Catalytic Activity of Immobilized Metalloporphyrins Prepared by Synchronously Synthesizing and Immobilizing Porphyrins on Polymeric Microspheres

Baojiao Gao, Jing Zhao, Yanbin Li

Department of Chemical Engineering, North University of China, Taiyuan 030051, People's Republic of China

ABSTRACT: A novel route to immobilize metalloporphyrins on polymeric supports was put forward, and it is the way to synchronously synthesize and immobilize porphyrins on polymeric microspheres, followed by metal salt coordination reaction. Copolymeric microspheres (GMA/MMA) of glycidyl methacrylate (GMA) and methyl methacrylate (MMA) were prepared, and then via the ring-opening reaction of the epoxy groups on GMA/MMA microspheres, parahydroxybenzaldehyde (HBA) was bond onto the microspheres, obtaining the modified microspheres HBA-GMA/MMA. Subsequently, the Adler reaction between solid-liquid phases was carried out with HBA-GMA/MMA microspheres and pyrrole as well as benzaldehyde derivate in a solution as coreactants. As a result, it was successfully realized to synchronously synthesize and immobilize porphyrin on the surfaces of GMA/MMA microspheres, resulting in three porphyrin-immobilized microspheres, PP-GMA/MMA (PP: phenyl porphyrin), CPP-GMA/MMA (CPP: 4-chlorophenyl porphyrin) and NPP-GMA/MMA (NPP: 4-nitrophenyl porphyrin). Further, the coordination reaction of these immobilized porphyrins with cobalt salt was conducted, obtaining three supported cobalt porphyrin catalysts, CoPP-GMA/MMA, CoCPP-GMA/MMA and CoNPP-GMA/MMA. The catalytic properties of these supported mettaloporphyrin catalysts were examined in the catalytic oxidation of ethylbenzene to acetophenone by dioxygen. The experimental results indicate: (1) the prepared three solid catalysts are effective in the catalytic oxidation of ethylbenzene to acetophenone by dioxygen; (2) for these polymer-supported metalloporphyrin catalysts, some factors, such as the substitute species on phenyl ring in the macrocycle, the immobilization density of metalloporphyrin and the added amount of the catalyst in the reaction system, affect the catalytic activity greatly; (3) the prepared supported metalloporphyrin catalysts have fine recycle and reuse property. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 406–416, 2011

Key words: glycidyl methacrylate; metalloporphyrin; synthesis; immobilization; catalytic oxidation

INTRODUCTION

Cytochrome P450s are a class of heme-containing monooxygenases that transfer an oxygen atom from molecular oxygen to a wide range of organic substrates.[1,2] Many researchers have used synthetic metalloporphyrins (MPs) as the mimic of heme proteins to catalyze a variety of hydrocarbon oxidations under mild conditions.[1,3–5] However, two problems associated with MPs as homogeneous catalysts are (1) they are easy to be deactivated by irreversible dimerization and oxidative self-destruction in the oxidizing media; (2) they as expensive catalysts can not be easily recovered after the reaction for reuse.[6–9] These drawbacks limit the practical application of MPs in both synthesis chemistry and industrial process heavily. One approach to resolve the two problems is to chemically support MPs on suitable insoluble supports, such as alumina, silica, zeolites, clays, and polymeric matrices.[9,10–12] The immobilization may prevent molecular aggregation or bimolecular self-destruction reactions, and is also associated with the easily recyclable solid catalysts, which can be reused.

Among various solid support materials, polymer supports have attracted much attention due to their inherent characteristics, and polymer-supported MPs catalysts are being researched widely. Inside organism, the natural oxidase is surrounded by polypeptide chains, and it can fully exert the catalytic action in a local hydrophobic microenvironment. In the structure of synthetic polymer-supported metalloporphyrin catalysts, in some respects, the macromolecular chains are analogous to the influence of the polypeptide chain in hemeproteins, and afford the catalyst a biomimetic hydrophobic microenvironment. The polymer effects produced by the biomimetic microenvironment not only can protect effectively the metalloporphyrin catalysts from

Correspondence to: B. Gao (gaobaojiao@126.com).

destruction and deactivation caused by self-oxidation and aggregation, but also can enhance the catalytic performance, such as catalytic activity and selectivity.[13–16] Generally, for preparing polymer-supported metalloporphyrin catalysts, it is needed to creating a connection between support polymers and porphyrins. Troublesome multistep polymer reactions are always needed for the functionalization of the support polymers, and it is also needed to make porphyrins to have reactivity.[17–20] Besides, various porphyrins need to be first synthesized and separated, and the processes of the synthesis and purification of porphyrins are also tedious.[21,22] Therefore, the conventional method to covalently link porphyrins onto polymeric supports suffers some disadvantages from complicated preparations of suitable porphyrins and polymer supports.

In this work, a novel and short cut to prepare supported MP catalysts is designed based on the copolymeric microspheres (GMA/MMA) of glycidyl methacrylate (GMA) and methyl methacrylate (MMA), several MP catalysts supported on GMA/MMA microspheres are successfully prepared, and their catalytic activities were mainly investigated. First, 4-hydroxybenzaldehyde(HBA)was bond onto the surface of GMA/MMA microspheres via ring-opening and ether-forming reaction of the epoxy groups of GMA/MMA microspheres with the hydroxyl groups of HBA, resulting in surface-modified microspheres HBA-GMA/MMA. Subsequently, the synchronic synthesis and immobilization of porphyrin on microspheres GMA/MMA were conducted through Adler reaction between solid-liquid phases using HBA-GMA/MMA microspheres, pyrrole, and benzaldehyde (or substituted benzaldehyde) in the solution as coreactants, and three phenyl porphyrin-immobilized microspheres were obtained. Finally, via coordination reaction, three supported cobalt porphyrin catalysts were obtained successfully. The catalytic activities of these catalysts for the oxidation of ethylbenzene to acetophenone by dioxygen were examined, and the result was very satisfactory. By adopting the method to synchronously synthesize and immobilize porphyrins on polymeric supports, various polymer-supported MP catalysts with different structures can be prepared as long as the substituted benzaldehydes with different structures are used as one reactant in the solution. Especially, for preparing the polymer-supported MP catalysts with electron-withdrawing substituents in macrocyclic rings, which are more stable and effective catalysts and are receiving much attention at present,[13,23] this method is very convenient. As long as the substituted benzaldehyde with electron-withdrawing substitute is used in the Adler reaction between solid-liquid phases, the polymer-supported MP catalysts with electron-withdrawing

substituents can be obtained. This study result supplies a new route to synthesize polymer-supported metalloporphyrin catalysts. As far as we know, this method is reported for the first time. In addition, there are several important findings about the catalytic property for the polymer-supported metalloporphyrin catalysts, such as the effect of the immobilization density of metalloporphyrin on the catalytic activity, the effect of the used amount of the catalyst, and so on. These findings are very significant for the development of the polymer-supported metalloporphyrin catalysts.

