

Immobilization of Manganoporphyrin on a Novel Polymeric Support and Catalytic Oxidation Characteristic of Supported Catalyst

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ABSTRACT: Monomer glycidyl methacrylate (GMA) was grafted on silica gel particles in the manner of "grafting from," and the grafted particles PGMA/SiO₂ was prepared. The grafted particles PGMA/SiO₂ is a kind of novel support for the immobilization of metalloporphyrin catalysts. In the presence of basic catalysts, the ring-opening reaction of the epoxy groups of the grafted PGMA occurred and the bonding of meso-tetra (4-hydroxyphenyl) porphyrin (THPP) on the particles PGMA/SiO₂ was realized, resulting in the bonded particles HPP-PGMA/SiO₂. Subsequently, the metallation of the bonded particles HPP-PGMA/SiO₂ was carried out via the coordination reaction between HPP-PGMA/SiO₂ and manganese salt, resulting in the supported manganoporphyrin (MnP) catalyst MnP-PGMA/SiO₂. The supported catalyst was used in the catalytic oxidation of ethyl benzene into acetophenone by molecular oxygen. In this article, the effects of various factors such as the species and amount of the cata-

lyst on the bonding process of THPP were studied because of the importance of the bonding reaction of THPP in the preparation of the catalyst MnP-PGMA/SiO₂. Finally, the catalytic performance of MnP-PGMA/SiO₂ in the catalytic oxidation process of ethyl benzene was investigated. The experimental results show that triethylamine is a suitable catalyst for the bonding of THPP on the grafted particles PGMA/SiO₂ and for the forming of MnP-PGMA/SiO₂. The supported catalyst MnP-PGMA/SiO₂ can effectively activate molecular oxygen, and obviously catalyze the oxidation process of ethyl benzene to acetophenone by molecular oxygen. It was found that the immobilization density of MnP on MnP-PGMA/SiO₂ has a great effect on the catalytic activity of the catalyst. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2764–2772, 2009

Key words: manganoporphyrin; immobilization; glycidyl methacrylate; silica gel; catalytic oxidation

INTRODUCTION

Metalloporphyrins (MPs) have been successfully used as model for the cytochrome-450 enzyme with respect to the oxidation of organic compounds such as hydrocarbons.^{1–3} However, metalloporphyrins as homogeneous catalysts have some disadvantages: for example, they may easily be destroyed during the course of the reaction leading to deactivation; these expensive catalysts cannot be easily recovered after the reaction for reuse.^{4–6} These disadvantages limit the practical application of metalloporphyrins in both synthetic chemistry and industrial process. These drawbacks can be overcome by immobilizing metalloporphyrins on suitable insoluble supports, such as alumina, silica, zeolites, clays, and polymeric matrices.^{7–10} Many studies confirm that immobilizing of metalloporphyrins on suitable support materi-

als not only improves the catalysts stability and the selectivity of the product but also promotes the easy recover and reuse of the catalysts.^{11–13} Among the various support materials, polymer supports have attracted much attention due to their some characteristics.

Inside organism, the natural oxidase is surrounded by polypeptide coils, and it exerts fully the catalytic action in a local hydrophobic microenvironment, which is formed by polypeptide chains. In the structure of synthetic polymer-supported metalloporphyrin catalysts, the macromolecular chains afford the catalyst a biomimetic hydrophobic microenvironment. The polymer effect of this biomimetic special microenvironment not only can protect effectively the metalloporphyrin catalysts from destruction and deactivation due to self-oxidation, but also can enhance the catalytic performance, such as catalytic activity and selectivity.^{4,14–16} To date, two classes of polymer supports for the immobilization of metalloporphyrin catalysts are mainly reported, synthetic polystyrene-based resins such as Merrifield and Argogel resins and natural polymer chitosan.^{17–19} In this work, a novel polymeric support PGMA/

