

Metalloporphyrin-Based Porous Coordination Polymers: Synthesis, Served as Heterogenous Catalysts and Dye Scavengers

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Abstract Six metalloporphyrin-based porous coordination polymers, $Mn^{II}(TCP)-Mn^{II}$ (CP1), $Fe^{III}(TCP)-Fe^{III}$ (CP2), $Co^{II}(TCP)-Co^{II}$ (CP3), $Ni^{II}(TCP)-Ni^{II}$ (CP4), $Cu^{II}(TCP)-Cu^{II}$ (CP5) and $Zn^{II}(TCP)-Zn^{II}$ (CP6), (TCP=5,10,15,20-tetra(4-(phenoxy-4-yl)butanoic acid) porphyrin tetravalent anion) were prepared and characterized. CP1, CP2, CP3, CP4 and CP6 are amorphous aggregation supported by SEM, TEM and powder XRD. **CP5** is a small particles aggregation with lower crystallinity. These coordination polymers exhibit effective dye scavenging and catalytic activities toward the oxidation of alkylbenzene to ketones, and can be reused by filtration with slight decreasing of catalytic activities.

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1 Introduction

Metalloporphyrins have been extensively studied in the past several decades for hydroxylation of alkanes and epoxidation of alkenes [1-7]. When used as homogeneous catalysts, unfortunately, they often suffer from quick degradation such as ligand oxidation or μ -oxo dimer formation [8]. Therefore, it would be advantageous to anchor and isolate catalytically active metalloporphyrins, prohibiting their oxidative degradations and self-dimerizations [2, 9-12]. Initially, metalloporphyrins were immobilized onto organic (e.g. polymers, ion-exchange resins) or inorganic supports (e.g. zeolites, silica, clays) with the interaction of organic covalent bonds [1, 3, 4, 13–15], electrovalent bonds or van der Waals interactions (physical adsorption) [2]. Although covalently bounded of polymers supported metalloporphyrin catalysts are much more stable than the inorganic supported entities, few suitable porphyrins or polymer supports could be qualified. Recently, crystalline metal-organic coordination frameworks (MOF) based catalysts were proposed and experimentally demonstrated [5, 6, 16-23], such as the well known PIZA-3, a capable and robust oxidation catalyst for the hydroxylation of a variety of linear and cyclic alkanes and the epoxidation of cyclic alkenes [16]. Despite attractive approaches to the construction of catalytic metalloporphyrins MOF developments, for instance heterogenization of well-defined homogeneous catalysts incorporated as MOF struts [17-19], MOF-encapsulation of molecular catalysts, and post-synthesis incorporation of catalytic metal sites [11], only few metalloporphyrins MOF have been shown to be both catalytically competent and porous with respect to chemical reactants [18, 20]. One of the problems encountered in building robust and catalytic MOF from porphyrins or metalloporphyrins, plaguily, is that amorphous coordination polymers tend to be generated, instead of crystalline frameworks. The metalloporphyrin-based coordination polymers (MpCP) is lower crystallinity or even amorphous coordination polymers, from which to distinguish crystalline frameworks. Similar to the well-known MOF, the MpCP is constructed from metalloporphyrins as metalloligand linkers and metal ions or metal ions clusters as nodes by bonding these two components with coordination bonds that is a type of chemical bonds. The metalloligand linkers, metalloporphyrins, that's one of the key factors of MpCP. On one hand, the metal ions situated in the centers of the metalloporphyrins can be changed arbitrarily according to your will. On the other hand, periphery substituent groups of the metalloporphyrins can be designed in accordance with the need to, such as length, rigid or flexible, and the atoms coordinating to nodes. Owning these two merits, metalloporphyrins render the MpCP materials more accessible to functionalize and structural design.