EXPERIMENTAL

Materials and instruments

Glyceryl methacrylate (GMA, Suzhou Nanhang Chemical Engineering Ltd., Province Jiangsu, China), Methyl methacrylate (MMA, Tianjing Ruijinte Chemical Ltd., Tianjing City, China) and Ethylene glycol dimethacrylate as crosslinker (EGDMA, Yantai Yunkai Chemical Engineering Ltd. Province Shandong, China) were all of analytical grade and distilled under vacuum before use. Parahydroxybenzaldehyde (HBA, Tientsin Tine Chemical Engineering Institute, 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, Beijing, China) was of analytical grade. Pyrrole (Fenke Chemical Reagent Company, Shanghai, China) was of analytical grade. All of other reagents were of analytical grade 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); Jasco V-50 UV/Vis spectrophotometer (Jasco Company, Japan); Thermo SOLAAR atomic absorption spectrometer (AAS, Thermo Company, USA); HP 6890 gas chromatograph (Beijing analytical Instrument Plant, Beijing, China).

Preparation and characterization of supported MP catalysts on GMA/MMA microsphers

Preparation of crosslinked microspheres GMA/MMA

According to the procedures described in Ref. 27, crosslinked microspheres GMA/MMA were prepared with suspension polymerization method, and the typical process is as follows. Two grams of polyvinyl alcohol (PVA) as disperser and 5 g of NaCl were dissolved in 100 mL of distilled water, forming water phase as continuous phase. The water phase was placed in a four-necked flask equipped with a

mechanical agitator, a condenser, a N_2 inlet and a thermometer. Three milliliters of GMA, 4 mL of MMA and 2 mL of EGDMA (crosslinker) were dissolved together, constituting oil phase as dispersion phase. The oil phase was added into the flask and the system was stirred sufficiently so as to fully disperse the oil phase into the water phase. The content was heated to 75°C, and 0.05 g of initiator AIBN dissolved in a little of toluene was added. The copolymerization was carried out at 75°C for 2 h with stirring under N_2 atmosphere, and then the temperature was enhanced to 85°C, and the reaction was performed for another 2 h. The white crosslinked microspheres GMA/MMA with translucence were obtained. Their structure was characterized by infrared spectrum.

Bonding HBA on GMA/MMA microsphers via ring-opening and ether forming reaction

HBA was bond onto the surfaces of GMA/MMA microsphers through ring-opening and ether forming reaction of the epoxy groups on the microsphers with the hydroxyl groups of HBA molecules, and the modified microsphers HBA-GMA/MMA were obtained. The typical process to prepare the modified microsphers is as follows. One gram of crossliked microspheres GMA/MMA was placed into a four-necked flask equipped with a mechanical agitator, a reflux condenser, a N_2 inlet and a thermometer, followed by addition of 25 mL N,N-dimethylformamide (DMF) as solvent. The GMA/MMA microspheres were allowed to be soaked for 24 h so as to be fully swelled. DMF solution (25 mL) in which 0.54 g of HBA was dissolved was added into the flask, and the reaction was performed under N_2 atmosphere at a constant temperature of 110°C with stirring for 12 h. After the reaction, the resultant microspheres were washed and dried in vacuum, resulting in the modified microspheres HBA-GMA/MMA. The residual content of HBA in the final solution was determined with UV spectrophotometry at 285 nm, and the bonding amount (g/g) of HBA on the microspheres HBA-GMA/MMA was calculated. The HBA-GMA/MMA microspheres used in this work had a HBA bonding amount of 0.22 g/g. The infrared spectrum of microspheres HBA-GMA/MMA was determined to confirm their structure.

Synchronously synthesizing and supporting porphyrins on GMA/MMA microspheres

Three porphyrin-immobilized microspheres were prepared using benzaldehyde, 4-chlorobenzaldehyde and 4-nitrobenzaldehyde as one reactant in the solution via synchronously synthesizing and immobilizing method, and the procedures are demonstrated

by taking the system with 4-nitrobenzaldehyde as one reactant as an example. The modified microspheres HBA-GMA/MMA (0.5 g) were soaked and swelled in 20 mL of dimethylsulfoxide (DMSO) in a reactor for 24 h, and 1.55 g of 4-nitrobenzaldehyde and 0.5 mL of lactic acid (catalyst) were added in turn. Ten milliliters of DMSO solution in which 0.9 mL of pyrrole was dissolved were added into a constant pressure dropping funnel. As the content in the reactor was heated to 135°C, DMSO solution of pyrrole began to be slowly added dropwise from the constant pressure dropping funnel, and the addition of the pyrrole solution was finished in 15–20 min. The Alder reaction between solid-liquid phases was carried out continuously at the constant temperature of 135°C for 7 h, and blue black microspheres were obtained. The product microspheres were washed repeatedly with DMF until there was no longer small molecular porphyrin (it formed in the solution) in the cleaning mixture after determination by UV-visible spectrophotometry. The final microspheres were dried to constant weight under vacuum, and they were the porphyrin-immobilized microspheres NPP-GMA/MMA, on which 4-nitrophenyl porphyrin (NPP) was immobilized.

The other two functional polymeric microspheres PP-GMA/MMA and CPP-GMA/MMA (they also were blue black) on which phenyl porphyrin (PP) and 4-chlorophenyl porphyrin (CPP) were immobilized, were prepared with the same process, and only benzaldehyde and 4-chlorobenzaldehyde were used as one reactant in DMF solution during the Alder reaction between solid-liquid phases.