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SiO₂ was used for the immobilization of manganoporphyrin (MnP). PGMA/SiO₂ was prepared by graft polymerizing of glycidyl methacrylate (GMA) onto the surface of silica gel particles (SiO₂). The immobilization of manganoporphyrin was realized through the ring-opening reaction of the epoxy groups of the grafted poly (glycidyl methacrylate) (PGMA) and subsequent coordination reaction between the bound porphyrin and MnCl₂, resulting in the supported catalyst MnP-PGMA/SiO₂. The supported manganoporphyrin catalyst MnP-PGMA/SiO₂ was used in the catalytic oxidation of ethyl benzene into acetophenone with molecular oxygen under ordinary pressure as oxidant and its catalytic performance was examined. The heterogeneous catalyst MnP-PGMA/SiO₂ exhibited high catalytic activity and selectivity. MnP-PGMA/SiO₂ combines well the advantages of polymer-supported manganoporphyrin catalysts with the many excellent properties of the inorganic carrier particle SiO₂, such as good mechanical property, high specific area, and fine thermal stability, which are very important in the heterogeneous catalytic process. Obviously, the grafted particles PGMA/SiO₂ is a kind of novel supports for the immobilization of metalloporphyrins, and this research helps us to develop further the heterogeneously supported manganoporphyrin catalysts used in the oxidation of hydrocarbons.

EXPERIMENTAL

Materials and instruments

Silica gel (120–160 mesh, an average diameter of 125 μm, Tsingtao Ocean Chemical Industry Ltd., Province Shandong, China) was of reagent grade; 3-methacryloxypropyl trimethoxysilane (MPS, Nanking Chuangshi Chemical Industry and Accessory Ingredient Ltd., Province Jiangsu, China) was of analytical purity grade; methane sulfonic acid (Beijing Jinlong Chemical Reagent Ltd., Beijing) was of chemical purity grade; glycidyl methacrylate (GMA, Mitsubishi Company, Japan) was of analytical purity grade, and was distilled under vacuum prior to use; azodiisobutyronitrile (AIBN, Shanghai Chemical Reagent Plant, Shanghai) was of analytical purity grade without further treatment; meso-tetra (4-hydroxyphenyl) porphyrin (THPP) was self-synthesized with Alder method; triethylamine (TEA, Tientsin Fuzhen Chemical Reagent Plant, Tientsin, China). Other chemicals were all commercial reagents with analytical pure.

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 (AAS,

Thermo Company, USA); HP 6890 gas chromatograph (GC, Beijing Analytical Instrument Plant).

Preparation and characterization of catalyst

Preparation and characterization of grafted particle PGMA/SiO₂

According to the procedure ascribed in Ref. 20, the graft polymerization of GMA on the surfaces of silica gel particles was performed, and the typical process was as follows. First, silica gel particles were treated with methane sulfonic acid to activate and produce more hydroxyl groups on the surfaces of silica gel particles. Afterwards, the surface modification of silica gel particles with coupling agent 3-methacryloxypropyl trimethoxysilane (MPS) was carried out at 50°C using a mixed solvent of ethanol and water in a volume ratio of 1 : 1, and the modified silica gel (denoted as MPS-SiO₂) on which double bonds were borne was obtained. Using AIBN as initiator and dimethyl formamide (DMF) as solvent, the graft polymerization of GMA on the surfaces of MPS-SiO₂ particles was carried out, and the grafted particles PGMA/SiO₂ were obtained. The infrared spectrum of PGMA/SiO₂ was determined with KBr pellet method to characterize its structure. The grafted particles PGMA/SiO₂ were swelled fully in acetone, and the amount of epoxy groups were measured with hydrochloric acid titrimetric method to determine the grafting degree of PGMA (g/100 g) on the surface of silica gel particles. The grafted particles PGMA/SiO₂ with a grafting degree of 25.8 g/100 g were prepared and used in this study.

Bonding THPP on PGMA/SiO₂ and characterization of product

Covalently bonding THPP on the grafted particle PGMA/SiO₂ was conducted in a four-necked bottle. One gram PGMA/SiO₂ was suspended in 40 mL of *N,N*-DMF. After swelling PGMA/SiO₂ for 12 h, 0.3 g THPP and a certain amount of the catalyst, TEA, were added. The bonding reaction was carried out at a constant temperature of 70°C for 8 h under mechanical stirring. After finishing the reaction, the product particles were washed repeatedly with DMF until no THPP in the cleaning mixture was detected with spectral absorption method. After vacuum drying, the obtained dull red product was namely the bonded particles HPP-PGMA/SiO₂ on which hydroxylphenyl porphyrin (HPP) was bound covalently. By collecting all filtrates and cleaning mixtures, the amount of the remaining THPP in these mixtures was determined with UV–Vis spectroscopy, and the bonding degree (μmol/g) of HPP on HPP-

PGMA/SiO₂ samples was determined. The chemical structure of HPP-PGMA/SiO₂ was characterized with infrared difference spectrometry.