Bearing all of the above in mind, and follow our previous studies [24] we designed a new porphyrin, 5,10,15,20-tetra(4-(phenoxy-4-yl)butanoic acid)porphyrin (H_2 TCP, see Scheme 1), given elongate and flexible periphery substituents. Such porphyrin bears flexibility substituents, on one hand, would be formed the steady structures of coordination polymers, in which the metalloporphyrins could be preferred orientation for the variability of the substituents' stretching direction. On the other hand, the polymers could change their structures accordingly on different substrate molecules in the processes of catalytic reactions, in order to respond to the different substrates. The MpCPs,



Scheme 1 Scheme of reaction for **a** synthesis of the methyl 4-(4-formylphenoxy) butanoate; **b** synthesis of metal-free porphyrins $H_2(TMEP)$ and $H_2(TCP)$

those are $Mn^{II}(TCP)-Mn^{II}$ (**CP1**), $Fe^{III}(TCP)-Fe^{III}$ (**CP2**), $Co^{II}(TCP)-Co^{II}$ (**CP3**), $Ni^{II}(TCP)-Ni^{II}$ (**CP4**), $Cu^{II}(TCP)-Cu^{II}$ (**CP5**) and $Zn^{II}(TCP)-Zn^{II}$ (**CP6**), were synthesized from the custom designed porphyrin and excess metal ions, of which the porphyrin cores can be in situ metalated readily with metal ions. These MpCPs exhibit catalytic activities and selectivities toward the oxidation of alkylbenzene, of which **CP1** catalytic performance is the best relatively, unfortunately, the yield declined slightly by reused. Without detectable catalysts leaching, fortunately, after three times consecutively reused. Meanwhile, the dye adsorption properties of the MpCPs have been examined, the **CP5** exhibits optimum performance relatively.

2 Experimental

2.1 Chemicals and Instruments

All solvents and reagents were used as received without further purification, except for pyrrole and *N*,*N*-dimethyl formamide (DMF) which were distilled before used. The 4-hydroxybenzaldehyde and methyl 4-bromobutyrate were commercially available from Beijing chemical reagents company. The alkylbenzene used as substrates were commercially available from ChengDu Kelong Chemical Reagent Company. The oxidant *tert*-butyl hydroperoxide (TBHP) was commercially available from Sinopharm Chemical Reagent Co., Ltd. The thin layer chromatography (TLC) was performed on silica gel GF254 plates. Chromatographic separations were carried out on silica gel (100–200 mesh).

UV-Vis spectra were measured on a Shimadzu UV1800 spectrophotometer. The mass spectrometry analyses (MS) were carried out using a MALDI-TOF MS (Shimadzu Biotech). Infrared spectra were obtained on a BEQ UZNDX₅50-FTIR spectrophotometer (Bruker) using KBr pellets. C, H, N elemental analyses were performed on a Vario EL-III apparatus (Bruker). ¹H NMR spectra were measured on a Varian INOVA-400 spectrometer (400 MHz, Varian, U.S.) by using tetramethylsilane (TMS) as an internal standard, with the chemical shifts relative to TMS. Scanning electron microscope (SEM) images were recorded on a Quanta 400FEG microscopes. Transmission electron microscopy (TEM) images were obtained using JEOL JEM-3010 microscopes. The powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 diffractometer using graphite monochromatic copper radiation (Cu Kα) at 40 kV, 30 mA over the 2θ range from 5° to 50°. Surface area experiments were performed at 77 K on a TriStar II 3020 apparatus (Micromeritics) using nitrogen as the probing gas. Thermal gravimetric analysis (TGA) were performed in flowing N₂ with a heating rate of 10°C min⁻¹ from 30 to 800°C on a Perkin-Elmer TGA-7 instrument. GC analyses were performed using a GC1100 chromatograph (PERSEE Beijing, China), N_2 as the carrier gas (35 cm³ min⁻¹) and equipped with a fused silica capillary 5% phenyl 95% dimethylpolysiloxane column (SE-54, 30m×0.32 mm).

2.2 Synthesis

2.2.1 Synthesis of Methyl 4-(4-Formylphenoxy) Butanoate

In a 100 mL three-necked flask, a mixture of 4-hydroxybenzaldehyde (2.49 g, 20 mmol), methyl 4-bromobutanoate

