

Hydroxylation of cyclohexane with molecular oxygen catalyzed by highly efficient heterogeneous Mn(III) porphyrin catalysts prepared by special synthesis and immobilization method

Baojiao Gao · Yingjun Chen · Qingjuan Lei

Received: 28 August 2011 / Accepted: 1 March 2012 / Published online: 9 June 2012
© Springer Science+Business Media B.V. 2012

Abstract A novel method to synthesize and immobilize porphyrins as well as manganese porphyrins on crosslinked polystyrene (CPS) microspheres was designed. The chloromethyl groups of chloromethylated CPS microspheres (CMCPS microspheres) were first oxidized to aldehyde groups via Kornblum oxidation reaction, obtaining aldehyde group-functionalized microspheres, and then, the synchronous synthesis and immobilization of porphyrins on CPS microspheres were carried out via the Adler reaction between solid–liquid phases, obtaining three kinds of functional microspheres, on which phenyl porphyrin (PP), *p*-chlorophenyl porphyrin (CPP) and *p*-nitrophenyl porphyrin (NPP) were immobilized. Finally, three manganese porphyrin-immobilized microspheres, MnPP–CPS, MnCPP–CPS and MnNPP–CPS, were prepared, these solid catalysts were used in the catalytic hydroxylation reaction of cyclohexane with molecular oxygen as oxidant, and their catalytic performances were mainly investigated in this work. Some surprising experimental results were obtained. The prepared immobilized manganese porphyrin catalysts display amazing catalytic activity and selectivity, and cyclohexane conversion can get up to 45 % and cyclohexanol selectivity in the reaction product can be up to 90–100 %.

Keywords Cyclohexane hydroxylation · Manganese porphyrins · Synthesis and immobilization · Crosslinked polystyrene microspheres · Activity and selectivity of catalyst

Introduction

Synthetic metalloporphyrins (MPs) have been extensively used as cytochrome P-450 models in the catalytic oxidations of organic compounds under mild conditions such as in alkene epoxidation and alkane hydroxylation [1–4]. However, for MPs as homogeneous catalysts, there are two drawbacks, and they limit the practical application of MPs in both synthesis chemistry and industrial process [5–8]: (1) the porphyrin ring is liable to oxidative self-destruction and the MPs are subject to aggregation through π – π interaction; (2) they as expensive catalysts can not be easily recovered after the reaction for reuse. The immobilization of MPs on solid supports can offer several advantages and effectively overcome the above shortcomings. The solid-supported MPs have higher stability and increased selectivity, and they can be recovered from reaction mixtures and reused. Among various solid support materials, polymer supports have attracted much attention due to their inherent characteristics. Inside organism, the natural oxidases are surrounded by polypeptide coils, and the local hydrophobic microenvironment formed by the polypeptide chains enables the natural oxidases to fully exert the catalytic action. The macromolecular chains in the structure of the synthetic polymer-supported MPs provide a biomimetic hydrophobic microenvironment to the MPs. The suitable microenvironment not only can effectively protect the metalloporphyrin catalysts from destruction and deactivation caused by self-oxidation and aggregation through π – π interaction, but also can enhance the catalytic performance, such as catalytic activity and selectivity [9–12].

Among the polymer supports that can be used for immobilizing MPs, polystyrene and its derivatives are often employed due to their cheapness, ready availability, mechanical robustness, chemical inertness and facile

B. Gao (✉) · Y. Chen · Q. Lei
Department of Chemical Engineering, North University of China, Taiyuan 030051, People's Republic of China
e-mail: gaobaojiao@126.com

functionalization [13–15]. For the most of polymer-supported catalysts, the immobilizations of MPs are always conducted via the reactions between the reactive groups of the support polymers and porphyrins. For this route, the preparation process is very troublesome. Generally, in order to creating the connection between support polymers and porphyrins, troublesome and multi-step polymer reactions are always needed for the functionalization of the support polymers, and tedious reactions are also needed in order to make porphyrins to have reactivity [16–18]. Besides, various porphyrins need to be firstly synthesized and then separated and purified. Therefore, the method to covalently link porphyrins onto polymeric supports has many drawbacks such as complicated preparations of suitable porphyrins and polymer supports, whose molecules contain reactive groups, as well as tedious synthesis, separation and purification processes of porphyrins.

In this work, a novel route to prepare immobilized MPs catalysts is designed based on the crosslinked polystyrene (CPS) microspheres, and the catalytic activities of the prepared immobilized MPs in cyclohexane hydroxylation with dioxygen as oxidant were mainly investigated. The chloromethyl groups of chloromethylated CPS microspheres (CMCPS microspheres) were firstly oxidated into aldehyde groups (AL group) via Kornblum reaction [19, 20], resulting aldehyde group-modified microspheres ALCPS; subsequently, synchronic synthesis and immobilization of porphyrins on CPS microspheres were realized successfully by using benzaldehyde (or substituted benzaldehyde), pyrrole in a solution and the microspheres ALCPS as the co-reactants via the Adler reaction between solid–liquid phases, obtaining functional microspheres on which porphyrins were immobilized; finally, several immobilized manganese [Mn(III)] porphyrins were prepared through the coordination reaction between these functional microspheres and manganese salt. The prepared immobilized Mn(III) porphyrins were used in the cyclohexane hydroxylation with molecular oxygen. In the present work, there are some important discoveries and they are briefly described as follows: (1) under mild conditions including at normal temperature and under ordinary pressure, and using molecular oxygen as oxidant, highly effective catalytic hydroxylation of cyclohexane can be carried out, and the conversion of cyclohexane can reach 45 %, displaying very high catalytic activity of the prepared immobilized Mn(III) porphyrins; (2) furthermore, the immobilized Mn(III) porphyrins prepared in this work exhibits excellent selectivity, and cyclohexanol content in the product occupies 90–100 %, whereas the content of cyclohexanone is very low; (3) the excellent performance of the prepared heterogenous metalloporphyrin catalysts arises from their special chemical structure, and around the immobilized MPs, there is a microenvironment analogous to polypeptide. To our knowledge, the immobilized MPs with such excellent catalytic

activity and selectivity are reported for the first time, and the concise and effective route to prepare immobilized metalloporphyrin catalysts is also first reported.

Experimental

Materials and instruments

CPS microspheres as starting microsphere material had a crosslinking degree of 4 %, and a grain size of 0.32–0.45 mm; CMCPS microspheres were self-synthesized [21] with 1,4-bis(chloromethoxy) butane as chloromethylation reagent, which was without carcinogenic toxicity, and had a chlorine content of 14 %; Dimethyl sulfoxide (DMSO, Tientsin University Chemical Reagent Plant, Tientsin City, China) was of analytical grade; Benzaldehyde (Tientsin University Chemical Reagent Plant, Tientsin City, China) was of analytical grade; 4-chlorobenzaldehyde (Alfa Aesar, USA) was of analytical grade; 4-nitrobenzaldehyde (Beijing Chemical Reagent Company, China) was of analytical grade; Pyrrole (Fenke Chemical Reagent Company, Shanghai, China) was of analytical grade; Cyclohexane (Tientsin University Chemical Reagent Plant, Tientsin City, China) was of analytical grade, and was distilled before use in order to remove any impurity. Other chemicals were all analytically pure reagents and were purchased from Chinese companies.

The instruments used in this study were as follows: Perkin-Elmer 1700 infrared spectrometer (IR, Perkin-Elmer Company, USA); Unic UV/Vis-2602 spectrophotometer (Unic Company, USA); Thermo SOLAAR atomic absorption spectrometer (AA, Thermo Company, USA); HP 6890 gas chromatograph (Beijing analytical instrument plant, China).

