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Magnetic Polymer Nanospheres Immobilizing Metalloporphyrins. Catalysis and Reuse to Hydroxylate Cyclohexane with Molecular Oxygen

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Abstract Magnetic polymer nanospheres immobilizing Co(II) porphyrin or Mn(III) porphyrin were synthesized and their catalytic activities in hydroxylating cyclohexane were comparably investigated. The catalytic results have shown that these magnetic nanospheres are highly efficient and recyclable catalysts and the nanospheres with Mn(III) porphyrin are more active than those with Co(II) porphyrin.

Keywords Magnetic polymer nanospheres · Co(II) porphyrin · Mn(III) porphyrin · Immobilize · Catalyst

1 Introduction

In the past two decades, interests in the field of metalloporphyrins used as catalysts for alkene epoxidation and alkane hydroxylation under mild conditions have mushroomed [1–5]. However, homogeneous metalloporphyrin catalysts are restricted in large-scale process for the drawbacks that they are inclined to an easy deactivation and difficult to recover from the reaction media. Meanwhile, metalloporphyrins are often expensive to purchase, synthesize and/or manipulate. To remedy these drawbacks, heterogeneous metalloporphyrins have been intensively researched.

In the field of heterogeneous catalysis, solid supported metalloporphyrins arouse much attention for they not only have increased stability and selectivity but can also be recovered from reaction media and reused. Among the supports that can be used to immobilize metalloporphyrins, polystyrene derivatives are often employed for their cheapness, ready availability, mechanical robustness, chemical inertness and facile functionalization. We, and also other research groups, have already made a great deal of efforts on the heterogeneous catalysis of polystyrene-supporting metalloporphyrins and the results show that they are more efficient catalysts than the non-supported metalloporphyrins [6–11].

However, although these solid supported catalysts can be recovered by filtration or precipitation through adding precipitating agents to the reaction media, these methods are time-consuming and energy-consuming. Furthermore, it causes a decrease of reaction yield and enantioselectivities [12, 13]. In the attempt to conquer such problems, magnetic polymer microspheres attract a great deal of interest due to their specific surface properties, and relatively rapid and effortless magnetic separation [14–18]. On the other hand, nanometer-sized catalyst supports have recently aroused our attention because of their high specific surface area and outstanding stability as well as activity in the liquid phase [19–24]. The combination of the magnetic separation of magnetic polymer microspheres and the special properties of nanometer-sized catalyst supports provides a good opportunity to design and synthesize novel polystyrene supporting metalloporphyrins to mimic the function of P450 enzymes.

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In this paper, magnetic polymer nanospheres immobilizing Co(II) porphyrin or Mn(III) porphyrin (designed as MPNSs(CoPP) and MPNSs(MnPP), respectively) were synthesized and characterized. These magnetic polymer nanospheres are of core/shell structure in which the core is composed of numerous Fe_3O_4 particles and the shell is composed of a copolymer of styrene with metalloporphyrin acrylate. The catalytic performances of these nanospheres for cyclohexane hydroxylation with molecular oxygen were evaluated comparing with those of non-supported metalloporphyrin acrylate. The influence of metal center on the catalytic activities of the nanospheres was also discussed.

2 Experimental

2.1 Materials

5-(4-Hydroxyl)phenyl-10,15,20-triphenylporphyrin (HPTPP) was synthesized in our laboratory according to [25]. All other reagents were commercially purchased.

2.2 Physical Measurements

Elemental analysis (C, H and N) were carried out on a Perkin-Elmer 240 Q elemental analyzer. ESI-MS were measured on a Thermo Finnigan LCQ DECA XP spectrometer. ^{1}H NMR spectra were recorded on a Varian Mercury-Plus 300 MHz spectrometer with $CDCl_3$ as solvent at room temperature and TMS as the internal standard. UV–Vis and IR spectra were recorded on a Shimadzu UV-3150 spectrophotometer and an EQUINOX 55 Fourier transformation infra-red spectrometer. The scanning electron microscopy (SEM) analyses were performed with a JSM-6330F Field Emission Scanning Electron Microscope. The particle sizes were measured by a Mastersizer 2000 Laser Particle Size Analyzer. IRIS(HR) inductively coupled plasma-atomic emission spectrometry (ICP) was used to determine the content of Mn(III) porphyrin acrylate and Fe_3O_4. Magnetic measurements were performed by using a XL-7 Magnetic Property Measurement System. Thermal analysis was performed with a Netzsch TG-209 Thermogravimetric Analyzer.

