPP/mesp-CTS, mesp-CTS and Fe TCPP

**TABLE 1** Binding energy of key elements in Fe TCPP/mesp-CTS, Fe TCPP and mesp-CTS

XPS	Existential form of the key elements	Binding energy/eV			
spectra		Fe TCPP/mesp-CTS	Fe TCPP	mesp-CTS	dBE /eV
Fe 2p	<i>Fe</i> –N	710.8 705.5	724.5 711.4		-13.7 -5.9
Cl 2p	<i>Cl</i> –Fe	199.1	200.0		-0.9
N 1 s	N-C = [N = C] N-Fe $NH_1 \text{ or } 2-C_{sp}^3$ $N = C_{sp}^2$	197.9 399.6 399.5 399.3 401.9	198.4 398.7 397.2	 397.7 400.9	-0.5 0.9 2.3 1.6 1.0
C 1 s	C = C C-C-NH <sub>1 or 2</sub> C = O, C-O	285.2 285.1 286.6	284.9  288.9	283.6 284.9	0.3 1.5 1.7,4.0

highest. The ethylbenzene conversion, TON, selectivity (ketone + alcohol), and yields subsequently respectively decreased, as the Fe TCPP amount continued to increase from 0.75 to 1.5 mg. The decrease in yields at high amount of Fe TCPP can be ascribed to that excessive addition of Fe TCPP may improve interactions between activated



**FIGURE 6** Effect of reaction temperature (a), reaction pressure (b), amount of Fe TCPP/mesp-CTS, and reaction time (d) on ethylbenzene oxidation catalyzed by Fe TCPP/mesp-CTS. Reaction conditions: (a) ethylbenzene, 200 ml; pressure, 0.8 MPa; Fe TCPP, 0.75 mg; air flow, 0.03 m<sup>3</sup>/h; rxn time, 4.0 h. (b) Ethylbenzene, 200 ml; temperature, 145 °C; Fe TCPP, 0.75 mg; air flow, 0.03 m<sup>3</sup>/h; rxn time, 4.0 h. (d) Ethylbenzene, 200 ml; temperature, 145 °C; pressure, 0.8 MPa; air flow, 0.03 m<sup>3</sup>/h; rxn time, 4.0 h. (d) Ethylbenzene, 200 ml; temperature, 145 °C; pressure, 0.8 MPa; air flow, 0.03 m<sup>3</sup>/h; rxn time, 4.0 h. (d) Ethylbenzene, 200 ml; temperature, 145 °C; pressure, 0.8 MPa; Fe TCPP, 0.75 mg; air flow, 0.03 m<sup>3</sup>/h



**FIGURE 7** Comparison of the catalytic activity of Fe TCPP/ mesp-CTS with that of Fe TCPP/macp-CTS for oxidation of ethylbenzene. Reaction conditions: Ethylbenzene, 200 ml; temperature, 145 °C; Fe TCPP, 0.75 mg; pressure, 0.8 MPa; air flow, 0.030 m<sup>3</sup>/h; reaction time, 4.0 h (left); situation of Fe TCPP/mesp-CTS recovered (right)

intermediates and suppress the formation of ketone and alcohol.  $^{\left[ 38\right] }$ 

Figure 6d illustrates changes in the ethylbenzene conversion, TON, selectivity and yields of ketone and alcohol with reaction time, for the ethylbenzene oxidation over Fe TCPP/mesp-CTS under an optimal temperature of 145 °C and pressure of 0.8 MPa. From 0 to 4 h, the yields increased with increasing reaction time. From 3.5 to 4 h, ethylbenzene conversion slightly increased from 21.1% to 24.2%, and the selectivity (ketone + alcohol) showed 69.1% at 4 h. According to the previous study, CTS could be destroyed with the increasing of reaction time at a high temperature, and Fe TCPP would be not protected by CTS and was easily destroyed by oxidant.<sup>[15,18]</sup> This would reduce the reuse times of Fe TCPP/mesp-CTS and decrease the catalysis for the ethylbenzene oxidation. So, the 4-h reaction time was chosen as the best time for ethylbenzene oxidation reaction.

### 3.3 | Comparison of the catalytic activity of Fe TCPP/mesp-CTS with Fe TCPP/macp-CTS etc.

To compare the catalysis of Fe TCPP/mesp-CTS with Fe TCPP/macp-CTS for the oxidation of ethylbenzene, the changes in ethylbenzene conversion and yields (ketone + alcohol) with reaction time were shown in Figure 7 (left). The increasing rate of ethylbenzene conversion and yields (ketone + alcohol) obtained from Fe TCPP/mesp-CTS were 6.1%/h and 4.6%/h, respectively, which were higher than those from Fe TCPP/macp-CTS. These differences were partly due to considerable differences in the specific surface area between Fe TCPP/ mesp-CTS and Fe TCPP/macp-CTS. The catalytic activity of Fe TCPP/mesp-CTS could increase with the increment of surface area. The larger the surface area, the more there were the sites for activating molecular oxygen, thus more ethylbenzene could be oxidized. Except for the mesocavity, there still was the especial CRC function in mesp-CTS-grafted iron porphyrin, which was similar to that in cytochrome P-450 enzyme. The function could -WILEY-Organometallic 9 of 11 Chemistry

improve the catalytic activity of Fe TCPP for hydrocarbon oxidation.