Preparation and characterization of aldehyde group-modified microspheres ALCPS

According to the procedures described in [22], aldehyde group-modified microspheres ALCPS were prepared via Kornblum reaction, and the typical process is as follows. One gram of CMCPS microspheres and 20 mL of DMSO as oxidant as well as solvent were added into a four-necked flask equipped with a mechanical stirrer, a reflux condenser, a thermometer and a N₂ inlet. After CMCPS microspheres were fully swelled for 24 h, 2 g of NaHCO₃ and 2.5 g of KI were added, followed by purging with nitrogen gas for about 30 min and raising the temperature to 110 °C, and the Kornblum oxidation reaction was carried out for 6 h under N₂ atmosphere at the constant temperature of 110 °C on an oil bath. After finishing the reaction, the resultant microspheres were collected by filtration, washed repeatedly with

distilled water to remove the inorganic salt physically attaching onto the microspheres, and dried under vacuum to a constant weight, obtaining the aldehyde group-modified CPS microspheres, ALCPS microspheres. The infrared spectrum of ALCPS microspheres was determined by KBr pellet method to confirm their chemical structure. Main IR (KBr, cm^{-1}): 670 (C–Cl of chloromethyl group $-\text{CH}_2\text{Cl}$) and 1,421 (C–H of chloromethyl group $-\text{CH}_2\text{Cl}$). The content of the residual chlorine was determined by using burning-Volhard method [21]. The conversion of chloromethyl groups into Al groups was calculated to be 88 mol%, implying the residual Cl element was 1.68 wt% ($14 \times 12 \% = 1.68 \text{ wt}\%$).

Synchronic synthesis and immobilization of porphyrins on CPS microspheres and characterization of porphyrin-immobilized microspheres

The synchronic synthesis and immobilization of porphyrins on CPS microspheres was actualized via Alder reaction [23, 24] between solid–liquid phases. Three kinds of porphyrins were immobilized onto CPS microspheres by using benzaldehyde and two substituted benzaldehydes, 4-chlorobenzaldehyde and 4-nitrobenzaldehyde, as a reactant in the solution, respectively. The detailed procedures are demonstrated by taking the benzaldehyde system as an example.

ALCPS microspheres (1 g) were added into a four-necked flask equipped with a stirrer, followed by adding 40 mL of DMSO. The microspheres were allowed to be sufficiently soaked and swelled for 24 h. Benzaldehyde (2.2 mL) and 1 mL of lactic acid as catalyst were added into the flask and dissolved in DMSO. 1.8 mL of pyrrole and 20 mL of DMSO were placed into a constant pressure dropping funnel, forming a uniform solution. The pyrrole solution begins to be added dropwise as the temperature of the reaction mixture in the flask was raised to 110 °C, and the addition was finished in 15–20 min. The Alders reaction between solid–liquid phases was carried out continuously at the constant temperature of 110 °C for 8 h. After ending the reaction, the product microspheres were filtered out and washed repeatedly with DMF until there was no longer small molecule porphyrin (formed in the solution) in the cleaning mixture (determined with spectrophotometric method). The final blue black microspheres were dried to constant weight under vacuum, and they were namely the functional microspheres phenyl porphyrin (PP)–CPS, on which PP was immobilized.

The other two porphyrin-immobilized microspheres, 4-chlorophenyl porphyrin (CPP)–CPS and 4-nitrophenyl porphyrin (NPP)–CPS, which also were blue black and on which CPP and NPP were immobilized, were prepared with the same process, and only 4-chlorobenzaldehyde or 4-nitrobenzaldehyde were used as one reactant in the solution in the Alder reaction between solid–liquid phases.

About the characterization of these porphyrin-immobilized microspheres, the following determinations were done.

- (1) The infrared spectra of these microspheres, PP–CPS, CPP–CPS and NPP–CPS, were determined with KBr pellet method to characterize their chemical structures. For all of PP–CPS, CPP–CPS and NPP–CPS microspheres, Main IR (KBr, cm^{-1}): 1018, 808 and 703 (porphyrin skeletal vibration) and 968 (N–H). For CPP–CPS, Main IR (KBr, cm^{-1}): 1,179 and 663 (C–Cl). For NPP–CPS, main IR (KBr, cm^{-1}): 1,536 and 1,348 ($-\text{NO}_2$).
- (2) In order to further confirm the chemical structures of these microspheres, the electronic absorption spectra (solid UV/Vis spectra) of these porphyrin-functionalized CPS microspheres were determined. For PP–CPS, Main peaks (nm): 423 (soret band); 516, 554, 595 and 647(Q bands). For CPP–CPS, Main peaks (nm): 418 (soret band); 515, 555, 597 and 648 (Q bands). For NPP–CPS, Main peaks (nm): 430 (soret band); 522, 561, 604 and 650 (Q bands).
- (3) The porphyrin immobilization amounts (mmol/100 g) of these functional microspheres were determined through the coordination reaction of the immobilized porphyrins with zinc salt [25]. Generally, by using the method of synchronic synthesis and immobilization of porphyrins on CPS microspheres, the porphyrin immobilization amounts were high, and the maximum immobilization amount could reach 23 mmol/100 g. However, for preparing immobilized metalloporphyrin catalysts, such high porphyrin immobilization amount is not needed actually because too high immobilization density of MPs on polymer supports will produce negative effect on the catalyst activity [25, 26].

Preparation of solid manganese porphyrin catalysts

40 mL of DMF and 1 g of PP–CPS microspheres were placed in a four-necked flask, and the microspheres were sufficiently swelled, followed by the addition of 1.1 g of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$. Under nitrogen atmosphere and with mechanical stirring, the coordination reaction was allowed to be carried out at the constant temperature of 110 °C. At the end, the resulting microspheres were filtered out, washed with ethanol and water and dried under vacuum, obtaining the immobilized catalyst in dark brown, MnPP–CPS. The Mn content ($\mu\text{mol/g}$) on MnPP–CPS was determined with atomic absorption spectroscopy (AAS), so the immobilized amount of MnPP on the microspheres MnPP–CPS was calculated and it was 45 $\mu\text{mol/g}$. Other two solid catalysts, MnCPP–CPS and MnNPP–CPS were

prepared with the same method, the immobilized amounts of manganese porphyrins were also determined by AAS, and they were 43 $\mu\text{mol/g}$ and 44 $\mu\text{mol/g}$, respectively.

In order to further confirm the chemical structures of these immobilized metalloporphyrins, their electronic absorption spectra (solid UV/Vis spectra) were determined. For MnPP–CPS, Main peaks (nm): 483 (soret band); 584 and 618 nm (Q bands). For MnCPP–CPS, Main peaks (nm): 479 (soret band); 582, and 624 (Q bands). For MnNPP–CPS, Main peaks (nm): 486 (soret band); 589 and 630 (Q bands).

Catalytic hydroxylation of cyclohexane with molecular oxygen

With molecular oxygen at normal pressure as oxidants, the three solid catalysts, MnPP–CPS, MnCPP–CPS and MnNPP–CPS, were used in the catalytic hydroxylation of cyclohexane at room temperature. The typical procedure is described as follows by taking the system with catalyst MnNPP–CPS as an example. Cyclohexane (20 mL) and solid catalyst MnNPP–CPS (0.70 g) were placed into a reactor (it was screened from light) equipped with a mechanical stirrer, a reflux condenser (it was longer and the rate of cooling water was rapider to prevent evaporation of cyclohexane), a thermometer and an O_2 inlet. Oxygen at normal pressure was passed into the mixture at a fixed flow rate. The oxidation reaction was performed at a constant temperature of 40 °C with stirring. The samples of the reaction mixture were taken at a certain time interval, and quantitatively analysed immediately by gas chromatograph with internal standard method by using chlorobenzene as the standard substance. The result indicated that the main product was cyclohexanol. The cyclohexane conversion and the yield of cyclohexanol were calculated quantitatively. After the oxidation reaction, the solid catalyst microspheres were collected by filtering, were soaked and washed with cyclohexane and ethanol in turn so as to completely remove the oxidation products physically attaching on the catalyst microspheres (the oxidation products in the cleaning mixture were determined by UV spectroscopy). And then, the recovered catalyst microspheres were reused in the oxidation reaction of cyclohexane to examine their recycle property.