2.3 Catalyst Preparation

2.3.1 Preparation of Fe_3O_4 Particles

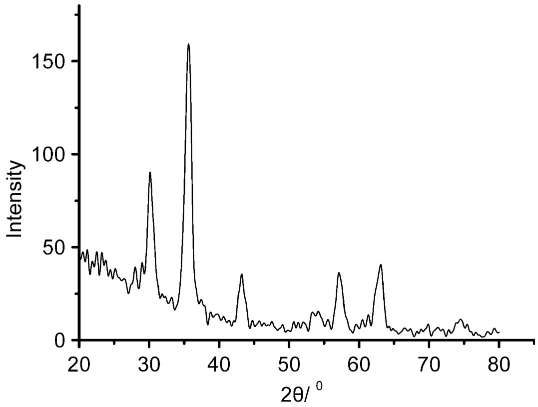


Fig. 1 XRD pattern of Fe_3O_4 particles

The magnetic fluid used in this work, Fe_3O_4 particles, was prepared by chemical coprecipitation of ferrous chloride and ferric chloride. 250 mL 4% fresh ammonia was refluxed in a 500 mL round flask at 80 °C under Ar atmosphere. 13.6 g $FeCl_3 \cdot 6H_2O$ and 5.0 g $FeCl_2 \cdot 4H_2O$ dissolved in 60 mL distilled water was added dropwise and the mixture was then refluxed for 2 h. After cooling the reaction mixture to room temperature, the products were separated in a magnetic field, washed with H_2O to neutrality and then redispersed in distilled water. The X-ray diffraction (XRD) pattern of the Fe_3O_4 particles is available in Fig. 1. The average diameter of the Fe_3O_4 particles obtained from XRD is ca. 8.96 nm [26].

2.3.2 Synthesis of Metalloporphyrin Acrylates

2.3.2.1 Porphyrin Acrylate Porphyrin acrylates, 5-(4-acryloxy)phenyl-10,15,20-triphenylporphyrin (APTPP), was synthesized by the method similar to [27, 28]. A mixture of 50 mL $CHCl_3$ and 0.2500 g HPTPP was stirred at 60 °C. 2.0 g acrylyl chloride dissolved in 5 mL $CHCl_3$ was added dropwise. After 2 h, the mixture was washed with 5% K_2CO_3 for several times and then evaporated to dryness. The crude material was purified on a silica gel chromatograph using $CHCl_3$ as eluent. APTPP was then obtained as a purple powder. Yield: 0.2172 g (76.3 wt.%). ^{1}H NMR ($CDCl_3$, 300 MHz), δ: 8.848(s, 8H, Pyrrole ring), 8.228(m, 8H, o-C_6H_5), 7.774(d, $J = 6.464$, 9H, m-C_6H_5, p-C_6H_5), 1.269(s, 3H, –COO–CH=CH_2), −2.770(s, 2H, Pyrrole N–H).

2.3.2.2 Metalloporphyrin Acrylates Co(II) porphyrin acrylate and Mn(III) porphyrin acrylate were synthesized by a reaction of $Co(Ac)_2$ or $Mn(Ac)_2$ with porphyrin acrylate. A typical reaction is described as following. 0.5 g $Co(Ac)_2$ and 1 g NaCl dissolved in 40 mL HAc were mixed with 20 mL $CHCl_3$ solution of APTPP (0.3180 g). The mixture was stirred at 65 °C for 8 h. Then, the reaction mixture was washed with H_2O and 1 M HCl for several times. After washing with H_2O to neutrality, drying over anhydrous Na_2SO_4 and concentrating via rotary evaporation, the residue was chromatographed on a silica gel column using $CHCl_3$ as eluent. Evaporation of solvent afforded CoAPTPP as an orange powder. Yield: 94.2 wt.%. (Found: C, 70.85; H, 4.03; N, 7.08% Calcd. for $C_{47}H_{30}N_4O_2CoCl{\cdot}H_2O$: C, 70.99; H, 4.06; N, 7.05%). ESI-MS [$CHCl_3$, *m/z*]: 741($[CoAPTPP]^+$).