To select suitable catalyst for the bonding reaction of THPP on the grafted particles PGMA/SiO₂, in this research, three kinds of catalysts, NaOH, Na₂CO₃, and triethylamine (TEA), were used. The effects of the species and of amount of the catalysts on the bonding reaction were studied.

Metallation of HPP-PGMA/SiO₂

One gram of the bonded particles HPP-PGMA/SiO₂ was suspended in 40 mL of a mixed solvent of acetone and *N,N'*-DMF (V/V = 1 : 1) in a four-necked bottle of 100 mL. After HPP-PGMA/SiO₂ was fully swelled, 2 g MnCl₂·4H₂O was added. Under nitrogen atmosphere and mechanical stirring, the content was heated, and the coordination chelation reaction was carried out at a reflux temperature of 64°C. After ending the reaction, the reaction mixture was cooled to room temperature, and the obtained solid product in greenish black was filtrated, washed repeatedly with water, and dried under vacuum, resulting in the supported catalyst MnP-PGMA/SiO₂. The Mn content (μmol/g) in MnP-PGMA/SiO₂ was determined with atomic absorption spectroscopy (AAS).

Ethyl benzene oxidation with molecular oxygen catalyzed by MnP-PGMA/SiO₂

In a reactor of 100 mL equipped with a mechanical stirrer, a reflux condenser, and a thermometer, 20 mL of ethylene benzene and the catalyst MnP-PGMA/SiO₂ with a certain amount were added. Oxygen at a fixed flow rate was bubbled through the mixture. The oxidation reaction was conducted at a constant temperature of 95°C under stirring. The mixture samples were taken at certain time intervals, were identified, and quantified immediately with gas chromatograph with internal standard method, using chlorobenzene as the standard substance. The main product was confirmed to be acetophenone. The acetophenone yield was calculated quantitatively. At the same time, the selectivity to acetophenone for the catalyst was examined.

By varying the used amount of the catalyst MnP-PGMA/SiO₂ and using the catalysts of different batches on which the immobilization density of MnP were different, the effects of the used amount and surface structure of the catalyst MnP-PGMA/SiO₂ on the oxidation process of ethyl benzene oxidation were studied.

RESULTS AND DISCUSSION

Process to prepare supported catalyst MnP-PGMA/SiO₂

In a solution polymerization system, the monomer GMA was graft-polymerized onto the surfaces of silica gel particles in the manner of "grafting from" by the aid of the mediacy action of the coupling agent MPS, and the grafted particles PGMA/SiO₂ was formed. There is a great deal of epoxy groups on the surface of the particle PGMA/SiO₂, so the ring-opening reaction between these epoxy groups and hydroxyl groups of THPP can occur in the presence of basic catalyst, leading to the bonding THPP on the grafted particle PGMA/SiO₂ and resulting in the bonded particles HPP-PGMA/SiO₂. Subsequently, the coordination chelation reaction between the bound porphyrin and manganese salt was carried out, leading to the metallation of the bound porphyrin and resulting in the supported manganoporphyrin catalyst MnP-PGMA/SiO₂. The process to prepare MnP-PGMA/SiO₂ is schematically shown in Scheme 1.