Results and discussions

Chemical process to synchronically synthesize and immobilize porphyrins on CPS microspheres and to prepare immobilized MPs

In the presence of NaHCO_3 as an alkaline substance, via Kornblum oxidation reaction, the chloromethyl groups on

CMCPS microspheres are oxidized by DMSO into aldehyde groups, and the modified microspheres ALCPS, for which a great deal of benzaldehyde groups are hung on the main chains, were obtained. These benzaldehyde groups can be used as the reactant for the synthesis of porphyrins. By the action of protonic acid catalyst such as lactic acid, the Alder reaction between solid–liquid phases, namely, the reaction between benzaldehyde groups on ALCPS microspheres and pyrrole as well as free benzaldehyde or substituted benzaldehyde (4-chlorobenzaldehyde or 4-nitrobenzaldehyde) in DMSO solution, is carried out. As a consequence, the synchronous synthesis and immobilization of porphyrins on CPS microspheres is realized, and the porphyrin-immobilized microspheres, PP–CPS, CPP–CPS and NPP–CPS, are prepared as benzaldehyde, 4-chlorobenzaldehyde or 4-nitrobenzaldehyde is used as one reactant in DMF solution, respectively. Finally, via the coordination reaction of the immobilized porphyrins with manganese salt, the three immobilized metalloporphyrin catalysts, MnPP–CPS, MnCPP–CPS and MnNPP–CPS (it needs to be pointed that original Mn(II) has been oxidated to Mn(III) [26]), were obtained. The above entire chemical processes of synchronously synthesizing and immobilizing porphyrins on CPS microspheres as well as the process of preparing immobilized MPs can be expressed schematically in Scheme 1. The chemical structures of these solid catalysts can be expressed graphically in Scheme 2.

Characterization of porphyrin-immobilized microspheres as well as metalloporphyrin-immobilized microspheres

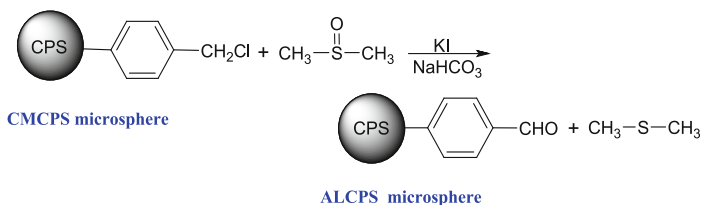
Infrared spectra of porphyrin-immobilized microspheres

Figure 1 gives the IR spectra of CMCPS and ALCPS microspheres, whereas Fig. 2 shows the IR spectra of the three porphyrin-immobilized microspheres, PP–CPS, CPP–CPS and NPP–CPS.

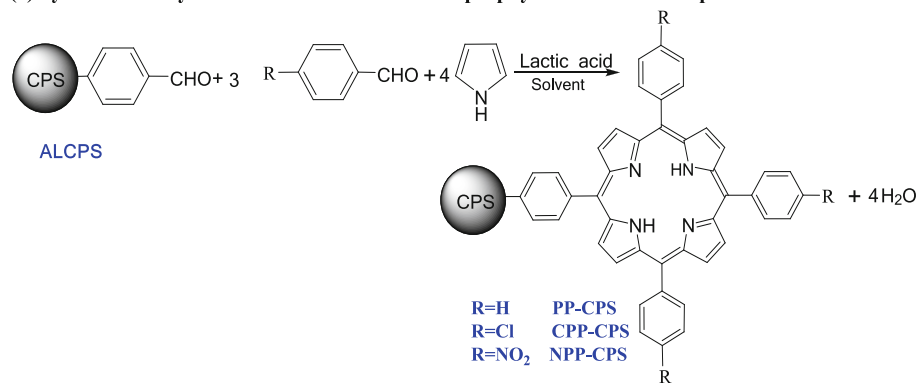
In the spectrum of CMCPS, except for displaying the characteristic absorption bands of polystyrene, there appear two characteristic absorption bands of chloromethyl group $-\text{CH}_2\text{Cl}$ at 1,421 and 670 cm^{-1} . In the spectrum of ALCPS, the absorptions of chloromethyl group at 1,421 and 670 cm^{-1} have been weakened greatly, and one new band at 1,673 cm^{-1} have appeared obviously. This new band is attributed to the stretching vibration absorption of C=O bond of aldehyde groups. Greatly weakening of chloromethyl group absorption bands and the appearance of the characteristic absorption band of aldehyde group adequately confirm that via Kornblum reaction, the pendant benzyl chloride groups of CMCPS has been transformed to pendant benzaldehyde groups, giving aldehyde group-modified CPS microspheres, ALCPS microspheres.

Scheme 1 Chemical process to realize immobilization of manganese porphyrin on CPS microspheres via a novel route

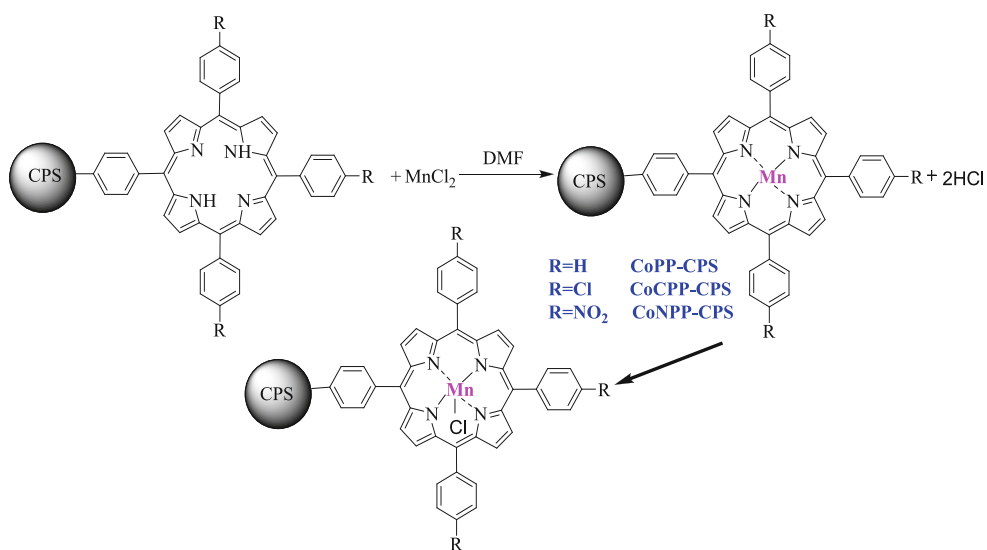
(1) Aldehyde group-functionalization reaction of CMCPs microspheres