MnAPTPP. Yield: 95.6 wt.%. (Found: C, 71.18; H, 4.09; N, 7.03% Calcd. for $C_{47}H_{30}N_4O_2MnCl{\cdot}H_2O$: C, 71.35; H, 4.08; N, 7.08%). ESI-MS [$CHCl_3$, *m/z*]: 737($[MnAPTPP]^+$).

2.3.3 Synthesis of MPNSs(CoPP) and MPNSs(MnPP)

The strategy to prepare these nanospheres is shown in Scheme 1. A total of 10.0 g magnetic fluid, 12.0 g styrene, 30 mg reactive Co(II) porphyrin acrylate or Mn(III) porphyrin acrylate, 3.0 g divinylbenzene, 1.5 g polyvinylpyrrolidone(K-30) (PVP K-30), 0.30 g 2,2′-AZo-bis-iso-butyronitrile (AIBN) and 100 mL H_2O/C_2H_5OH were mixed in a 250 mL round-bottomed flask equipped with a reflux condenser. The mixture was stirred at 70 °C for 20-24 h under a N_2 atmosphere. The product was washed with 1 M HCl solution to remove the unenclosed Fe_3O_4 and then with acetone to remove the residual metalloporphyrin acrylate. The final product was separated by applying an additional magnetic field (0.42 T) and dried for 24 h at 60 °C in vacuum.

Magnetic polymer nanospheres without metalloporphyrins used in the controlled experiment were similarly prepared, replacing metalloporphyrin acrylate by methyl acrylate.

2.4 Catalytic Experiments for Cyclohexane Hydroxylation

Cyclohexane hydroxylation in the metalloporphyrin–O_2–ascorbate system was carried out in a specially constructed reaction vessel at (30.0 ± 0.1) °C [6, 7, 28–34]. The catalytic system consists of MPNSs(CoPP), MPNSs(MnPP) or non-supported metalloporphyrin acrylate, coreductant (3.0 mmol ascorbate, 4.0×10^{-2} mmol thiosalicylic acid), substrate (5.55 mmol cyclohexane), acetone/water (9:1, 10 mL) and pure oxygen (101 kPa). The products were detected by Gas Chromatography (GC-7890II) using *p*-chlorotoluene as internal standard.

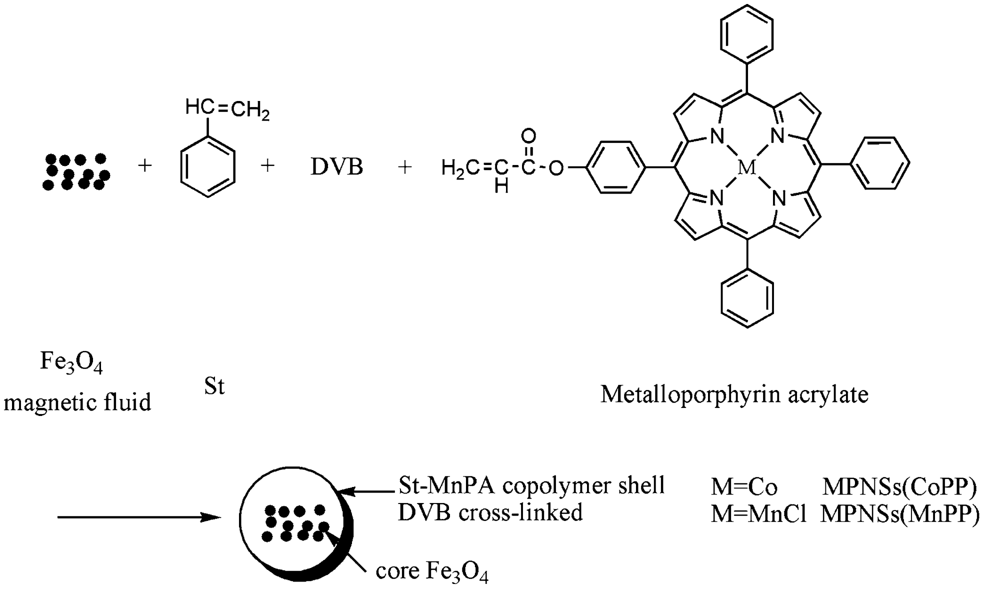
The magnetic polymer nanospheres were separated from the reaction media by adding an external magnetic field (0.42 T). The cyclohexane hydroxylation catalyzed by recovered nanospheres was performed under identical conditions.