The infrared spectra of these microspheres, PP-GMA/MMA, NPP-GMA/MMA and CPP-GMA/MMA, were determined with KBr pellet method to characterize their chemical structures. To further confirm the chemical structures of these microspheres, the solid UV/Vis electronic adsorption spectra were determined.

The immobilized amounts (mmol/g) of porphyrins on these functional microspheres were determined through the coordination reaction of the immobilized porphyrin with zinc salt[25]: the coordination reaction of an aqueous $ZnCl_2$ solution with a given amount with the sample of the porphyrin-immobilized microspheres was allowed to be carried out, and the Zn^{2+} ion content in final solution was analyzed with EDTA complexometric titration method so as to indirectly determine the immobilized amount of porphyrin on these functional polymeric microspheres.

Preparation of supported cobalt porphyrin catalysts

Forty milliliters of DMF and 0.5 g of the functional polymeric microspheres NPP-GMA/MMA (or

PP-GMA/MMA and CPP-GMA/MMA) were placed in a four-necked flask, and the microspheres were sufficiently swelled, followed by the addition of 1 g of CoCl$_2$·6H$_2$O. Under nitrogen atmosphere and with mechanical stirring, the coordination reaction was allowed to be carried out at the constant temperature of 110°C for 8 h. At the end, the resulting microspheres were filtered out, washed with ethanol and distilled water, and dried under vacuum, resulting in the supported cobalt porphyrin catalyst CoNPP-GMA/MMA. Another two kinds of supported cobalt porphyrin catalysts, CoPP-GMA/MMA and CoCPP-GMA/MMA, were prepared.

To confirm the formation of the supported MPs, the solid UV/Vis electronic adsorption spectra of the above three kinds of cobalt porphyrin-supported microspheres, CoPP-GMA/MMA, CoCPP-GMA/MMA and CoNPP-GMA/MMA, were determined. The Co contents on these microspheres were determined with atomic absorption spectroscopy (AAS), so the immobilization amounts (μmol/g) of cobalt porphyrins, CoPP on CoPP-GMA/MMA, CoCPP on CoCPP-GMA/MMA and CoNPP on CoNPP-GMA/MMA, were calculated. By controlling the coordination reaction time, the solid catalysts with different immobilization amounts (i.e., immobilization density) of MPs were prepared.

Oxidation reaction of ethylbenzene catalyzed by solid cobalt porphyrin catalysts

The solid catalyst PP-GMA/MMA, CPP-GMA/MMA, and CoNPP-GMA/MMA were used in the catalytic oxidation of ethylbenzene by dioxygen to examine their catalytic activities. The procedures are described as follows by taking the system with catalyst CoNPP-GMA/MMA as an example. Ethylbenzene (20 mL) and 0.316 g of the solid catalyst CoNPP-GMA/MMA containing 10.46 μmol of CoNPP were placed into a reactor equipped with a mechanical agitator, a reflux condenser, a thermometer and an O$_2$ inlet. Oxygen at ordinary pressure was bubbled through the mixture at a fixed flow rate. The oxidation reaction was performed at a constant temperature of 120°C under stirring. The samples of the reaction mixture were taken at a certain time interval, and identified and quantificationally analyzed immediately by gas chromatograph with internal standard method using chlorobenzene as the standard substance. The result indicated that the main product was acetophenone, and its yield was calculated.

Examining effects of several factors on catalytic activity of solid catalysts

In this work, the catalytic properties of the prepared three supported metalloporphyrin catalysts, CPP-GMA/MMA, PP-GMA/MMA, and CoNPP-GMA/MMA were investigated in more detail, and the effects of several factors on the catalytic activity were investigated, including the effects of the catalyst species, the used amount of the catalyst and the immobilization density of metalloporphyrin. In addition, the reuse and stability experiments of the catalysts were performed. The reaction was carried out as described above, and every time, the reaction was carried out for 10 h. At the end of the reaction, the catalyst was collected by filtration, fully washed with ethanol and dried in vacuum, and then reused. The determined acetophenone yield was regarded as an index of evaluating the catalyst stability. The tested catalysts were consecutively used six times, and no cobalt was detectable in the filtrates by atomic absorption spectrometry.
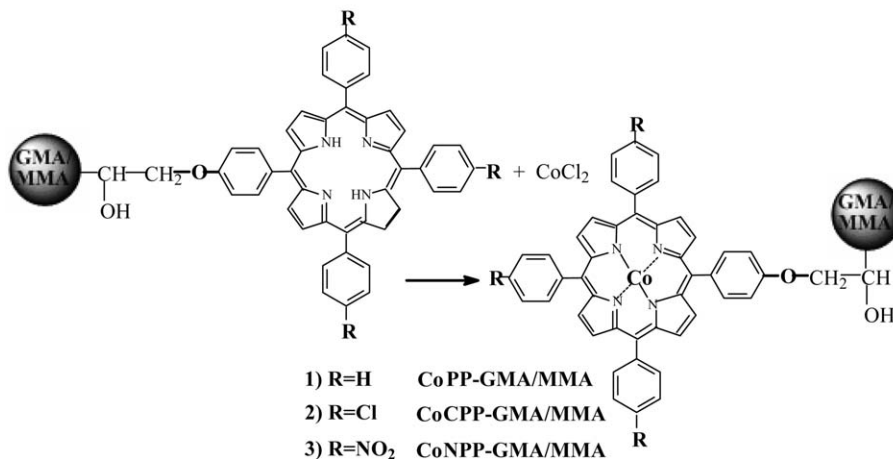
RESULTS AND DISCUSSION

Chemical process to realize synchronic synthesis and immobilization of porphyrins on GMA/MMA microspheres

Via suspension copolymerization of two monomers, GMA and MMA, and crosslinker EGDMA, the crosslinked copolymeric microspheres GMA/MMA were obtained. There are a mass of epoxy groups on the surfaces of the microspheres GMA/MMA, and this lays the foundation of synchronously synthesizing and immobilizing porphyrins on GMA/MMA microspheres. The chemical structure of the microspheres GMA/MMA is schematically expressed in Scheme 1.