Compd	EDS			UV–Vis	IR			GC-MS		
	С	N	0	M (%) Mass (%)	$\lambda_{ m max}$, nm	$\overline{v^{s}_{COO}}^{-}$ cm ⁻¹	$ u_{\rm Mn-N} $ cm ⁻¹	$\omega_{ m N-H}$ cm ⁻¹	Found amu	Calcd amu
	Mass (%)	Mass (%)	Mass (%)							
H ₂ (TMEP)					421, 519, 554, 593, 650			966	1079.5 ^a	1078.4
H ₂ (TCP)					419, 518, 555, 595, 651			978	1023.4 ^a	1022.4
CP1	55.32	9.05	14.05	21.63	389, 468, 542, 584	1344	995			
CP2	56.26	8.30	13.43	22.01	403, 469, 544, 594	1337	991			
CP3	57.70	7.65	15.65	21.65	423, 549, 593	1342	995			
CP4	52.88	7.28	14.53	25.31	420, 550, 592	1343	997			
CP5	53.67	7.19	14.38	24.76	435, 551, 590	1329	988			
CP6	53.79	7.16	14.78	24.27	420, 550, 590	1337	991			

Table 1 Data of EDS, UV-Vis, FT-IR and GC-MS spectra of porphyrins and CP1-CP6

^a[M+H]⁺ charged

(3.67 mL, 20 mmol) and dried K₂CO₃ (2.78 g, 20 mmol) was stirring in distilled DMF (30 mL) at 80 °C under a nitrogen atmosphere for 6 h. The reaction mixture was decanted into cold water to remove the K₂CO₃. When K₂CO₃ dissolved completely, the mixture extracted with ethyl acetate. The organic layer was washed with NaCl saturated aqueous solution, dried over MgSO₄ and evaporated to remove most of ethyl acetate. Amount of cold water was added in the oily residual, the crude product, white precipitate was present. Finally, acicular crystal transparent of desired product, methyl 4-(4-formylphenoxy) butanoate, was obtained by recrystal with ethanol. Yield: 52%; Mp: 65 °C; elemental analysis Calcd. for C₁₂H₁₄O₄: C, 64.85; H, 6.35; found: C, 65.13; H, 6.32.

2.2.2 Synthesis of $H_2(TMEP)$ and $H_2(TCP)$

Methyl 4-(4-formylphenoxy) butanoate (6.67 g, 30 mmol) was dissolved in propionic acid (120 mL), and was heated to reflux at 140 °C. Then distilled pyrrole (2.70 mL, 40 mmol) was added dropwise and the mixture was refluxed for 1 h. When cooling to room temperature, $\sim 80\%$ of the solvent was evaporated and 40 mL ethanol was added. Then the mixture was cooled overnight in refrigerator and collected the crude product by suction filtration. The crude product was purified by chromatography on a silica-gel column with CH2Cl2 as the eluent solvent, and collected the first band, a desired purple solid of compound H₂(TMEP) was obtained. Yield: 15%; Mp: >250°C; elemental analysis Calcd. for C₆₄H₆₂N₄O₁₂: C, 71.23; H, 5.79; N, 5.19; found: C, 71.04; H, 6.03; N, 5.15; MS observed $[M+H]^+$: 1079.5 amu, calculated M: 1078.4 amu; UV–Vis (nm, CH₂Cl₂) λ_{max} : 421 (Soret band), 519, 554, 593, 650 (Q bands); FT-IR (cm⁻¹): 2952, 1734, 1606, 1508, 1472, 1244, 1174, 1051, 966, 808. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.85 (8H, Pyrrole-H), 8.10 ~ 7.08 (16H, Ar-H),

4.81, 4.78 (2H, $-H_2C-COO-$), 2.74 ~ 2.70 (3H, CH₃), 2.32, 2.28 (2H, $-OCH_2-$), 1.61 (2H, $-CH_2-$), -2.77 (2H, N–H).

H₂(TCP) was obtained by alkaline hydrolysis of the H₂(TMEP). H₂(TMEP) (0.20 g, 0.18 mmol) was dissolved in tetrahydrofuran (15 mL), and KOH aqueous solution (25 mL, 10%) was added, then heated to reflux. The reaction progress was monitored by TLC. After the reaction, most of tetrahydrofuran was removed by vacuum distillation, and a lot of distilled water was added in residue, dissolved it. Finally, amount of H₂(TCP) precipitated from the solution which acidized with concentrated HCl to pH 3. The product was washed with distilled water and ethanol until the filtrate to colorless. Yield: 95 %; Mp: >250 °C; Elemental analysis Calcd. for C₆₀H₅₄N₄O₁₂: C, 70.44; H, 5.32; N, 5.48; Found: C, 70.91; H, 5.56; N, 4.95; MS observed $[M+H]^+$: 1023.4 amu, calculated M: 1022.4 amu; UV–Vis (nm, DMF) λ_{max} : 423 (Soret band), 520, 558, 594, 651 (Q bands); FT-IR (cm⁻¹): 3101, 2964, 1711, 1593, 1501, 1474, 1250, 1167, 1024, 978, 814.