3 Results and Discussion

3.1 Characterization of Magnetic Microspheres

The surface morphology and the average diameter of MPNSs(CoPP) and MPNSs(MnPP) were obtained by SEM whose results are given in Fig. 2. The SEM images of the magnetic microspheres show uniformity and spherical morphology with an average diameter of ca. 200 nm. Figure 2 also gives the size distributions of these magnetic nanospheres, which are determined by the particle size analysis and are polydisperse, with more than 80% in the 100–300 nm range.

Scheme 1 The preparation of MPNSs(CoPP) and MPNSs(MnPP)



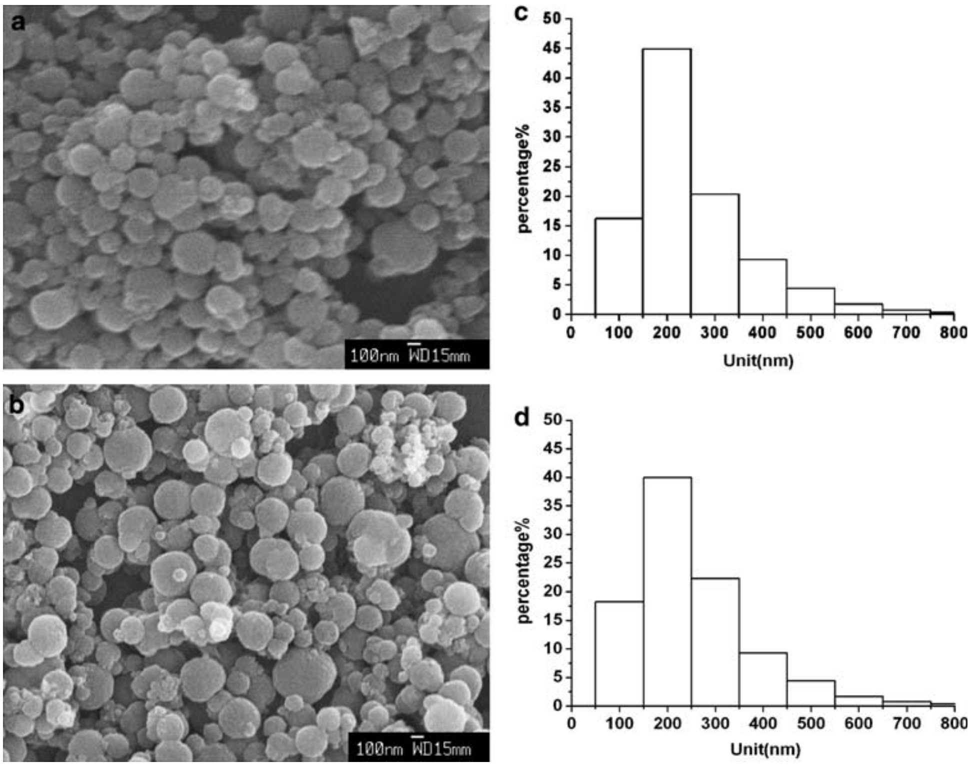


Fig. 2 SEM images of MPNSs(MnPP) (**a**) and MPNSs(CoPP) (**b**); Size distribution histograms of MPNSs(MnPP) (**c**) and MPNSs(CoPP) (**d**)