The compound containing hydroxyl group as nucleophilic reagent can attack epoxy group, and enables ring-opening reaction of epoxy group to occur. HBA molecule not only contains hydroxyl group, but also is a Brønsted acid in itself, so that it can easily react with the hydroxyl group on GMA/MMA microspheres in the absence of proton acid to form the modified microspheres HBA-GMA/MMA. In succession, with the action of protonic acid
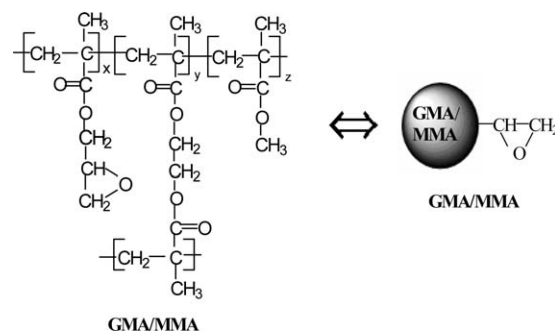
Scheme 1 Chemical structure of crosslinking microspheres GMA/MMA.

(1) Bonding p-Hydroxybenzaldehyde on GMA/MMA microspheres

HBA-GMA/MMA
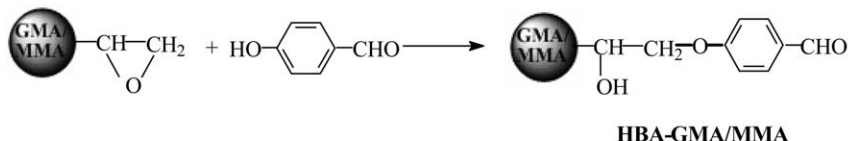
(2) Sychronistically synthesizing and immobilizing porphyrin on GMA/MMA microspheres

1): R=H   PP-GMA/MMA
2): R=Cl   CPP-GMA/MMA
3): R=NO₂   NPP-GMA/MMA
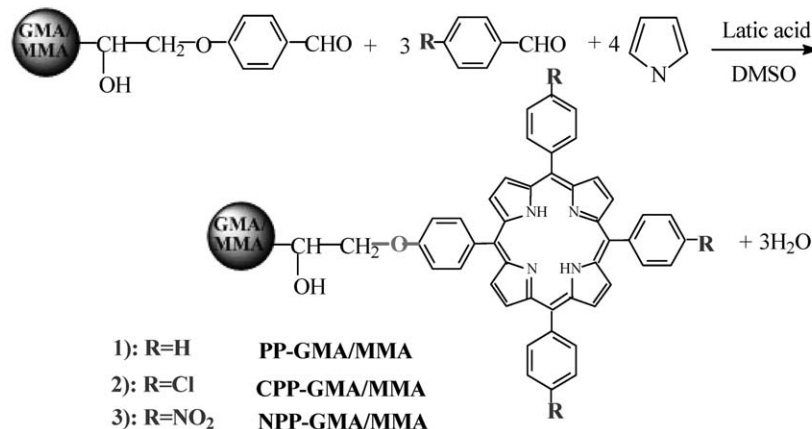
(3)Coordination reaction to form immobilized metalloporphyrins

1) R=H   CoPP-GMA/MMA
2) R=Cl   CoCPP-GMA/MMA
3) R=NO₂   CoNPP-GMA/MMA

Scheme 2 Chemical process to prepare immobilized MPs by synchronistically synthesizing and immobilizing porphyrins on GMA/MMA microspheres.

catalyst (lactic acid), the Alder reaction between solid-liquid phases, namely, the reaction between HBA on HBA-GMA/MMA and pyrrole as well as free benzaldehyde or substituted benzaldehyde in DMF solution, is carried out. As a consequence, the synchronous synthesis and immobilization of porphyrins on GMA/MMA microspheres is realized, and the porphyrin-immobilized microspheres, PP-GMA/MMA, CPP-GMA/MMA, and NPP-GMA/MMA, are prepared as used benzaldehyde, 4-chlorobenzaldehyde or 4-nitrobenzaldehyde as one reactant in DMF solution. Finally, via the coordination reaction of the immobilized porphyrins with cobalt salt, the three supported MPs catalysts, CoPP-GMA/MMA, CoCPP-GMA/MMA, and CoNPP-GMA/

MMA, were obtained. The entire chemical process to prepare the supported MPs can be schematically expressed in Scheme 2.

Characterization of two classes of functional microspheres

Infrared spectra of porphyrin-immobilized microspheres

Figure 1 gives the FTIR spectra of GMA/MMA and HBA-GMA/MMA, whereas Figure 2 shows the FTIR spectra of the three porphyrin-immobilized microspheres, PP-GMA/MMA, CPP-GMA/MMA, and NPP-GMA/MMA.
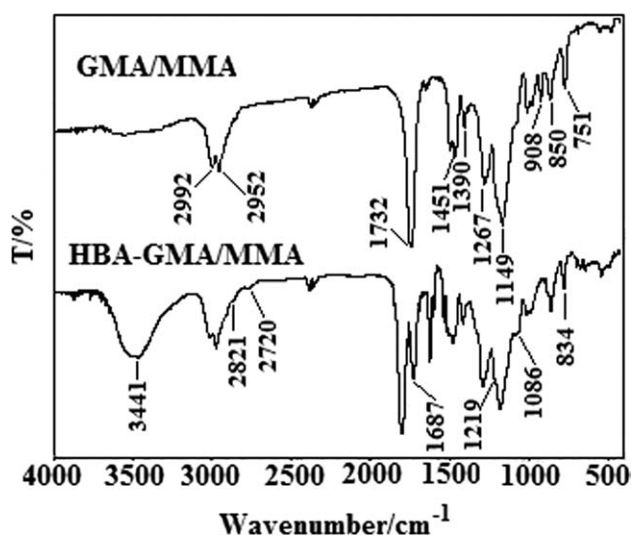
Figure 1 FTIR spectra of GMA/MMA and HBA-GMA/MMA microsphe.

In the spectrum of GMA/MMA, the characteristic absorption bands of the two monomer units and crossliker unit are shown, and it needs to be mentioned that there are two characteristic absorption bands of epoxy group at 908 and 850 cm^{-1}.