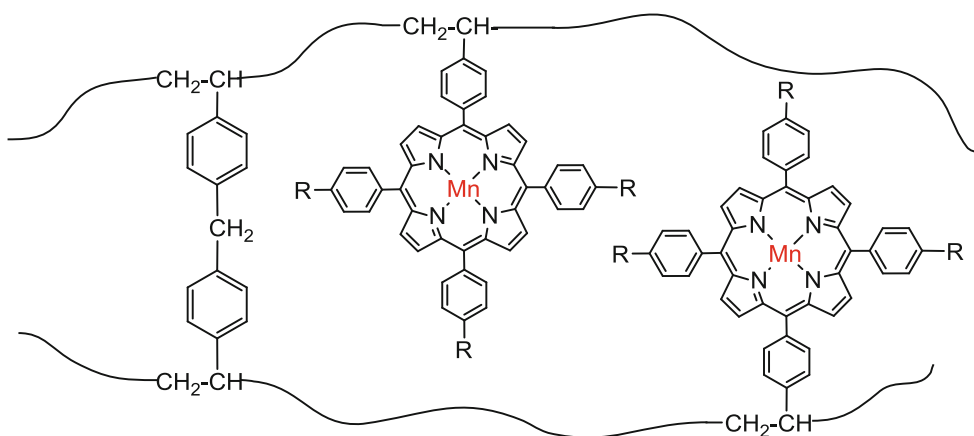
(2) Synchronistic synthesis and immobilization of porphyrin on CPS microspheres



(3) Coordination reaction to form immobilized metalloporphyrins



Scheme 2 Chemical structure of manganese porphyrin-immobilized microspheres



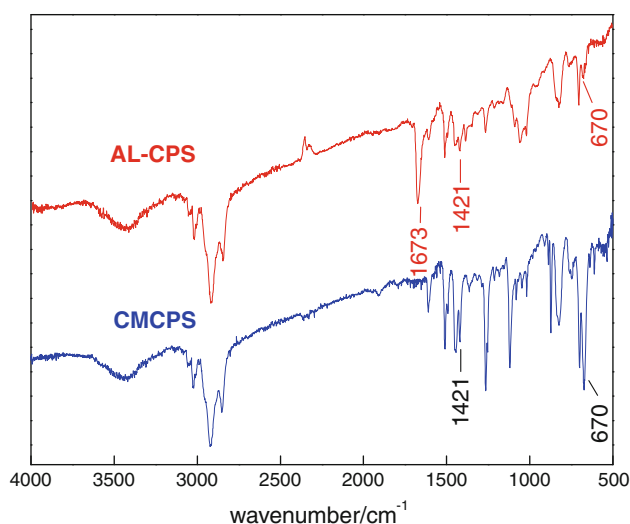


Fig. 1 FTIR spectra of CMCPs and ALCPs microspheres

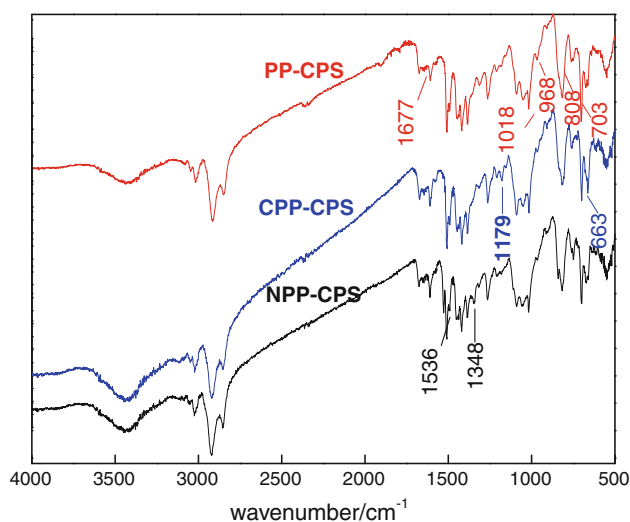


Fig. 2 FTIR spectra of three kinds of porphyrin-immobilized microspheres

In the spectra of PP-CPS, CPP-CPS and NPP-CPS, those characteristic absorption bands of aldehyde groups as described above have been disappeared completely, whereas the characteristic absorption bands of porphyrin skeletal vibration have appeared at 1018, 808 and 703 cm^{-1} . Especially, the vibration absorption of N-H bond on the inner ring of porphyrin has appeared at 968 cm^{-1} , and this is an important proof of the formation of porphyrin. The characteristic absorptions of benzene ring are strengthened greatly owing to the overlap of the absorption bands of polystyrene and the outer rings of porphyrin. Besides, in the spectrum of CPP-CPS, the characteristic absorption band of C-Cl bond appear at 1,179 and 663 cm^{-1} , and in the spectrum of NPP-CPS, the characteristic absorption bands of nitro groups exhibit at 1,536 and 1,348 cm^{-1} . The above changes of absorption

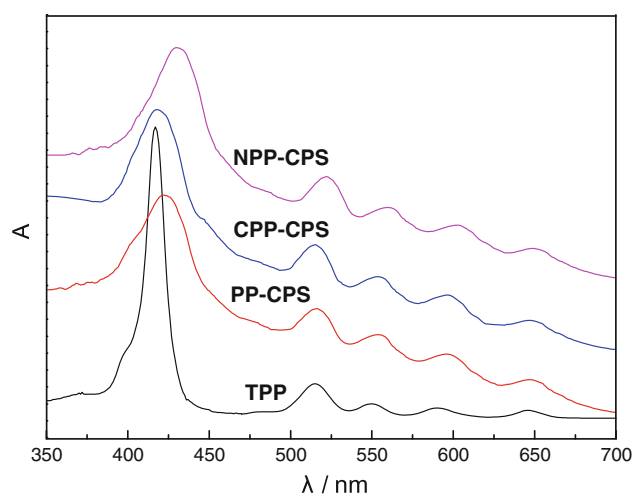


Fig. 3 Electronic absorption spectra of porphyrin-immobilized microspheres

bands sufficiently reveal that the Alder reaction between ALCPs microspheres and pyrrole as well as benzaldehyde or substituted benzaldehyde in the solution has been occurred, and the synchronous synthesis and immobilization of porphyrins on CPS microspheres have been achieved, forming porphyrin-immobilized microspheres, PP-CPS, CPP-CPS and NPP-CPS.

Electronic absorption spectra of porphyrin-immobilized microspheres

The synchronous synthesis and immobilization of porphyrins on CPS microspheres were further confirmed by solid UV-Vis spectroscopy. The spectra for the solid microspheres, PP-CPS, CPP-CPS and NPP-CPS as well as the spectrum of the small molecule porphyrin, tetraphenyl porphyrin (TPP), in chloroform solution, are shown in Fig. 3.

For TPP, a Soret band and four Q bands are visible at 418 nm and at 515, 550, 590 and 645 nm. For PP-CPS microspheres, a Soret band and four Q bands at 423 nm and at 516, 554, 595 and 647 nm, are also observed in the UV-Vis spectrum, and they are basically identical with that of TPP and only have slight shifts, implying the immobilization of PP on the CPS microspheres. For the other two kinds of porphyrin-immobilized microspheres, CPP-CPS and NPP-CPS, a Soret band and four Q bands can also be observed similarly, and they are also almost identical with that of the corresponding small molecule porphyrins in solutions (tetrachlorophenyl porphyrin, TCPP, and tetranitrophenyl porphyrin, TNPP). For CPP-CPS and NPP-CPS, the position differences of the corresponding absorption bands in comparison with that of PP-CPS are caused by the existence of diverse substituents on the outer rings of the immobilized porphyrins, like as small molecule

porphyrins. In word, UV–Vis spectra of the three kinds of porphyrin-immobilized microspheres further prove that the synchronous synthesis and immobilization of porphyrins on CPS microspheres have been realized.

Electronic absorption spectra of metalloporphyrin-immobilized microspheres

The presence of metalloporphyrin on CPS microspheres was confirmed by UV–Vis spectroscopy. The spectra of the small molecule manganese tetraphenyl porphyrin (MnTPP) in chloroform solution and solid MnPP–CPS, MnCPP–CPS and MnNPP–CPS are shown in Fig. 4.