The solid UV–Vis spectra of MPNSs(CoPP) and MPNSs(MnPP), shown in Fig. 3, exhibited Soret band at 428 and 480 nm, respectively, similar to those of the starting Co(II) porphyrin and Mn(III) porphyrin, indicating the existence of metalloporphyrins in the magnetic nanospheres and that the porphyrin rings were not significantly affected by anchoring it to the support. Slight redshifts (about 2–3 nm) in Soret bands were observed for the solid metalloporphyrin nanospheres comparing the metalloporphyrins in the solution. This red shift probably results from a stereochemical provoking loss of aromatic stability of the porphyrin in covalently attachment to the solid surface. The changes in the porphyrin ring planarity lead to a destabilization of the HOMO, but not of the LUMO orbital of the porphyrin molecule, resulting in a decrease in the HOMO–LUMO energy gap, which is responsible for the red-shift of the Soret band [35–38]. Meanwhile, the Q bands of these solid-supported metalloporphyrins, around 580 and 660 nm, were similarly red-shifted for about 2 nm [35–39].

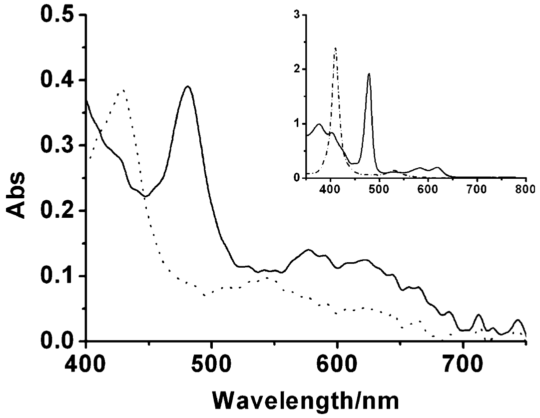


Fig. 3 Solid state UV–Vis absorption spectra of MPNSs(CoPP) (*dotted line*) and MPNSs(MnPP) (*straight line*). Inset: absorption spectrum of CoPP (*dotted line*) and Mn(III)PP (*straight line*) in $CHCl_3$

IR spectra of these nanospheres (Fig. 4) are dominated by the vibrational bands of styrene and metalloporphyrin acrylate. For example, the bands in the region of 3100–2900 cm^{-1}, three bands at 1600.7, 1490.8 and 1446.4 cm^{-1} and double bands at 757.9 and 700.1 cm^{-1} in the IR spectra of both MPNSs(CoPP) and MPNSs(MnPP) can be attributed to the benzene rings in styrene. Two bands at 1024.1 and 1744.3 cm^{-1} corresponding to the C–O stretching and C=O stretching of Co(II) porphyrin acrylate, respectively, are clearly shown in Fig. 4a. These contributions directly argue for the existence of styrene and metalloporphyrin acrylate in the nanospheres.

Thermostabilities of the nanospheres have been determined by using thermogravimetric analysis (TGA). The TG curves (Fig. 5) give us the information that MPNSs(CoPP) and MPNSs(MnPP) degrade at 240 and 259 °C, respectively. This indicates that these nanospheres are thermally stable up to almost 240 °C, exhibiting relatively high thermostabilities. The organic parts decompose