In the spectrum of HBA-GMA/MMA, the absorption bands of epoxy group at 908 and 850 cm^{-1} have disappeared, and the various characteristic bands of benzene ring (at 1600, 1492, 756, and 700 cm^{-1}) have appeared. Added to this, it is more important that four new bands at 3441, 1687, 1219, and 1086 cm^{-1} appear. The band at 1687 cm^{-1} is attributed to the stretching vibration absorption of C=O bond of aldehyde group, the bands at 1219 and 1086 cm^{-1} should be corresponding to the asymmetrical stretching and symmetrical stretching absorptions of C—O—C bond of aromatic ether group, and the bands at 3441 cm^{-1} should be ascribed to the vibration absorptions of secondary hydroxyl —OH that is formed after ring-opening of the epoxy group. The above facts show that the ring-opening and ether-forming reaction between the epoxy groups of GMA/MMA microspheres and hydroxyl groups of HBA has been occurred, HBA has been bound on GMA/MMA microspheres, and the surface-modified microspheres HBA-GMA/MMA microspheres have been obtained.

In the spectra of the three porphrins-supported microspheres, PP-GMA/MMA, CPP-GMA/MMA, and NPP-GMA/MMA, the characteristic absorption band of aldehyde group at 1687 cm^{-1} as described above has been disappeared completely, and the characteristic absorption bands of porphyrin have appeared at 1348, 1451, 1040, and 963 cm^{-1}. The first three bands at 1348, 1451, and 1040 cm^{-1} are attributed to porphyrin, whereas the last band at

963 cm^{-1} should be corresponding to the vibration absorption of N—H bond on the inner ring of porphyrin, and this is an important symbol of the formation of porphyrin.

Besides, as compared the spectrum of CPP-GMA/MMA as well as with the spectrum of NPP-GMA/MMA with the spectrum of PP-GMA/MMA, two characteristic absorption bands of C—Cl bond exhibits at 1175 and 675 cm^{-1} for CPP-GMA/MMA; whereas in the spectrum of NPP-GMA/MMA, two characteristic absorption bands of nitro groups exhibit at 1551 and 1378 cm^{-1}.

The above changes of absorption bands reveal that the Alder reaction between HBA-GMA/MMA 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 GMA/MMA microspheres have been realized, forming porphyrin-immobilized polymeric microspheres, PP-GMA/MMA, CPP-GMA/MMA, and NPP-GMA/MMA.

Electronic absorption spectra of porphyrin-immobilized microspheres

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

In the chloroform solution of TPP [Fig. 3(a)], a Soret band and four Q bands are visible at 421 nm and at 515, 550, 590, and 645 nm. For PP-GMA/MMA
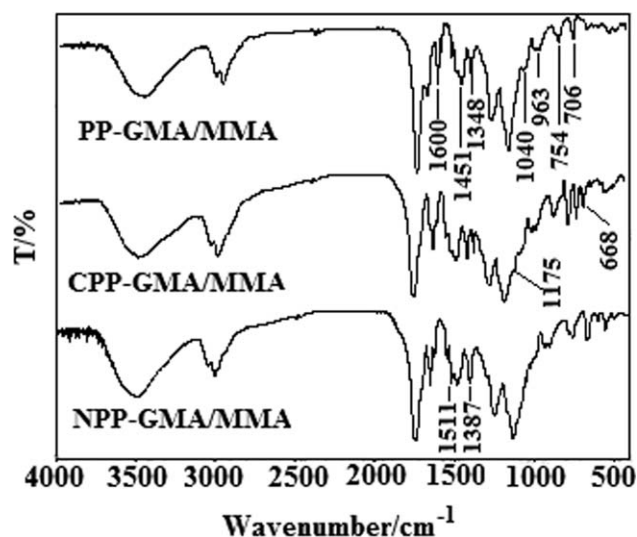

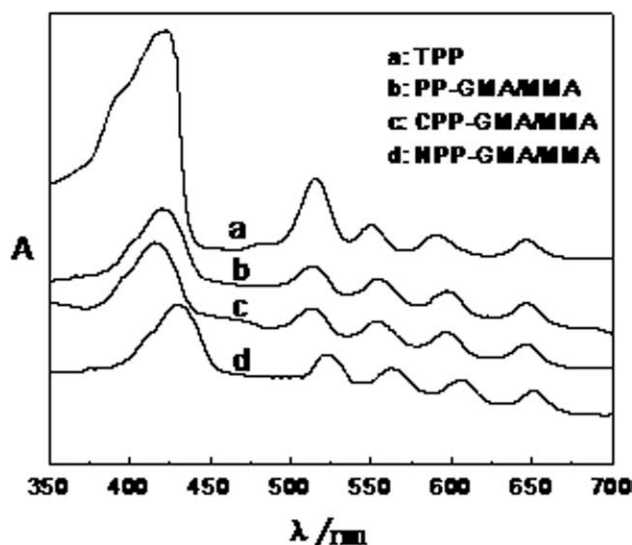**Figure 2** FTIR spectra of three porphyrin-immobilized microspheres.

Figure 3 Electronic absorption spectra of porphyrin- immobilized microspheres.

microspheres, a Soret band and four Q bands at 420 nm and at 514, 553, 595, and 646 nm, are also observed in the UV-Vis spectrum [Fig. 3(b)], and they are basically identical with that of TPP and only have slight shifts, implying the immobilization of PP on the microspheres. For the other two kinds of porphyrin-immobilized microspheres, CPP-GMA/MMA and NPP-GMA/MMA [Fig. 3(c,d)], a Soret band and four Q bands can also be observed similarly, and they are also almost identical with the corresponding the small molecule porphyrins in solutions (tetrachlorophynyl porphyrin, TCPP, and tetranitrophynyl porphyrin, TNPP). For CPP-GMA/ MMA and NPP-GMA/MMA, the position differences of the corresponding absorption bands in comparison with that of PP-GMA/MMA 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 GMA/ MMA microspheres have been realized.

Electronic absorption spectra of metalloporphyrin-immobilized microspheres

The presence of MP on PP-GMA/MMA microspheres as well as on CPP-GMA/MMA and NPP-GMA/MMA microspheres was confirmed by UV-Vis spectroscopy. The spectra for the small molecule cobalt phenyl porphyrin (CoPP) in solution, solid CoPP-GMA/MMA, CoCPP-GMA/MMA and CoNPP-GMA/MMA are shown in Figure 4.