According to Table 2, the 1<sup>ST</sup>-run-obtained conversion and the average conversion (22.8%) and yields of ketonealcohol (15.5%) were still higher than those values (21.5% and 15.0%) of Fe TCPP/macp-CTS after 5 cycles. Secondly, when mesp-CTS was used as catalyst or no catalyst was used, the conversion of ethylbenzene and the yields (ketone + alcohol) were lower than 4.1% and 3.5%, respectively, and these results were attributed to the auto-oxidation of ethylbenzene. Under the same reaction conditions, using the Fe TCPP/mesp-CTS as catalyst for the first run (Table 2), the catalytic power for Fe TCPP/mesp-CTS was almost the same as that of Fe TCPP. This result indicated that the catalytic activity of Fe TCPP was maintained. However, when Fe TCPP was ligated on the mesp-CTS, the CRC would work. During the catalytic oxidation process, the surface of Fe TCPP/mesp-CTS was scorched. Therefore, a very small part of Fe TCPP was lost in the recovered process, resulting in the decrease of recovered amount of iron porphyrin (Figure 7 right). However, the TON had increased more than 5 times when

 TABLE 2
 Catalytic activity of reused Fe TCPP/mesp-CTS, Fe TCPP/macp-CTS and Fe TCPP

Catalysts	Run	Conversion/%	Selectivity/%	Ton/(×10 <sup>5</sup> )	Yields/%
Fe TCPP/mesp-CTS	1	24.4	74.3	4.0	18.2
	2	21.5	66.1	4.6	14.2
	3	24.1	69.4	7.3	16.7
	4	22.1	65.2	10.1	14.4
	5	21.7	64.6	22.7	14.0
	Av.	22.8	67.9	9.7	15.5
CTS or no catalyst	1	<4.1	<84.8	-	<3.5
Fe TCPP	1	24.0	73.8	3.1	18.4
Fe TCPP/macp-CTS	1	21.5	69.6	2.8	15.0

Reaction conditions: ethylbenzene, 200 ml; temperature, 145 °C; Fe TCPP, 0.75 mg; pressure, 0.8 MPa; air flow, 0.030 m<sup>3</sup>/h; reaction time, 4.0 h.



SCHEME 1 Plausible mechanism of ethylbenzene oxidation over Fe TCPP/ mesp-CTS

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the grafted catalyst was reused from  $1^{\text{st}}$  to  $5^{\text{th}}$  run. The average values of TON ( $22.7 \times 10^5$ ) was more than 3 times of those ( $3.1 \times 10^5$  and  $2.8 \times 10^5$ ) for the Fe TCPP and Fe TCPP/macp-CTS catalysts. The results are attributed to the above coordination and mesocavity, which resulted in the above stability and activation of Fe TCPP, which has some reason as following.

Lyons proposed a hypothetical catalytic mechanism of hydrocarbon oxidation over iron porphyrin, which was similar to that of the P-450 enzyme.<sup>[39]</sup> According to the previous studies,<sup>[23,40,41]</sup> it is believed that the catalytic mechanism for hydrocarbon oxidation over the supported M TCPP are similar to that of M TCPP:

With the negative dBEs of Fe and Cl ion, the repulsive Coulomb force between elements of like charge between the Fe ion and the chloride ion of ClFe<sup>III</sup> TCPP/mesp-CTS was bigger than that of ClFe<sup>III</sup> TCPP. Therefore, chlorine radical was produced for the ClFe<sup>III</sup> TCPP/mesp-CTS more easily than the ClFe<sup>III</sup> TCPP when the ClFe<sup>III</sup> TCPP/ mesp-CTS was heated<sup>[34]</sup> (Scheme 1). The simultaneously generated Fe<sup>II</sup> TCPP/mesp-CTS radical would immediately react with  $O_2$  to form  $\bullet O_2 Fe^{III}$  TCPP/mesp-CTS, and then reacted with the Fe<sup>II</sup> TCPP/mesp-CTS to form an  $O = Fe^{IV}$  TCPP/mesp-CTS. The  $O = Fe^{IV}$  TCPP/ mesp-CTS intermediately oxidized a H-C bond of ethylbenzene, forming [mesp-CTS/TCPP Fe<sup>III</sup>OHPh-CHCH<sub>2</sub>•]. Whereafter, ethyl benzene radical and hydroxyl radical escaped, causing the subsequent reduction of Fe<sup>III</sup> to Fe<sup>II</sup> species. Then, the radical chain reactions was occurred: [Ph-CHCH<sub>3</sub>]• reacted with •OH radicals to produce 1phenylethanol, Ph-CHOHCH<sub>3</sub>.And another part of the radicals reacted with O<sub>2</sub> to produce ethylbenzene hydroperoxide, Ph-CH(OOH)CH<sub>3</sub> discomposed acetophenone and water. Finally, the reduction-obtained Fe<sup>II</sup> species, Fe<sup>II</sup> TCPP/mesp-CTS reacted with chlorine radical, going back to the starting catalyst materials, ClFe<sup>III</sup> TCPP/mesp-CTS.

#### 4 | CONCLUSION

Fe TCPP was successfully immobilized on mesoporous chitosan by acylation and coordination. The catalytic activity of Fe TCPP for the oxidation of ethylbenzene was improved by modeling the nano-cavity and regulation-catalysis function via the coordination of cysteine to iron center in the cytochrome P450 enzyme. The coordination changed the BEs of iron center in Fe TCPP, and thus improved the catalytic activity, stability and reusability of Fe TCPP for ethylbenzene oxidation. The utilization of mesoporous CTS improved the touching chance of Fe TCPP with  $O_2$  and ethylbenzene, profiting the oxidation of substrate. This shows that Fe TCPP/mesp-CTS can

mimic the nano-cavity and coordinate regulation-catalysis function of cytochrome P-450 enzyme.

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