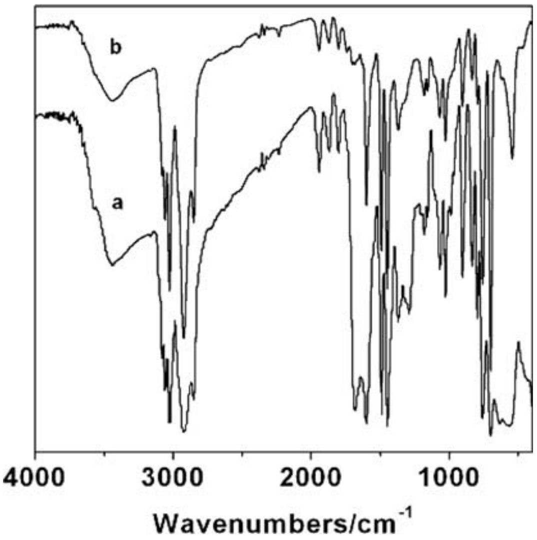


Fig. 4 IR spectra of MPNSs(CoPP) (a) and MPNSs(MnPP) (b)

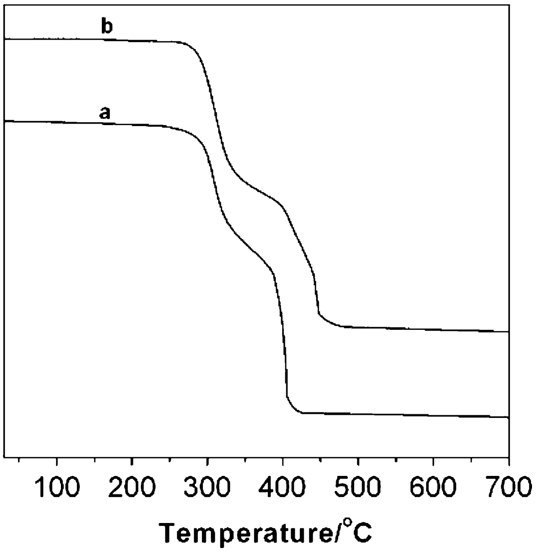


Fig. 5 TG curves of MPNSs(CoPP) (a) and MPNSs(MnPP) (b)

completely at 430 and 480 °C for MPNSs(CoPP) and MPNSs(MnPP), respectively.

The contents of metalloporphyrin acrylate in the magnetic nanospheres were calculated from the contents of Co or Mn, which can be obtained using ICP. Meanwhile, the contents of Fe_3O_4 were similarly calculated. The results are given in Table 1 from which we can get the quantitative information of the core and shell in the nanospheres.

An important characteristic of these nanospheres is that they are superparamagnetic and have excellent magnetic responsibility which plays an essential role in their effortless recovery. Magnetization curves (Fig. 6) show that all of these magnetic nanospheres exhibit superparamagnetic behavior with zero coercivity and remanence because the diameter of the magnetic Fe_3O_4 fluid used in the preparation of these nanospheres is 8.96 nm which is smaller than the critical particle size of Fe_3O_4 particles [40]. The saturation magnetizations of MPNSs(CoPP) (3.51 emu/g) and MPNSs(MnPP) (5.65 emu/g) are lower than that of Fe_3O_4 nanoparticles, which are due to the copolymer coating of the Fe_3O_4 nanoparticles in nanospheres [25, 41]. What's more, it was experimentally observed that these nanospheres dispersed in water are rapidly attracted (<1 min) by a conventional magnet placed close to the reaction vessel (Fig. 7), demonstrating the efficacy of magnetic separation.

Table 1 Contents of metalloporphyrin acrylate and Fe_3O_4

Catalyst	Content of metalloporphyrin acrylate (%)	Content of Fe_3O_4 (%)
MPNSs(MnPP)	0.29	11.28
MPNSs(CoPP)	0.16	7.35

3.2 Hydroxylation of Cyclohexane Catalyzed by MPNSs(CoPP) and MPNSs(MnPP)

Cyclohexanol and cyclohexanone are usually reported and widely admitted as the main products of the cyclohexane hydroxylation in the metalloporphyrin–O_2–ascorbate system under mild condition [6, 7, 27–33]. No obvious catalytic results were observed in the controlled experiments (data not shown), indicating that the effect of Fe_3O_4 embedded in the nanospheres on catalysis of the nanospheres is negligible. The kinetic curves of turnover numbers for MPNSs(CoPP) and MPNSs(MnPP) are shown in Fig. 8, from which we can find that the curves have a similar trend that enhance rapidly and reach maximum values after about 3 h. The turnover numbers have unchanged values with further increasing of