2.2.3 Synthesis of M(TCP)-M ($M = Mn^{II}$, **CP1**; Fe^{III}, **CP2**; Co^{II}, **CP3**; Ni^{II}, **CP4**; Cu^{II}, **CP5**; Zn^{II}, **CP6**)

A mixture of H_2TCP (0.010 g, 0.01 mmol), Mn(CH₃COO)₂·4H₂O (0.015 g, 0.06 mmol) and DMF (4 mL) was stirred, and then sealed in a 10 mL Teflonlined stainless steel reactor, kept under autogenous pressure at 90 °C for 72 h. The dark-purple precipitate of reaction was filtered and washed with water, DMF, CH₂Cl₂ and ethanol to remove any unreacted monomer. The target product Mn^{II}(TCP)-Mn^{II} (**CP1**) was dried at 45 °C under vacuum for 12 h. **CP2, CP3, CP4, CP5** and **CP6** were prepared following the procedure described for **CP1** except that Fe(NO₃)₃ (0.015 g, 0.06 mmol), Co(CH₃COO)₂·4H₂O (0.015 g, 0.06 mmol), Ni(CH₃COO)₂·4H₂O (0.015 g, 0.06 mmol), Cu(CH₃COO)₂·H₂O (0.012 g, 0.06 mmol)



Fig. 1 UV-Vis spectra of CP1-CP6 in solid

and $Zn(CH_3COO)_2 \cdot 2H_2O(0.013 \text{ g}, 0.06 \text{ mmol})$ were used instead of $Mn(CH_3COO)_2 \cdot 4H_2O$.

2.3 Oxidation Procedure and Catalysts Reuse

All the oxidation reactions were carried out in a sealed vial. A mixture of alkylbenzene (1.2 mmol), TBHP (3.6 mmol) and the catalyst (**CP1–CP6**, 0.02 mmol, 5 mg) in water (2.5 mL) was stirred at 80 °C for 24 h. When time up, the results of reaction were examined by GC. ¹H NMR and MS spectral data confirmed the identities of the product. The catalyst was recovered by centrifugation, washed with water and ethanol successively, and dried in vacuum at 45 °C to remove the solvent for several hours before new utilization under similar reaction conditions.

After the use of catalyst for three consecutive times, the ketone yield declined slightly and the selectivity remained over 99%. The leaching experiments were made in the same conditions described above, after 24 h of reaction the catalyst was isolated by centrifugation and no characteristic spectrum of the porphyrin or metalloporphyrin was detectable in the supernatant by UV–Vis.

2.4 Dye Adsorption Tests

Two typical dye molecules methylene blue (MB) and rhodamine B (RB) were used to examine the adsorption properties of **CP1–CP6** in further study. **CP1–CP6** (5 mg) was added to dye aqueous solution (10 mL, 50 mg L⁻¹) with continuously stirring at room temperature for 24 h, respectively. The solution and adsorbent were separated by



Fig. 2 Illustration of CP1-CP6, assembled from metalloligands and metal ions nodes

centrifugal, and the concentration of dye in solution was determined by UV-Vis.

3 Results and Discussion

3.1 Synthesis and Characterization of H₂(TMEP) and H₂(TCP)

In order to ensure that the designed porphyrin bears long flexible substituents, as shown in Scheme 1, the aldehyde with the substituents, methyl 4-(4-formylphenoxy) butanoate, was synthesized firstly. It is known that Adler synthesis is a convenient strategy for preparing porphyrin derivatives by the condensation of pyrrole and aldehyde [25–29]. So that the metal-free tetr-methyl ester porphyrin, H₂(TMEP), was prepared by condensation of pyrrole with methyl 4-(4-formylphenoxy)butanoate in hot propionic acid. The metal-free tetr-carboxylic porphyrin, H₂(TCP), was obtained by hydrolysis of H₂(TMEP) in KOH aqueous solution.