In the UV–Vis spectrum of MnTPP, one soret band and two Q bands are visible at 478 nm, and at 581 and 618 nm. For solid MnPP–CPS, there is no significant changes in the positions of soret band and two Q bands. For MnCPP–CPS and MnNPP–CPS, their spectra are also basically identical with that of the corresponding small molecule MPs (manganese tetrachlorophenyl porphyrin MnTCPP and manganese tetranitrophenyl porphyrin MnTNPP) in solutions. The above fact proves that the three immobilized MPs, MnPP–CPS, MnCPP–CPS and MnNPP–CPS, have been obtained via the coordination reactions of the porphyrin-immobilized microspheres with manganese salt.

Catalytic characters of immobilized metalloporphyrin catalysts in cyclohexane hydroxylation by molecular oxygen

Catalytic activity and selectivity

The catalyst MnNPP–CPS microspheres (0.70 g) with a MnNPP immobilization density of 43 $\mu\text{mol/g}$ (it need to be

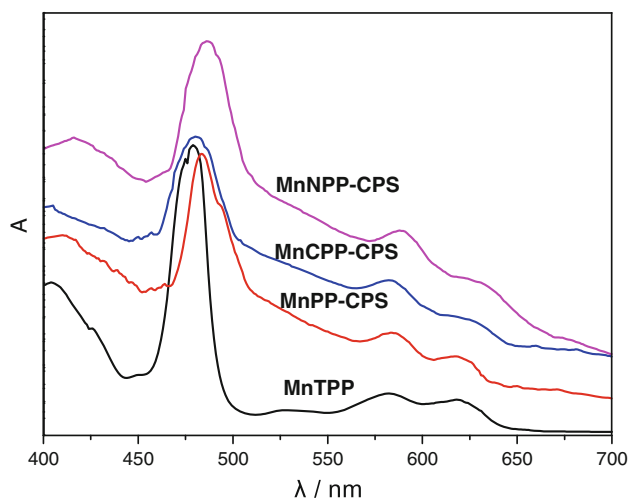


Fig. 4 Electronic absorption spectra of manganese porphyrin-immobilized microspheres

pointed that here MnNPP–CPS microspheres with a lower MnNPP immobilization density intentionally were used because the lower immobilization density of metalloporphyrin on the polymer microspheres afforded the immobilized metalloporphyrin higher catalytic activity of [26]) were added into the system described in “Catalytic hydroxylation of cyclohexane with molecular oxygen” section, and the actual added amount of MnNPP was 30 μmol . The oxidation reaction of cyclohexane was performed at room temperature and normal pressure. Figure 5a gives the variation curve of cyclohexane conversion with time, and Fig. 5b presents the variation curves of cyclohexanol and cyclohexanone yields with time as well as the variation curve of cyclohexanol selectivity.

Figure 5a indicates that there is nearly no reaction to occur for the system without catalyst, whereas for the system, in which the immobilized metalloporphyrin is added, cyclohexane conversion enhances continuously. This fact fully display that the catalyst MnNPP–CPS can effectively catalyze the oxidation reaction of cyclohexane by molecular oxygen. The reaction mechanism is still not

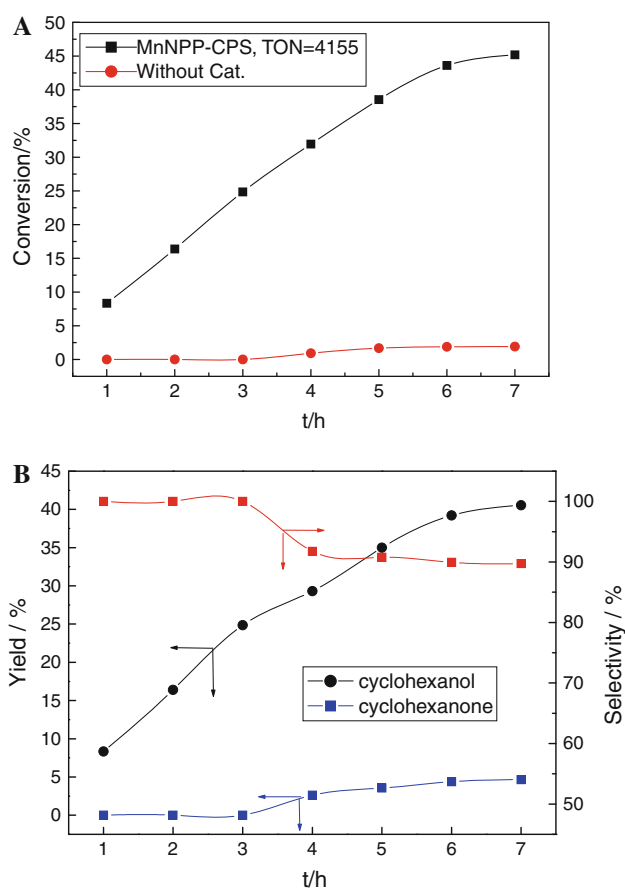


Fig. 5 a Variation of cyclohexane conversion with time with MnNPP-CPS as catalyst. Temperature: 40 °C; Dioxygen pressure: normal pressure. **b** Variation of yields of two products with time. Temperature: 40 °C; Dioxygen pressure: normal pressure

well established, and different pathways that could lead to the hydroxylation of alkanes with molecular oxygen catalyzed by immobilized metalloporphyrins were proposed [27–29]. By referring the mechanism proposed by Gray and coworkers [29], we think that the reaction of hydroxylation reaction of cyclohexane runs via a radical chain mechanism, in which alkyl hydroperoxide is an intermediate. Alkyl hydroperoxide species is decomposed efficiently by metalloporphyrins, and then a radical chain mechanism unfolds, resulting in the product cyclohexanol. Because the metalloporphyrin sites are fixed in the immobilized metalloporphyrin structure, it is impossible to form the peroxo-bridged M–O–O–M dimer. Therefore, the model of the active oxo species is not suitable to the present system.

More importantly, Fig. 5 displays that the immobilized manganese porphyrin prepared in this work possesses extraordinarily high catalytic activity and selectivity: (1) After the reaction of 7 h at room temperature and pressure, cyclohexane conversion achieves 45.2 % unexpectedly, and the turnover number (TON) is 3,229; (2) Before 3 h in the reaction (cyclohexane conversion is 25 %), cyclohexanol is the sole product, and namely, here cyclohexane is converted into cyclohexanol with 100 % selectivity; (3) After the reaction of 3 h, another product, cyclohexanone, begins to be produced, but its yield is very low and only is 2.6 %. Here the selectivity of cyclohexanol still maintains a high value of 90 %.

About the oxidation of cyclohexane with molecular oxygen catalyzed by immobilized MPs, there are many reports in the literature. However, the reported systems have the following several common points [30, 31]: (1) The conversions of cyclohexane are not all high, and generally, are about 10 %; (2) The contents of cyclohexanol and cyclohexanone are similar, and even there are other side products in the product, indicating poor selectivity; (3) The most of the reactions are conducted in a high-pressure container (0.8 MPa) and at high temperature (140 °C); (4) For a few reaction systems performed at normal pressure and temperature, some assistant agents with reducibility are needed to be added [13].

By contrast, the immobilized metalloporphyrin catalysts prepared in this work display amazing catalytic activity and selectivity, and it depends on the chemical structure of these catalysts. It can be seen from Scheme 2 that there are two unique structure factors for the catalysts prepared in this work: (1) In the structure of the solid catalysts, metalloporphyrin rings directly are hung on the main chains of polystyrene, and they are very close to the hydrophobic main chains. (2) At the same time, metalloporphyrin rings are enveloped in the hydrophobic cross-linked networks, and the microenvironment is very similar to polypeptide caves around cytochrome P-450. As is well

known, the key steps [32] in the catalytic cycle that cytochrome P-450 catalyze hydroxylation of substrates with molecular oxygen are all related to the hydrophobic microenvironment—the hydrophobic cavity formed in three-dimensional structure of the protein part. According to this point of view, it is not difficult to explain MnNPP–CPS has the extraordinarily high catalytic activity. It is believed that the structure of MnNPP–CPS as described above provides a suitable microenvironment for the “accommodation” of porphyrin catalytic centers and thus remarkably enhances the catalytic capability of Mn(III) porphyrins under the mild conditions.