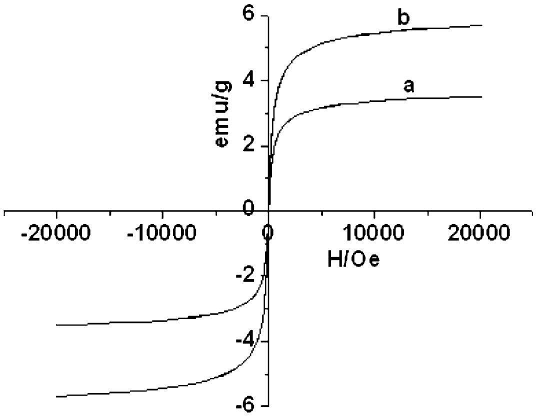


Fig. 6 Magnetic hysteresis loops of MPNSs(CoPP) (a) and MPNSs(MnPP) (b)

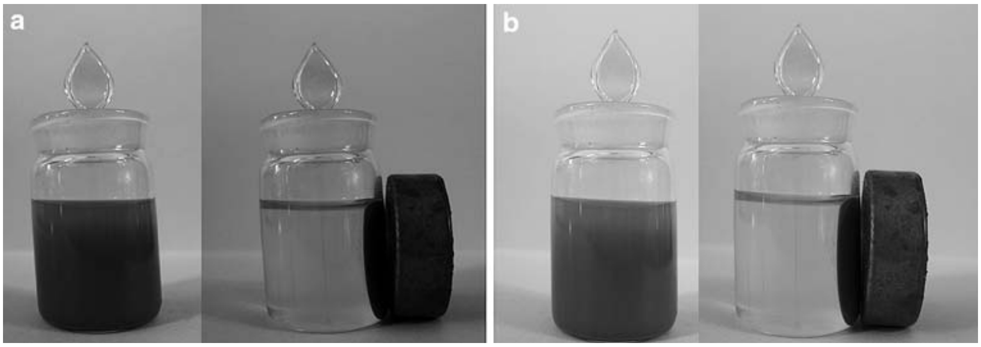


Fig. 7 Illustration of the magnetic separation of MPNSs(CoPP) (**a**) and MPNSs(MnPP) (**b**) from the liquid media

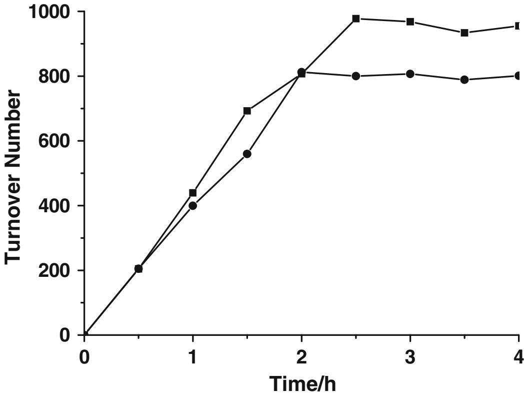


Fig. 8 Changes of the turnover numbers of MPNSs(CoPP) (●) and MPNSs(MnPP) (■) calculated from the reaction products with catalytic time

reaction time. These results further suggest that the by-products of this reaction, such as cyclohexanediol, dicyclohexyl, hexanedioic acid and esters, are negligible [42, 43] and 3 h may be the optimum reaction time in the experiments of cyclohexane hydroxylation catalyzed by these nanospheres.