UV–Vis spectroscopy is a convenient method, through which can quickly determine the formation of the porphyrin ring. The UV–Vis spectra of H₂(TMEP) and H₂(TCP) have Soret band at 421 and 419 nm, and Q bands located at 519, 554, 593, 650 and 518, 555, 595, 651 nm, respectively (see Table 1 and Fig. S1 in Supplementary Material). These characteristic spectral data of porphyrin derivatives are similar to Spellane [30], Kadish [31] reports and our previous studies [24]. In the infrared spectra of H₂(TMEP) and H₂(TCP), absorption bands of $\nu_{\text{Benzene ring in}}$ the regions of 1606, 1508, 1472 cm⁻¹, $\nu_{C=0}$ in 1734 cm⁻¹,



Fig. 3 SEM images of CP1 (a), CP2 (b), CP3 (c), CP4 (d), CP5 (e) and CP6 (f)



Fig. 4 TEM images of CP1 (a), CP2 (b), CP3 (c), CP4 (d), CP5 (e) and CP6 (f)



Fig. 5 Powder XRD pattern of CP1-CP6



Fig. 6 TGA of CP1-CP6

 $\omega_{\rm N-H}$ in 966 cm⁻¹ for H₂(TMEP) and $\nu_{\rm Benzene ring}$ in 1593, 1501, 1474 cm⁻¹, $\nu_{\rm C=0}$ in 1711 cm⁻¹, $\omega_{\rm N-H}$ in 978 cm⁻¹ for H₂(TCP) accordingly (see Fig. S2 and Table S1). The UV–Vis and infrared spectra provide limited information as to the formation of different porphyrin derivatives, but these are not the case for the mass spectral (MS) data which are quite definitive. The MS data in accordance with the expected value of H₂(TMEP) and H₂(TCP), which are also consistent with the elemental analysis and ¹H NMR of H₂(TMEP) [31–33] (see Table 1, Scheme 1 and Fig. S6). All the above, indicating the isolated porphyrins, H₂(TMEP) and H₂(TCP), are consistent with the structures illustrated in Scheme 1.

3.2 Synthesis and Characterization of M(TCP)-M (M=Mn^{II}, CP1; Fe^{III}, CP2; Co^{II}, CP3; Ni^{II}, CP4; Cu^{II}, CP5; Zn^{II}, CP6)

The MpCPs, **CP1**, **CP2**, **CP3**, **CP4**, **CP5** and **CP6**, were prepared from the custom designed porphyrin $H_2(TCP)$ and excess metal ions in DMF under solvothermal. Meanwhile, the porphyrin cores were in situ metalated with the metal ions. In Fig. 1, the UV–Vis spectra of **CP1–CP6** show the characteristics of metalloporphyrins. The Soret bands of **CP1** and **CP2** blue shift, respectively, to 389 and 403 nm, and those of **CP3–CP6** red shift slightly to 423, 420, 435 and 420 nm. All O bands of CP1-CP6 were reduced to two ones. It is suggested that the porphyrins of CP1-CP6 are metalated, and MpCPs are mainly composed of M(TCP) units. Although most of the absorption bands observed in the infrared spectra of CP1-CP6 are due to the porphyrins themselves, the subtle differences between the spectra of the custom-designed porphyrins and CP1-CP6 suggest that the structure distinction of them. An infrared spectral feature common to $H_2(TMEP)$ and H₂(TCP) is a wagging vibration absorption band of $\omega_{\rm N \ H}$ in the regions of 966 and 978 cm⁻¹ (Table 1). These bands are present in each spectrum of metal-free porphyrin and absent from those of CP1-CP6. Meanwhile, a stretching vibration absorption band of ν_{Mn-N} in the region of 988–997 cm⁻¹ is present in each spectrum of CP1-CP6 and absent from that of the metal-free porphyrin (Table 1) [34]. These subtle differences between the infrared spectra of the porphyrins and CP1-CP6 indicate that metal cations are locating at the cores of porphyrins and coordinating to four nitrogen atoms in the MpCPs, which are consistent with the UV-Vis spectra of **CP1–CP6**. In addition, it can be seen the $v_{C=0}$ absorptions of $H_2(TMEP)$ and $H_2(TCP)$ in the region of 1734 and 1711 cm⁻¹, as shown in Fig. S2 and Table S1, those are absent from spectra of CP1-CP6. Meanwhile, $\nu_{\rm COO}^{\rm s}$ absorption bands of **CP1–CP6** are present in the region of 1340 cm⁻¹, which indicate that the peripheral carboxyl of M(TCP) are ligating the nodes of metal ions (Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}) in CP1-CP6. Consequently, the recommended structure of CP1-CP6 is shown in Fig. 2, metalloligands of M(TCP) combine with nodes of metal ions (Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}) forming the extension structure.