In the chloroform solution of Cobalt tetraphynyl porphyrin (CoTPP) [Fig. 4(a)], a Soret band and a

Q band are visible at 407 nm and at 528nm. For solid CoPP-GMA/MMA, no significant changes in the positions of Soret band (at 406 nm) and Q band (at 527nm) are observed in the UV-Vis spectrum [Fig. 4(b)]. For the other two supported MPs CoCPP-GMA/MMA and CoNPP-GMA/MMA [Fig. 4(c,d)], we have observed the Soret bands at 407 nm and the Q band at 523nm, and the Soret bands at 432 nm and the Q band at 544 nm, and the spectra of the two supported MPs on GMA/MMA are also almost identical with the corresponding MPs in homogenous solutions (Cobalt tetrachlorophynyl porphyrin, CoTCPP, and Cobalt tetranitrophynyl porphyrin, CoTNPP). The above fact proves that the three supported MPs, CoPP-GMA/MMA, CoCPP-GMA/ MMA, and CoNPP-GMA/MMA, have been obtained via the coordination reactions of the porphyrin-immobilized microspheres with cobalt salt.

Catalytic property of supported metalloporphyrin catalysts

Effect of substitute on phenyl ring in macrocycle on catalytic activity

Some study results that metalloporphyrin catalysts are used in the catalytic oxidation of ethylbenzene by molecular oxygen have been reported.[26–29] Now, we used the supported metalloporphyrin catalysts, CoPP-GMA/MMA, CoCPP-GMA/MMA, and CoNPP-GMA/MMA, in the catalytic oxidation of ethylbenzene by molecular oxygen under ordinary pressure at 120°C. It needs to be pointed out that for the used three catalysts, the immobilization density of cobalt porphyrins were similar each other, and they were 66.18 μmol/g for CoPP-GMA/MMA, 64.49 μmol/g for CoCPP-GMA/MMA, and 64.25
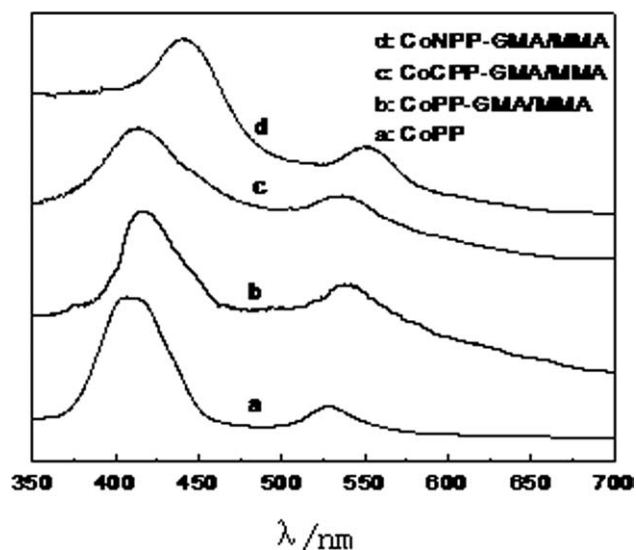

Figure 4 Electronic absorption spectra of metalloporphyrin-immobilized microspheres.
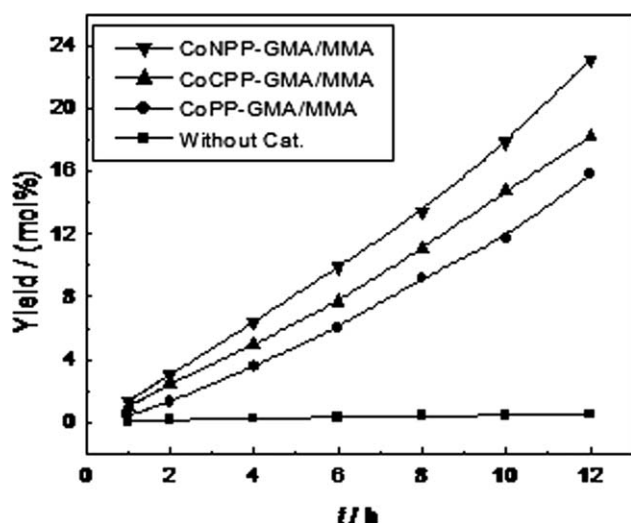
Figure 5 Variation of acetophenone yield with time using three different catalysts. Temperature: 120°C; Used amount of solid catalyst: 0.316g (amount of Cobalt porphyrin: 20.93μmol).

μmol/g for CoNPP-GMA/MMA. Besides, the added amounts of cobalt porphyrins (μmole number) in the three catalytic oxidation systems were also identical, 20.93μmol. The reaction product was identified and analyzed via gas chromatographic (GC) method. The experimental results showed that the main product of the oxidation was acetophenone with a percent of 98% (a little of by-product, α-methyl benzalcohol). The variations of the acetophenone yields with the reaction time for the three catalytic oxidation systems are displayed in Figure 5.

As no cataltst was added into the reaction system, only little acetophenone is produced as shown in Figure 5; whereas as a little of catalyst was added, a certain amount of acetophenone was produced; further, the yield of acetophenone increases rapidly with the reaction time; for the CoNPP-GMA/MMA system, after 12 h, the yield of acetophenone gets up to 23%. Obviously, the three supported cobalt porphyrin catalysts, CoPP-GMA/MMA, CoCPP-GMA/MMA, and CoNPP-GMA/MMA, can effectively activate molecular oxygen, and make ethylbenzene to be oxidized into acetonphenone by molecular oxygen under the mild condition, evidently displaying their higher catalytic activity.

It also can be found from Figure 5 that the catalytic activities of the three catalysts are different. The catalytic activity of CoNPP-GMA/MMA is the highest among the three catalysts, CoCPP-GMA/MMA ranks the second, and CoPP-GMA/MMA is the catalyst with the worst activity. The possible reason for this is as follows. Nitro group and halogen atom are electron-withdrawing substitutes. 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.[30,31] Therefore, CoNPP-GMA/MMA and CoCPP-GMA/MMA have higher catalytic activity than CoPP-GMA/MMA.