The results of cyclohexane hydroxylation catalyzed by MPNSs(CoPP), MPNSs(MnPP) (fresh and recovered) and non-supported porphyrins (Co(II) and Mn(III) porphyrin acrylate) after reaction for 3 h are listed in Table 2. As shown in Table 2, the total turnover numbers of the magnetic nanospheres are about 215–308 times larger than those of the non-supported metalloporphyrin acrylate. This is probably due to the suitable microenvironment provided by the nanospheres. As is well known, the hydrophobic microenvironment produced by the protein chain folded around the binding site of cytochrome P450 plays an important role in the process of hydroxylating substrate [6]. However, under mild conditions, homogeneous metalloporphyrins have limited catalytic activities to hydroxylate substrate when using molecular oxygen as oxidant, which may be caused by the lack of this hydrophobic microenvironment. It is believed that the nanospheres provide suitable microenvironment for the “accommodation” of porphyrin catalytic centers [6–11] and thus remarkably enhance the catalytic capability of metalloporphyrin.

From Table 2, one can also clearly observe that the metalloporphyrin nanospheres, which are reused for up to

Table 2 The catalytic performances of MPNSs(CoPP), MPNSs(MnPP), Co(II) porphyrin and Mn(III) porphyrin acrylate to hydroxylate cyclohexane after reaction for 3 h

Catalysts[a]	Catalytic times	Product amount (μmol) (turnover number[b])		
		Cyclohexanol	Cyclohexanone	Total
MPNSs(CoPP)	1	45.3(567)	23.5(294)	68.8(861)
	2	43.0(538)	22.1(276)	65.1(814)
	3	44.1(551)	21.2(265)	65.3(816)
	4	45.6(570)	20.7(259)	66.3(829)
	5	42.9(536)	23.1(289)	66.0(825)
MPNSs(MnPP)	1	55.2(709)	16.4(211)	71.6(920)
	2	54.0(693)	17.8(229)	71.8(922)
	3	57.0(732)	16.8(216)	73.8(949)
	4	57.6(740)	14.6(187)	72.2(928)
	5	63.2(812)	10.3(133)	73.5(945)
Co(II) porphyrin acrylate	1	2.98(2.31)	1.15(0.89)	4.13(3.20)
Mn(III) porphyrin acrylate	1	3.14(2.43)	1.31(1.01)	4.45(3.44)

five times through recovering from the reaction media by effortless magnetic separation, still show relatively high stabilization in catalytic results. Meanwhile, the spectra of the filtrates isolated from the reaction mixtures did not show any band related to metalloporphyrins, indicating no leaching of the complex from the support during reaction. The results above evidence the expended catalytic life of these magnetic nanospheres.

It is interesting that the turnover numbers of MPNSs(MnPP) $>$ MPNSs(CoPP) (Table 2; Fig. 8) under identical conditions. This trend is similar to our previous research on the catalysis of non-supported metalloporphyrin and probably related to the different characteristics of the metal center in the two metalloporphyrins [30]. As is well known, the binding of dioxygen to the low valent metal complex is a significant step in hydroxylation of cyclohexane catalyzed by metalloporphyrins. Muneyuki Tsuda et al. have investigated the activities of metalloporphyrins to bind with O_2 using density-functional theory (DFT) [44]. Their calculated results have shown that the contributions from *d* electrons of Mn(III) in Mn(III) porphyrins are more advantageous for O_2 binding than those from Co(II) in Co(II) porphyrin. This conclusion is in agreement with the theoretical results that the *d* orbital occupancies decrease from Mn to Co across the Periodic Table [45]. It seems that the higher activity of Mn(III) porphyrin than Co(II) porphyrin to react with O_2 plays an essential role in the higher catalytic efficiency of MPNSs(MnPP) than MPNSs(CoPP).

4 Conclusion

Magnetic polymer nanospheres immobilizing Mn(III) porphyrin or Co(II) porphyrin can be easily synthesized by copolymerization of styrene with metalloporphyrins in the presence of Fe_3O_4 magnetic fluid, bearing core/shell structures with satisfying morphology, thermostability and magnetic responsibility. These nanospheres are useful catalysts for cyclohexane hydroxylation, with higher efficiency than non-supported metalloporphyrins. Moreover, these new catalysts, which can be effectively and effortlessly recovered, can retain their high catalytic activities after being recycled five times. Based on these results, it is expected that these magnetic polymer nanospheres immobilizing metalloporphyrins will be new promising catalysts in cyclohexane hydroxylation.

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