The above two structure factors of MnNPP–CPS at least lead to three effects [10]: (1) The hydrophobic main chains similar to polypeptide matrix of P-450 can concentrate the reaction substrate nearby the active sites of the catalyst, and this will accelerate the oxidation reaction and offers the catalysts very high catalytic activity; (2) The wrapping and isolating action of the crosslinked networks will effectively protect metalloporphyrin from its self-aggregation and oxidative destruction, and this makes the catalyst to consistently maintain high activity; (3) The hydrophobic (or lipophilic) matrix will make the product cyclohexanol to rapidly depart from the active sites of the catalyst, the deep oxidation of cyclohexanol is avoided, and it enables the catalyst to exhibit high selectivity of cyclohexanol in the oxidation reaction of cyclohexane.

Effect of substitute on outer ring of MPs on catalytic activity

The three solid catalysts with a given amount, MnPP–CPS, MnCPP–CPS and MnNPP–CPS, the metalloporphyrin immobilization densities of which were similar (MnPP–CPS, 45 $\mu\text{mol/g}$; MnCPP–CPS, 44 $\mu\text{mol/g}$; MnNPP–CPS, 43 $\mu\text{mol/g}$), were added into the system described in “Catalytic hydroxylation of cyclohexane with molecular oxygen” section, and the actual added amounts of the three MPs, MnPP, MnCPP and MnNPP, were made to be the same (30 μmol). Under the same reaction conditions, the catalytic hydroxylation reactions of cyclohexane were carried out, and the variation curves of cyclohexane conversions with time for the three catalytic oxidation systems are presented in Fig. 6.

It can be found in Fig. 6 that the catalytic activities of the three catalysts are different. The catalytic activity of MnNPP–CPS is the highest among the three catalysts, MnCPP–CPS ranks the second, and MnPP–CPS is the catalyst with the worst activity. This is closely related to the electron-withdrawing and releasing property of the substituents on the outer ring of phenyl porphyrins. It is known well that the immobilized MPs on whose outer rings electron-withdrawing substituents are linked are called the

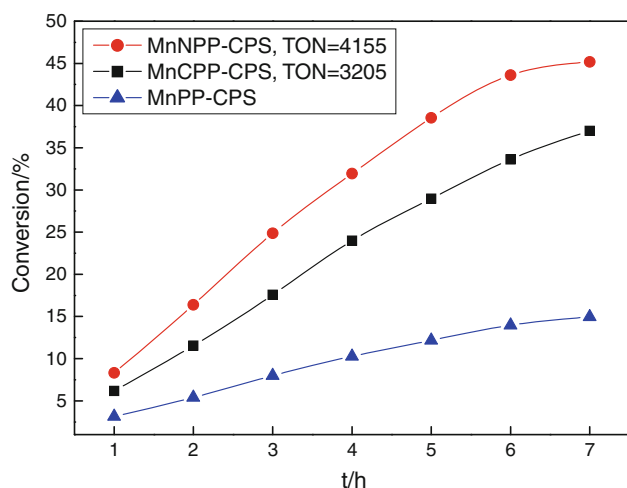


Fig. 6 Variation of cyclohexane conversion with time using different catalysts. Temperature: 40 °C; Dioxygen pressure: normal pressure

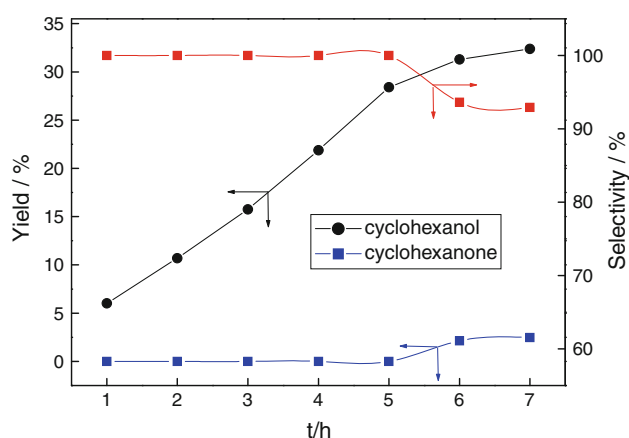


Fig. 7 Variation of yields of two products with time with MnCPP-CPS as catalyst. Temperature: 40 °C; Dioxygen pressure: normal pressure

second-generation metalloporphyrin catalysts, and they are more efficient catalysts for oxidation of hydrocarbons. The possible reason is that the electron-withdrawing substituents bring about an increase of the half-wave potential of the MPs and thus protect the macrocyclic ligand from oxidative self-destruction, resulting in the high catalytic efficiency [11, 33]. Both nitro group and halogen atom are electron-withdrawing substituents, especially, nitro group is a strong electron-withdrawing substitute, so MnNPP-CPS and MnCPP-CPS have higher catalytic activity than MnPP-CPS. In Fig. 7, the remarkably high catalytic selectivity of MnCPP-CPS is also demonstrated like as that of MnNPP-CPS displayed in Fig. 5b.

Figure 7 shows the following facts: (1) Before the reaction of 5 h (cyclohexane conversion is 29 %), cyclohexanol is the sole product, and namely here cyclohexane

is converted into cyclohexanol with 100 % selectivity; (2) After the reaction of 5 h, another product, cyclohexanone, begins to be produced, but its yield is also very low and only is 2.5 %. Here the selectivity of cyclohexanol still maintains a high value of 93 %. In a word, the facts observed in both Figs. 5b and 7 sufficiently illustrate the outstanding selectivity of the prepared immobilized manganese porphyrins in the oxidation reaction of cyclohexane, and more than 90 % of cyclohexane that has reacted is converted into cyclohexanol.

Effect of used amount of catalyst on catalytic activity

The catalyst MnNPP-CPS with a MnNPP immobilization density of 43 $\mu\text{mol/g}$ and the catalyst MnCPP-CPS with a MnCPP immobilization density of 44 $\mu\text{mol/g}$ were used in the catalytic hydroxylation reactions of cyclohexane, respectively. By fixing other reaction conditions and changing the added amount of the solid catalysts so as to change the actual used amount (μmol) of MPs, the oxidation reactions of cyclohexane were conducted so as to examine the effect of the used amount of MPs on the catalytic activity of the catalysts. Figure 8a gives cyclohexane conversion curves as different amounts of solid catalyst MnNPP-CPS were added into the systems and different amounts of MnNPP were used. The cyclohexane conversion data in 7 h are taken from Fig. 8a, and the relationship curve between the cyclohexane conversion and the used amount of MnNPP is presented in Fig. 8b. Similarly, for the catalyst MnCPP-CPS, the relationship curve between the cyclohexane conversion and the used amount of MnCPP is also shown in Fig. 8b.