Effect of immobilization density of cobalt porphyrin on catalytic activity

Fixed other reaction conditions (ethylbenzene: 20 mL; temperature: 120°C; added amount of Cobalt porphyrin: 20.93 μmol), the catalytic oxidation reactions were performed using the CoNPP-GMA/MMA catalysts with different immobilization densities of CoNPP and the catalysts CoCPP-GMA/MMA with different immobilization densities of CoCPP, so as to examine the effect of the immobilization density of metalloporphyrin on the catalytic activity for the polymer-supported metalloporphyrin catalysts. Figure 6 presents acetophenone yield curves of the systems with CoNPP-GMA/MMA. The yield data in 12 h are taken from Figure 6, and the relationship curve between the acetophenone yield and the immobilization density of CoNPP is given in Figure 7.

It can be found from Figures 6 and 7 that as the catalyst CoNPP-GMA/MMA with a smaller immobilization density of CoNPP is used, the yield of acetonephenone is greater, implying higher catalytic activity. In contrast, as the catalyst CoNPP-GMA/MMA with a larger immobilization density of CoNPP is used, the catalytic activity of CoNPP-GMA/MMA is lower. Perhaps, this reflects the effect of the macromolecule microenvironment similar to polypeptide on the activity of the biomimetic
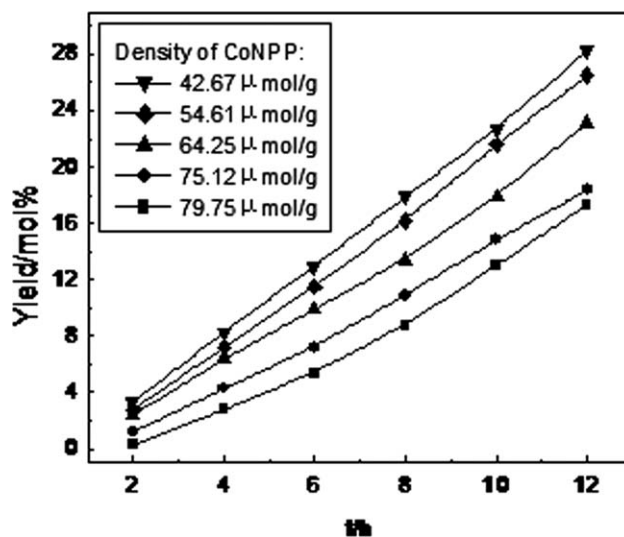

Figure 6 Variation of acetophenone yield with time using CoNPP-GMA/MMA catalysts with different immobilization densities of CoNPP. Temperature: 120°C; Added amount of CoNPP in system: 20.93 μmol.
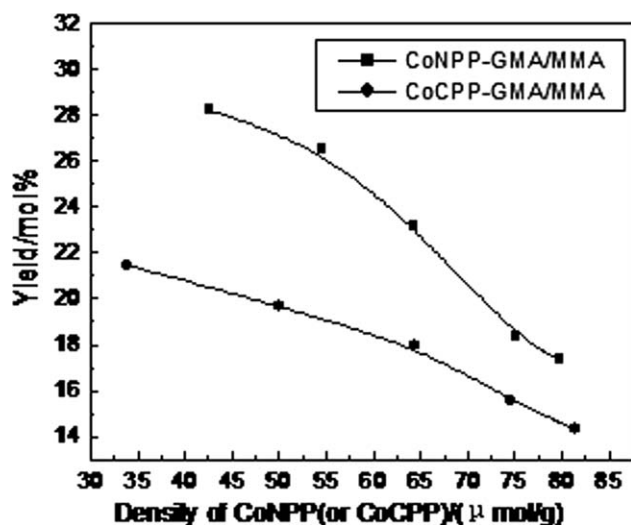
Figure 7 Acetophenone yield as function of immobilization densities of CoNPP or CoCPP. Reaction time: 12 h.

Figure 8 Variation of acetophenone yield with time using different added amounts of CoNPP-GMA/MMA (expressed as added amount of CoNPP. Reaction temperature: 120°C.

catalysts. The possible reason for this is that the sufficient and excellent polymer microenvironment can effectively protect metalloporphyrin and prevent it from destruction and deactivation, resulting in high catalytic activity. It is obvious that when the immobilization density of metalloporphyrin on the polymer-supported metalloporphyrin catalyst is smaller, the effect of the polymer microenvironment is more outstanding. The effect of the immobilization density of metalloporphyrin on the catalytic activity for the polymer-supported metalloporphyrin catalysts was found for the first time in our previous study,[32] and in this work, this finding is again confirmed.

For the CoCPP-GMA/MMA systems, the relationship curve between acetophenone yield in 12 h and the immobilization density of CoCPP is also given in Figure 7, and the similar experimental results are exhibited, namely, the catalyst CoCPP-GMA/MMA with a smaller immobilization density of CoCPP has higher catalytic activity.

Effect of used amount of catalyst on catalytic activity

The Catalyst CoNPP-GMA/MMA with 42.67 μmol/g of immobilization density of CoNPP and the CoCPP-GMA/MMA with 33.94 μmol/g of immobilization density of CoCPP were used in the catalytic oxidation reactions. By fixing other reaction conditions (ethylbenzene: 20 mL; temperature: 120°C) and changing the added amount of the solid catalysts, the oxidations were conducted so as to examine the effect of the used amount of the catalyst on the catalytic activity. For CoNPP-GMA/MMA systems, Figure 8 displays the acetophenone yield curves as different amounts of solid catalyst CoNPP-GMA/MMA were added into the systems (the amounts of
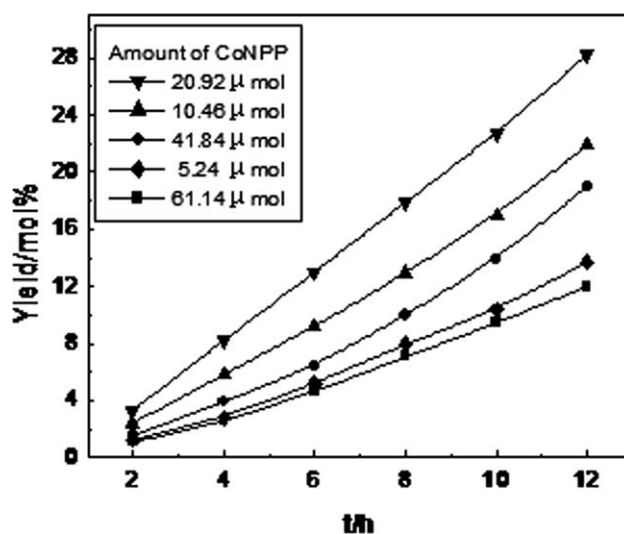
CoNPP-GMA/MMA had been transformed into the amount of CoNPP). The yield data in 12 h are taken from Figure 8, and the relationship curve between the acetophenone yield and the added amount of CoNPP is given in Figure 9.