Figures 3 and 4 show the SEM and TEM images of **CP1–CP6**. The morphologies of **CP1, CP2** and **CP6** are spherical particles, they are aggregations made up of different shape of smaller particles actually, which can be seen from the TEM images (Fig. 4a, b, f). The morphology of **CP3** is willow leaf shape, and **CP4** is long granular particles. The powder XRD patterns indicate that **CP1, CP2, CP3, CP4** and **CP6** are amorphous aggregations (see Fig. 5). **CP5** is also an aggregation with uniform particle size, and PXRD showed that it is a substance has a certain degree of crystallinity.

BET specific surface areas and most probable poresizes of the **CP1–CP6** based N_2 adsorption data are summarized in Table 2. **CP1–CP6** have similar isotherm profiles, and show type II ones with almost no hysteresis loops (Figs. S7, S8, S9, S10, S11, S12). In addition, the wide ranges of pore-sizes of **CP1–CP6** indicate that the pores are primarily attributed to the accumulation of particles, which can also be seen from the SEM and TEM images. These suggest that the adsorption occurred

Catalysts	Substrates	Products	Yield ^a , % 1st, 2nd, 3rd	Selectivity ^a , % 1st, 2nd, 3rd	Specific surface area ^b , m ² g ⁻¹	Most probable pore size ^b , nm
CP1		0 I	82.1, 79.4, 78.1	>99, >99, >99	116.4	25
	$\bigcirc \frown$		56.0, 55.2, 54.0	>99, >99, >99		
			85.0, 83.2, 80.0	>99, >99, >99		
CP2	\bigcirc		75.2,74.2,72.3	>99, >99, >99	98.8	30
	$\bigcirc \frown$		48.0, 47.1, 46.2	>99, >99, >99		
			56.0, 55.3, 54.0	>99, >99, >99		
CP3	\bigcirc		68.1, 66.0, 65.0	>99, >99, >99	109.8	25
	$\bigcirc \frown$		37.5, 37.0, 36.0	>99, >99, >99		
			20.3, 20.0, 19.8	>99, >99, >99		
CP4	\bigcirc		5.0, 4.5, 4.3	>99, >99, >99	59.8	19
			4.5, 4.0, 4.0	>99, >99, >99		
			4.0,4.0,3.9	>99, >99, >99		
CP5	\bigcirc		61.0, 60.0, 58.1	>99, >99, >99	119.4	25
			32.5, 30.2, 30.0	>99, >99, >99		
			18.2,18.1,18.0	>99, >99, >99		
CP6	\bigcirc		34.9, 34.0, 33.2	>99, >99, >99	105.8	34
	$\bigcirc \frown$		23.4, 23.0, 22.1	>99, >99, >99		

 Table 2
 Oxygenation of alkylbenzene with TBHP catalyzed by CP1–CP6

Table 2 (continued)

Catalysts	Substrates	Products	Yield ^a , % 1st, 2nd, 3rd	Selectivity ^a , % 1st, 2nd, 3rd	Specific surface area ^b , m ² g ⁻¹	Most probable pore size ^b , nm
		0 U	22.5, 22.0, 22.0	>99, >99, >99		
Blank		o V V	Trace	>99		
	$\bigcirc \frown$		Trace	>99		
			Trace	>99		

Reaction conditions: alkylbenzene (1.2 mmol), TBHP (3.6 mmol), catalyst (5 mg), H₂O (2.5 mL), temperature 80 °C, time 24 h

^aGC yield based on starting substrate

^bBET specific surface area of catalysts before the 1st cycle, N₂ adsorption isotherm measurements at 77 K





mainly on the external of particles. So, presumably, catalytic reactions likewise occur on the particles surface of the MpCPs.