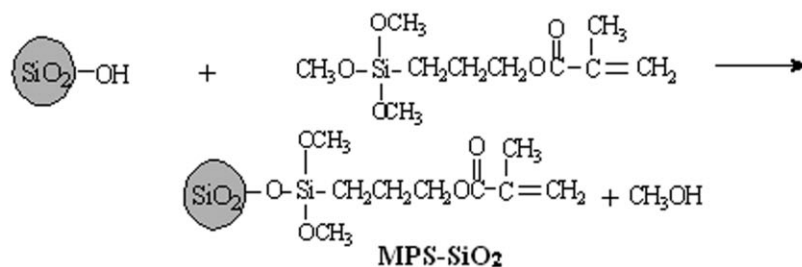
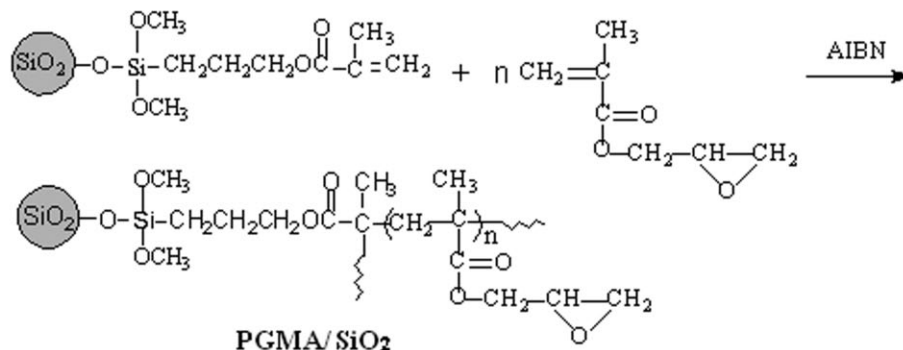
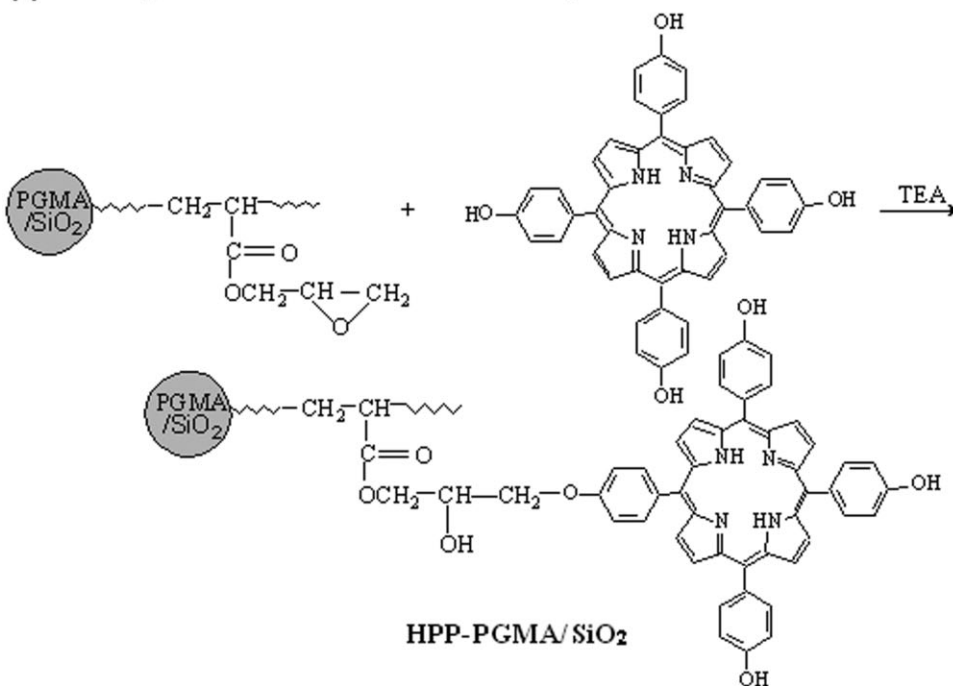
IR spectrum of HPP-PGMA/SiO₂

Figure 1 gives the IR spectra of PGMA/SiO₂ (1) and HPP-PGMA/SiO₂ (2), and their difference spectrum (3) is also displayed. In the spectrum of PGMA/SiO₂, the band at 1100 cm⁻¹ is the stretching vibration absorption of Si—O—Si bond of SiO₂, and this band covers up many absorptions of PGMA because the band at 1100 cm⁻¹ is wide and strong. The band at 1725 cm⁻¹ is the vibration absorption of ester carbonyl group C=O, the bands at 1482 and 1397 cm⁻¹ are the absorptions of >CH₂ and —CH₃, and the band at 907 cm⁻¹ is the absorption of epoxy groups of PGMA. In the spectrum of HPP-PGMA/SiO₂, the main characteristic absorptions of PGMA are displayed, but the characteristic absorptions of HPP are difficult to be recognized. Thus, the difference spectrometry is adopted. The difference spectrum in Figure 2 is a magnified result. In the difference spectrum, the characteristic absorptions of HPP are displayed basically: the band at 3313 cm⁻¹ is ascribed to the absorptions of N—H bond of pyrrole ring, and 1360, 998, and 731 cm⁻¹ correspond to the absorptions of the skeletal vibration of porphyrin ring. The above IR data show that the bonding reaction of THPP on PGMA/SiO₂ has occurred and the composite bonded particles HPP-PGMA/SiO₂ have been formed.