From Fig. 8a and b, a special effect of the used amount of MPs on the catalytic activity of the catalysts can be found: as the used amount of the MPs is smaller, the cyclohexane conversion increases rapidly with the used amount of the MPs, and this is similar to the common heterogeneous catalytic reaction systems; when the used amount of the MPs is increased to 30 μmol , maximum conversions of cyclohexane appear, 45 % for MnNPP and 35 % for MnCPP, implying the optimal used amount of MnNPP or MnCPP for this reaction system is 30 μmol ; as the used amount of the MPs is over 30 μmol , the conversion of cyclohexane turns to decrease with increasing the used amount of the MPs; as the used amount is very great, the conversion yield of cyclohexane seems to be very low. Obviously, the excessive addition of manganese porphyrin catalysts will inhibit the catalytic activity, and this is apparently different from the common heterogeneous catalysts. This special behavior of biomimetic catalysts also were found by another research group [34] as well as in our previous work [26]. The reason for this needs to be further studied.

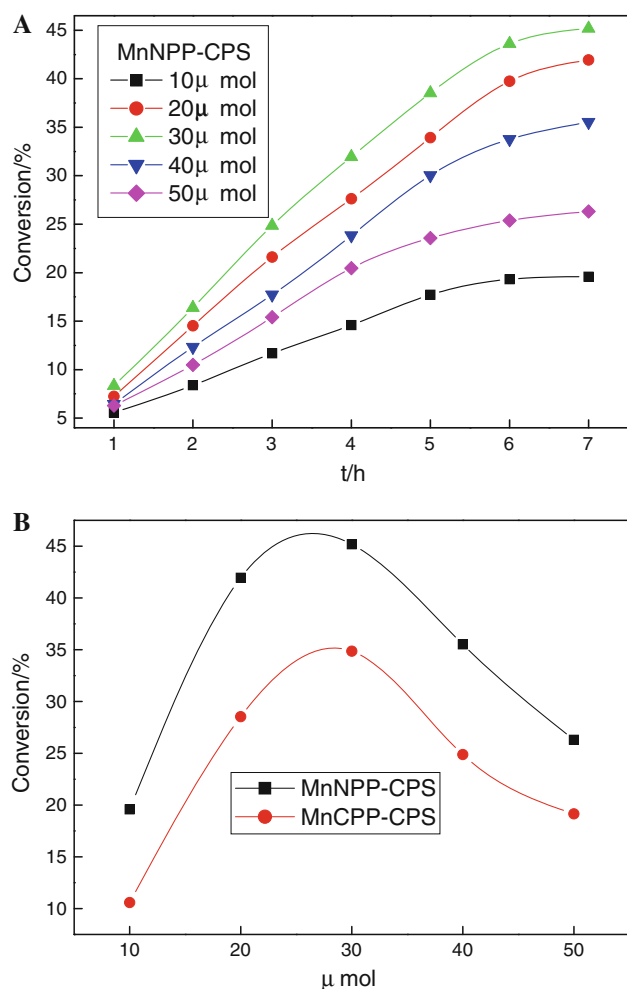


Fig. 8 **a** Variation of cyclohexane conversion with time with different used amounts of manganese porphyrins. Temperature: 40 °C; Dioxygen pressure: normal pressure. **b** Variation of cyclohexane conversion with used amount of manganese porphyrins. Reaction time: 7 h

Recycle and reuse property of catalyst

The recycle and reuse experiments for the prepared solid catalysts were conducted to examine their stability. The solid catalysts MnNPP-CPS and MnCPP-CPS, which had been used, were soaked and washed with cyclohexane and ethanol to remove the oxidation products attaching on the solid catalysts, and then were reused. Figure 9 shows the cyclohexane conversion in 7 h as a function of the number of cycle for the two solid catalysts. It can be observed from Fig. 9 that during the consecutive reusing of 6 times, the catalytic activities of the two immobilized MPs catalysts remain stable. Furthermore, except for the secondary time, the catalytic activities of the two catalysts increase tardily, and as a consequence, the activities of the sixth time are higher than that of the first time, displaying the excellent reuse performance. During the use process of six cycles,

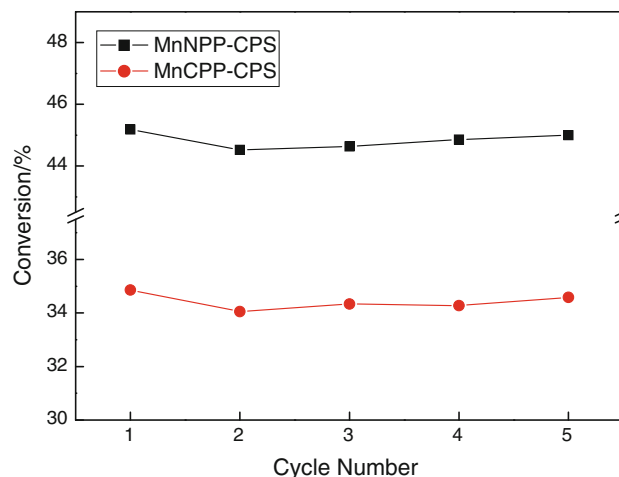


Fig. 9 Cyclohexane conversion in 7 h as function of cycle number. Temperature: 40 °C; Dioxygen pressure: normal pressure

the color of the solid catalysts kept in dark brown, and the detection result of atomic absorption spectrometry indicated that no metalloporphyrin was detached, showing that the immobilized metalloporphyrin catalysts prepared in this work are stable and robust.

Conclusions

In our investigation, the immobilized metalloporphyrin catalysts were prepared by synchronously synthesizing and immobilizing porphyrins on crosslinked polystyrene microspheres, resulting in the heterogenous metalloporphyrin catalysts with a unique structure that was similar to the natural metalloporphyrin encompassed by polypeptide chains. It is the special chemical structure that makes the prepared immobilized manganese porphyrin catalysts have extraordinarily high catalytic activity and excellent selectivity in the hydroxylation reaction of cyclohexane by molecular oxygen. 45 % of cyclohexane conversion and 90–100 % of cyclohexanol selectivity were obtained in 7 h.

References

- Mirkhani, V., Moghadam, M., Tangestaninejad, S., Kargar, H.: Mn(Br₂TPP)Cl supported on polystyrene-bound imidazole: an efficient and reusable catalyst for biomimetic alkene epoxidation and alkane hydroxylation with sodium periodate under various reaction conditions. *Appl. Catal. A* **303**, 221–229 (2006)
- Połowicz, J., Pamin, K., Haber, J.: Influence of manganese tetraarylporphyrins substituents on the selectivity of cycloalkanes oxidation with magnesium monoperoxyphthalate. *J. Mol. Catal. A Chem.* **257**, 154–157 (2006)
- Machado, G.S., de F Castro, K.A.D., Wypych, F., Nakagaki, S.: Immobilization of metalloporphyrins into nanotubes of natural