Thermogravimetric analysis was taken to examine the thermal stability of **CP1–CP6**. As can be seen in Fig. 6, **CP1, CP3** and **CP4** have similar mass loss processes, the first mass loss should be attributed to solvent molecules. With the temperature increased there are plateaus, subsequently, the second weight loss began in 240, 230 and 300 °C for the **CP1, CP3** and **CP4**, respectively, which should correspond to decomposition of polymers structures. So that stable state can be maintained for the **CP1, CP3** and **CP4** below 240, 230 and 300 °C. **CP2, CP5** and **CP6** underwent continuous processes of weight loss, there is no plateau. However, the stable state of **CP2, CP5** and **CP6** could be maintained below 360, 290 and 320 °C, since there are inflection points in the TGA curves of the MpCPs in the temperatures.

3.3 Alkylbenzene Oxidation with TBHP Catalyzed by CP1–CP6

To assess the catalytic properties of the new heterogeneous catalysts, the oxidation of alkylbenzene were carried out using TBHP as the oxidant. In Table 2 are summarized the results of ethylbenzene, propylbenzene and diphenylmethane oxidation catalyzed by **CP1–CP6**, respectively. It is show that all of **CP1–CP6** exhibited catalytic activities toward the oxidation of the three substrates to ketones, and the selectivities were over 99% indicating the products were almost ketones. Among them, the catalytic performance of **CP1** was the best to all of the three substrates, however, that of **CP4** was the worst. This result is consistent with our previous researches, which is quite possibly because the **CP1** is based on manganese porphyrin, and the high catalytic activities of manganese porphyrins have been confirmed Table 3Oxygenation ofethylbenzene with TBHPcatalyzed by CP1–CP6 andother catalysts

Catalysts	Ethylbenzene	Selectivity, %	Tempera-	Time, h		
	conversion, %	Acetophenone	Other products	ture, °C		
CP1	82.1	>99	_	80	24	
CP2	75.2	>99	_	80	24	
CP3	68.1	>99	_	80	24	
CP4	5.0	>99	_	80	24	
CP5	61.0	>99	_	80	24	
CP6	34.9	>99	_	80	24	
$Mn^{III}(F_{10}CPp)-Ni^{II}$ [24]	82	>99	_	65	12	
$[(pymox-Me_2)RuCl_2]^+BF_4^-$ [36]	95	83 ^a	_	20	16	
5 wt% Ag/SiO ₂ [37]	38	88	12 ^b	120	12	
CeO ₂ nanorods [38]	88	65	35 ^e	105	120	
Si/Al- <i>pr</i> -NH- <i>et</i> -N = methyl- 2-pyridylketone-Mn [39]	67	93	2.7 ^c , 4.3 ^d	80	24	
Pd-nanoparticles [40]	92.3	93.5	0.5 ^c , 6.0 ^d	130	24	
MnSBA-15 [41]	25	37	62 ^d	80	8	
Mn-MCM-41 [42]	60	39	10 ^c , 50 ^d	80	24	
CNCr-2 [43]	45	69	30 ^d	70	8	
Co/MCM-41 [44]	26	85	9.1 ^c , 5.9 ^d	80	24	
Zr-K-OMS-2 [45]	62	98	2.0 ^d	65	10	
NMC [46]	88.3	53.4	_	80	24	
[Co(TCPp)]·2DMF [47]	83.1	>99	_	80	20	
ZJU-18 [48]	>99	>99	-	65	48	
CoZnAl-MMO/Al ₂ O ₃ [49]	69.5	80.4	12.1°, 7.5 ^d	120	12	

NMC nitrogen-doped mesoporous carbons

^aIsolated product yields

^b1-Phenylethanol

^cBenzaldehyde

^dOther products

^e1-Phenyl-ethyl-tert-butyl-peroxide



Fig. 7 Catalysts reuse of CP1-CP6

by predecessors' researches [1–7, 35]. Accordingly, we tentatively speculate that the catalytic activities of the **CP1–CP6** could be attributed to the M(TCP) units which are immobilized by ligating to nodes of metal ions (Mn^{II} , Fe^{III}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}) in the MpCPs to prevent their self-dimerization and oxidative degradation. In the three substrates, the conversion rate of ethylbenzene is relatively high for smaller molecule size. But the MpCPs have no size selectivity, because all of them have catalytic abilities for the substrates, which suggest that the catalytic reactions occur on the surface of the MpCPs particles.