Effects of various factors on bonding reaction of THPP on PGMA/SiO₂

Effect of species of catalyst

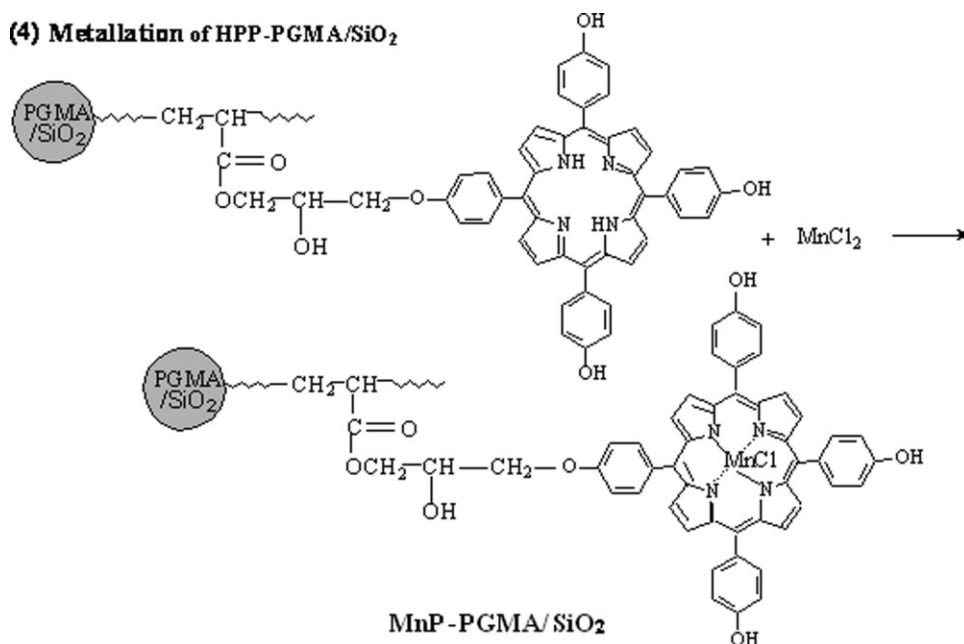
The bonding of THPP on PGMA/SiO₂ was realized via the ring-opening reaction between the epoxy

(1) Surface modification of silica gel particle**(2) Graft-polymerization of GMA on MPS-SiO₂****(3) Bonding reaction of THPP on PGMA/SiO₂**

Scheme 1 Schematic expression of process to prepare MnP-PGMA/SiO₂.

groups of the grafted PGMA and hydroxyl groups of THPP in the presence of basic catalyst. In this investigation, three basic catalysts, NaOH, Na₂CO₃, and TEA, were tested, and they have basicity with different strengths. Figure 2 shows the bonding degree of HPP of the bonded particles HPP-PGMA/

SiO₂ as a function of the reaction time. It can be seen that under the same conditions such as the used amount of the catalyst and reaction temperature, at the earlier stage of the reaction, the rate of bonding reaction is the rapidest as NaOH is used as the catalyst resulting in the greatest bonding degree of HPP.

(4) Metallation of HPP-PGMA/SiO₂

Scheme 1 Continued

However, as the reaction is carried out to a certain time (about 5 h), the rates of the bonding reaction in the three systems are changed, and the rate of the bonding reaction in the system with TEA turns the rapidest, resulting in the crossing of the three curves. The appearance of this phenomenon can be explained as follows. Among the three catalysts, the basicity of NaOH is the strongest, that of Na₂CO₃ follows, and that of TEA is the weakest. Thus, their catalytic abilities for the ring-opening reaction of epoxy groups are in the same sequence. As a result, the reaction rate at the earlier stage of the reaction is the rapidest as used NaOH, whereas the reaction rate is the slowest as used TEA. There are four sym-

metrical hydroxyl groups on the outside ring of THPP. The crosslinking between PGMA macromolecules grafted on SiO₂ will occur consequentially along with the progress of the bonding reaction, and this will result in crosslinked PGMA with porphyrin as crosslinking bridges. This crosslinking bridges will produce steric hindrance for the further bonding of THPP on the grafted particles PGMA/SiO₂. As NaOH is used, the rapider rate of the bonding reaction leads to the rapid increase of the bonding degree of HPP at the earlier stage of the reaction, and this will result in prematurely and severely forming of the crosslinking bridges. Consequently, as the reaction is carried out to a certain time, the rate of the bonding reaction turns slow owing to the