- halloysite toward selective catalysts for oxidation reactions. *J. Mol. Catal. A Chem.* **283**, 99–107 (2008)
4. Huang, G., Liu, S.-Y., Guo, Y.-A., Wang, A.-P., Luo, J., Cai, C.-C.: Immobilization of manganese tetrphenylporphyrin on boehmite and its catalysis for aerobic oxidation of cyclohexane. *Appl. Catal. A* **358**, 173–179 (2009)
 5. Moghadam, M., Tangestaninejad, S., Habibi, M.H.: A convenient preparation of polymer-supported manganese porphyrin and its use as hydrocarbon monooxygenation catalyst. *J. Mol. Catal. A Chem.* **217**, 9–12 (2004)
 6. Naik, R., Joshi, P., Umbarkar, S., Deshpande, R.K.: Polystyrene encapsulation of manganese porphyrins: highly efficient catalysts for oxidation of olefins. *Catal. Commun.* **6**, 125–129 (2005)
 7. Rahiman, A.K., Rajesh, K., Bharathi, K.S., Sreedaran, S., Narayanan, V.: Manganese(III) porphyrin-encapsulated Ti, Si-mesoporous molecular sieves as heterogeneous catalysts for the epoxidation of alkenes. *Appl. Catal. A* **314**, 216–225 (2006)
 8. Moghadam, M., Tangestaninejad, S., Mirkhani, V., Mohammadpoor-Baltorkb, I., Kargar, H.: Mild and efficient oxidation of alcohols with sodium periodate catalyzed by polystyrene-bound Mn(III). *Bioorg. Med. Chem.* **13**, 2901–2905 (2005)
 9. Lindsay Smith, J.R., Iamamoto, Y., Vinhado, F.S.: Oxidation of alkanes by iodobenzene (PhIO) catalysed by supported Mn(III) porphyrins: Activity and mechanism. *J. Mol. Catal. A Chem.* **252**, 23–30 (2006)
 10. Gotardo, M.C.A.F., Guedes, A.A., Schiavon, M.A., José, N.M., Yoshida, I.V.P., Assis, M.D.: Polymeric membranes: the role this support plays in the reactivity of the different generations of metalloporphyrins. *J. Mol. Catal. A Chem.* **229**, 137–143 (2005)
 11. Rebelo, S.L.H., Gonçalves, A.R., Pereira, M.M., Simões, M.M.Q., Neves, M.G.P.M.S., Cavaleiro, J.A.S.: Epoxidation reactions with hydrogen peroxide activated by a novel heterogeneous metalloporphyrin catalyst. *J. Mol. Catal. A Chem.* **256**, 321–323 (2006)
 12. Du, C.-P., Li, Z.-K., Wen, X.-M., Wu, J., Yu, X.-Q., Yang, M., Xie, R.-G.: Highly diastereoselective epoxidation of cholest-5-ene derivatives catalyzed by polymer-supported manganese(III) porphyrins. *J. Mol. Catal. A Chem.* **216**, 7–12 (2004)
 13. Fu, B., Yu, H.-C., Huang, J.-W., Zhao, P., Liu, J., Ji, L.-N.: Mn(III) porphyrins immobilized on magnetic polymer nanospheres as biomimetic catalysts hydroxylating cyclohexane with molecular oxygen. *J. Mol. Catal. A Chem.* **298**, 74–80 (2009)
 14. Huang, J.-W., Mei, W.-J., Liu, J., Ji, L.-N.: The catalysis of some novel polystyrene-supported porphyrinatomanganese(III) in hydroxylation of cyclohexane with molecular oxygen. *J. Mol. Catal. A Chem.* **170**, 261–265 (2001)
 15. Brulé, E., de Miguel, Y.R., Hiic, K.K.: Chemoselective epoxidation of dienes using polymer-supported manganese porphyrin catalysts. *Tetrahedron* **60**, 5913–5918 (2004)
 16. Ribeiro, S.M., Serra, A.C., Gonsalves, A.M.d'.A.R.: Covalently immobilized porphyrins as photooxidation catalysts. *Tetrahedron* **63**, 7885–7891 (2007)
 17. Vinodu, M.V., Padmanabhan, M., Polym, J.: Electronic effect of polymeric environments on metalloporphyrins. *J. Polym. Sci. Part A Polym. Chem.* **39**, 326–334 (2001)
 18. Mukherjee, M., Ray, A.R.: Biomimetic oxidation of L-arginine with hydrogen peroxide catalyzed by the resin-supported iron(III) porphyrin. *J. Mol. Catal. A Chem.* **266**, 207–214 (2007)
 19. Kornblum, J.W., Powers, O.J.: Flavonoids of citrus. II. Isolation of a new flavonol from lemons. *J. Am. Ceram. Soc.* **79**, 6562–6563 (1957)
 20. Kornblum, J.W., Powers, O.J.: A new and selective method of oxidation. the conversion of alkyl halides and alkyl tosylates to aldehydes. *J. Am. Ceram. Soc.* **81**, 4113–4114 (1959)
 21. Lü, C.-L., Gao, B.-J., Liu, Q., Qi, C.-S.: Preparation of two kinds of chloromethylated polystyrene particle using 1,4-bis (chloromethoxy) butane as chloromethylation reagent. *Colloid Polym. Sci.* **286**, 553–561 (2008)
 22. Chen, Y.-J., Gao, B.-J., Wan, M.: Aldehyde group-functionalization modification of crosslinked polystyrene microspheres and immobilization of phenyl porphyrins. *Chin. Chem. Bull.* **73**, 1110–1115 (2010). (in Chinese)
 23. Adler, A.D., Longo, F.R., Shergalis, W.: Mechanistic investigations of porphyrin syntheses I. Preliminary studies on meso-tetra-phenylporphyrin. *J. Am. Ceram. Soc.* **84**, 3145–3149 (1964)
 24. Adler, A.D., Sklar, L., Longo, F.R.: A mechanistic study of the synthesis of meso-tetra-phenylporphyrin. *J. Heterocycl. Chem.* **5**, 669–678 (1968)
 25. Gao, B.-J., Zhang, G.-H., Li, Y.-B., Du, R.-K.: Synchronously synthesizing and immobilizing porphyrins on crosslinked polystyrene microspheres and preliminary study on catalytic activity of supported metalloporphyrins. *Polym. Adv. Technol.* **20**, 1183–1189 (2009)
 26. Gao, B.-J., Wang, R.-X., Zhang, Y.: Immobilization of mangano-porphyrin on a novel polymeric support and catalytic oxidation characteristic of supported catalyst. *J. Appl. Polym. Sci.* **112**, 2764–2772 (2009)
 27. Haber, J., Matachowski, L., Pamin, K., Połtowicz, J.: Manganese porphyrins as catalysts for oxidation of cyclooctane in Lyons system. *Mol. Catal. A Chem.* **162**, 105–109 (2000)
 28. Połtowicz, J., Pamin, K., Matachowski, L., Serwicka, E.M., Mokaya, R., Xia, Y., Olejniczak, Z.: Oxidation of cyclooctane over Mn(TMPyP) porphyrin-exchanged Al, Si-mesoporous molecular sieves of MCM-41 and SBA-15 type. *Catal. Today* **114**, 287–292 (2006)
 29. Birnbaum, E.R., Grinstaff, M.W., Labinger, Y.A., Bercaw, J.E., Gray, H.B.: On the mechanism of catalytic alkene oxidation by molecular oxygen and halogenated iron porphyrins. *J. Mol. Catal.* **104**, L119–L122 (1995)
 30. Haber, J., Matachowski, L., Pamin, K., Połtowicz, J.: Supported polyhalogenated metalloporphyrins as catalysts for the oxidation of cycloalkanes with molecular oxygen in Lyons system. *Catal. Today* **91–92**, 195–198 (2004)
 31. Huang, G., Li, T.-M., Liu, S.-Y., Fan, M.-G., Jiang, Y.-X., Guo, Y.-A.: A robust boehmite-supported cobalt tetraphenylporphyrin catalyst for aerobic oxidation of cyclohexane. *Appl. Catal. A* **371**, 161–165 (2009)
 32. Mansuy, D.: Cytochrome P450 and synthetic models. *Pure Appl. Chem.* **59**, 759–770 (1987)
 33. Moreira, M.S.M., Martins, P.R., Curi, R.B., Nascimento, O.R., Iamamoto, Y.: Iron porphyrins immobilised on silica surface and encapsulated in silica matrix: a comparison of their catalytic activity in hydrocarbon oxidation. *J. Mol. Catal. A Chem.* **233**, 73–81 (2005)
 34. Guo, C.-C., Liu, X.-Q., Liu, Y., Liu, Q., Chu, M.-F., Zhang, X.-B.: Studies of simple μ -oxo-bisiron(III)porphyrin as catalyst of cyclohexane oxidation with air in absence of cocatalysts or reductants. *J. Mol. Catal. A Chem.* **192**, 289–294 (2003)