From Figures 8 and 9, a special effect of the used amount of the catalyst on the catalytic activity can be found: the acetophenone yield increases rapidly with the amount of the catalyst as the used amount of the catalyst is smaller, and this is similar to the common heterogeneous catalytic reaction systems; when the catalyst amount is enhanced to a certain amount (10.46 μmol of CoNPP), a maximum yield of
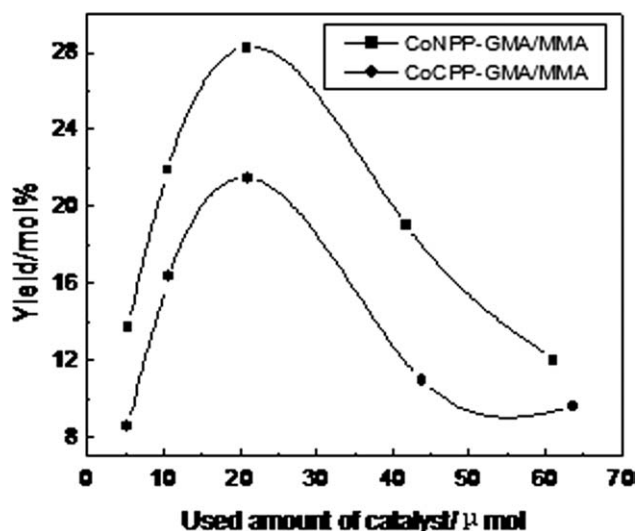

Figure 9 Acetophenone yield as function of added amounts of CoNPP or CoCPP. Reaction time: 12 h.
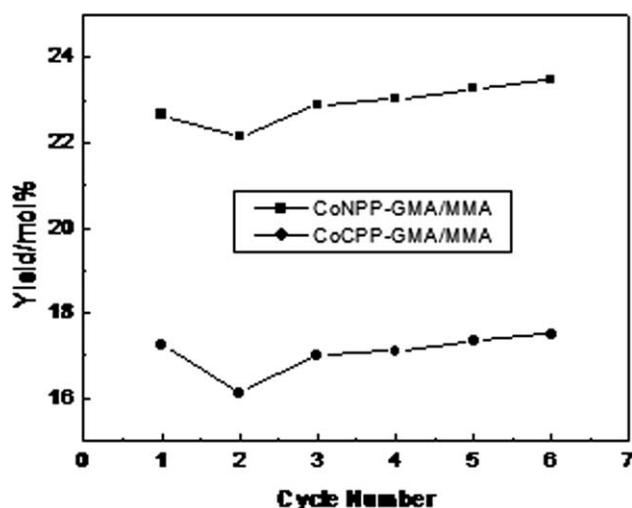
Figure 10 Acetophenone yield in 10 h as function of cycle number.

acetophenone (28%) appears, implying 10.46 μmol is the optimal used amount of CoNPP; subsequently, the acetophenone yield turns to decreasing with continuatively increasing the catalyst amount; as the catalyst amount is very great, the yield of acetophenone seems to be very low. Apparently, the excessive addition of cobaltoporphyrin catalyst will inhibit the catalytic activity, and this is different from the common heterogeneous catalysts. This special phenomenon of biomimetic catalysts also were found by another research group[33] as well as in our previous work.[32] The reason for this needs to be further studied, and up to now, it still can not be explained clearly.

For the CoCPP-GMA/MMA systems, the relationship curve between the acetophenone yield in 12 h and the amount of CoCPP is also given in Figure 9, and the similar experimental results are displayed, but then for the CoCPP-GMA/MMA systems, the optimal used amount of CoCPP is about 10.57 μmol, and the corresponding maximum yield of acetophenone is 21%.

Recycle and reuse property of catalyst

The recycle and reuse experiments for the prepared solid catalysts were conducted to examine their stability. Figure 10 shows the acetophenone yield in 10 h as a function of the number of cycle for the catalyst CoNPP-GMA/MMA with 42.67 μmol/g of immobilization density of CoNPP and the catalyst CoCPP-GMA/MMA with 33.94 μmol/g of immobilization density of CoNPP. It can be observed that during the consecutive reuse of six times, the catalytic activity of the two immobilized metalloporphyrin catalysts increases except the secondary time, leading to that the activity of the sixth time is higher

than that of the first time, exhibiting excellent reuse performance. This behavior seems to be also different from common heterogeneous catalysts, and this phenomenon was also found in our previous study.[32] For this special phenomenon of biomimetic catalysts, we are seeking the reason, and the further investigation result will be reported in future.

CONCLUSIONS

In this article, a new route to prepare metalloporphyrin catalysts supported on polymeric microspheres is put forward, and it is to synchronously synthesize and immobilize porphyrins on polymeric microsphers GMA/MMA, followed by the coordination reaction of metal salt. Three kinds of polymer-supported cobalt porphyrin catalysts, CoPP-GMA/MMA, CoCPP-GMA/MMA, and CoNPP-GMA/MMA were prepared. These catalysts were used in the catalytic oxidation of ethylbenzene to acetophenone by molecular oxygen, and exhibited high catalytic activity. In this study, some special phenomena (or facts) were found (1) The catalyst with electron-withdrawing substitutes in macrocyclic rings has higher catalytic activity; (2) The used amount of the biomimetic catalysts seems to have an optimal value in a given reaction system, and excessive addition of the biomimetic catalysts results in reduced yield of acetophenone; (3) For the polymer-supported metalloporphyrin catalysts, the immobilization density of metalloporphyrin has an effect on the yield of acetophenone. The catalyst with a smaller immobilization density of metalloporphyrin provides a higher yield of acetophenone; (4) The prepared polymer-supported metalloporphyrin catalysts have excellent recycle and reuse property. The above findings are significant and important for the applications of polymer-supported metalloporphyrin catalysts.

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