In view of only ketones were formed as main products and no other product was found to be forming, as shown in Scheme 2, alkylbenzene oxidation with TBHP should follow a free radical mechanism in the presence of **CP1–CP6** catalysts (see Fig. S16). Possibly, the **CP1–CP6** catalysts act as an initiator in the homolysis of *t*-BuOOH (TBHP) into free alkoxy (*t*-BuO·) and alkylperoxy radicals (*t*-BuOO·) [37, 38]. Subsequently, oxidation

Table 4	The adsorption
capacitie	s of CP1-CP6 for the
dyes of M	AB and RB

Dyes	$\begin{array}{c} \textbf{CP1} \\ \textbf{Q} \ (mg \ g^{-1}) \end{array}$	$\begin{array}{c} \textbf{CP2} \\ Q \ (mg \ g^{-1}) \end{array}$	$CP3 Q (mg g^{-1})$	$CP4 Q (mg g^{-1})$	$\begin{array}{c} \textbf{CP5} \\ Q \ (mg \ g^{-1}) \end{array}$	$\begin{array}{c} \mathbf{CP6} \\ \mathbf{Q} \ (\mathrm{mg \ g}^{-1}) \end{array}$
MB	83	96	89	80	99	92
RB	88	95	85	78	98	89

takes place at the α -carbon of the alkylbenzene [39]. Formation of the product ketones have been illustrated in Scheme 2.

Considering the higher conversion rate of ethylbenzene in the three substrates, in Table 3, the catalysts examined in the present work and the other ones in previous literatures used for oxidation of ethylbenzene with TBHP are compared under different conditions. When the ethylbenzene conversion (82.1%) and selectivity to acetophenone (>99%) obtained in this work were compared with other published data, it can be observed that the catalyst of **CP1** employed here behaves in a comparable way, or even better, in most cases with respect to other catalysts.

The stabilities of the heterogeneous catalysts **CP1–CP6** were examined through repeated oxidations of the three substrates using TBHP (see Fig. 7). The catalysts were isolated, washed exhaustively with water, DMF and ethanol, successively, and dried before being used for the fresh substrates and TBHP. There is a certain degree of decreasing of catalytic activities, when the catalysts were consecutively reused three times, however, without detectable catalysts leaching.

3.4 Dye Adsorption Tests

Dyes are extensively used to produce attractive colours in industries such as textile, paper-making, cosmetic and leather. Furthermore, dyes form highly chronic toxicity complexes by combining with various heavy metal oxides in wastewater, which should be treated before discharged. In addition, adsorption and separation of dyes in wastewater is a potential application of MOF [50, 51]. So here, we employed the most commonly used two dyes, methylene blue (MB) and rhodamine B (RB), to investigate dye adsorption properties of the MpCPs. In aqueous solutions of MB and RB (50 mg L^{-1}), the MpCPs of **CP1–CP6** were added parallelly. For 24 h continuous stirring at room temperature, the colours of the solutions turned lighter and clearer compared to those of the original. Simultaneously, the concentrations of MB and RhB were monitored by the UV-Vis spectra as shown in Fig. S14 and S15. The results show that **CP1–CP6** were capable of uptaking organic dyes including RB and MB, among which the adsorption capacity of CP5 for both of MB and RhB is the highest (see Table 4).

4 Conclusion

This work presents six heterogeneous catalytic MpCPs of **CP1-CP6** based on M(TCP) units, which were very easily prepared from commercially available compounds, able to selectively oxidize alkylbenzene exclusively to ketones. The high catalytic efficiency observed for **CP1–CP6** may be attributed to M(TCP) units immobilized in the MpCPs, owing to prohibit their self-dimerization and oxidative degradation. Although, the ketone yields were declining slightly for consecutively reused, the selectivity remained over 99% and without detectable catalysts leaching. The catalysts are robust toward the oxidation reactions of alkylbenzene and easily recovered by simple filtration. Furthermore, the dye adsorption properties of CP1-CP6 have been examined, show that the MpCPs were capable of uptaking both of RB and MB, among which the adsorption capability of CP5 is optimum.

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