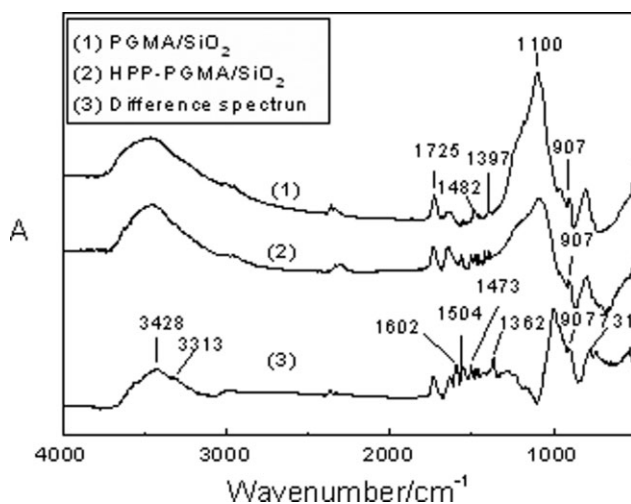


Figure 1 FTIR spectra of PGMA/SiO₂ and HPP-PGMA/SiO₂ and their difference spectrum.

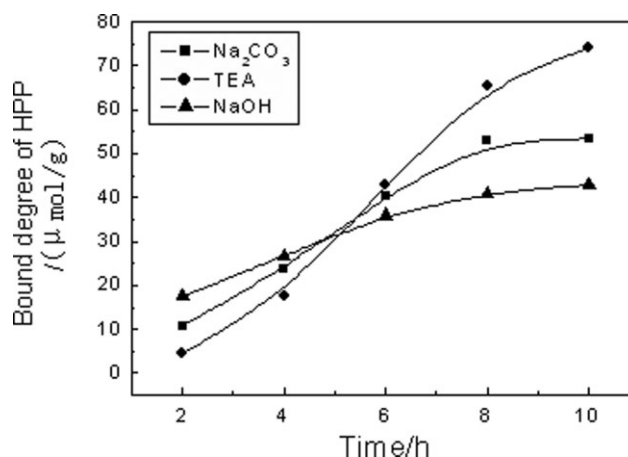


Figure 2 Variation of bonding degree of HPP with time with different catalysts DMF: 40 mL; PGMA/SiO₂: 1 g; THPP: 0.3 g; Catalyst: 0.0142 mol; *T* = 70°C.

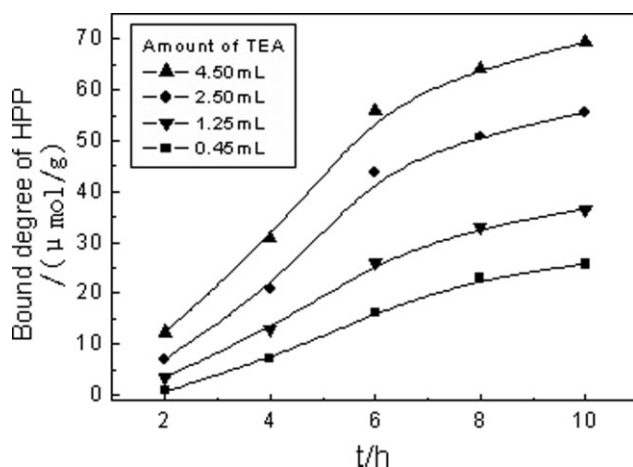


Figure 3 Variation of bonding degree of HPP with time with different amounts of TEA DMF: 40 mL; PGMA/SiO₂: 1 g; THPP: 0.3 g; *T* = 70°C.

steric hindrance of the crosslinking bridges. Whereas as TEA is used, the bonding reaction of THPP is gentle, and the crosslinking extent of the grafted PGMA always is weaker in the reaction system compared with the other two systems, the systems with NaOH or Na₂CO₃ as catalyst. Although the rate of the bonding reaction of THPP is slow at the earlier stage in the system used TEA, the total result of bonding THPP on the grafted particles is better than that in the other two systems. Therefore, in this investigation, TEA was selected as a suitable catalyst for the preparation of the bonded particles HPP-PGMA/SiO₂.

Effect of amount of catalyst

By varying the used amount of the catalyst TEA and by fixing other conditions (PGMA/SiO₂: 1 g; DMF: 40 mL; THPP: 0.3 g; temperature: 70°C), the bonding reactions were performed. Figure 3 gives the bonding degree of HPP as a function of the reaction time as different amounts of the catalyst TEA were used. The following facts can be observed: (1) At the earlier stage of the reaction, the bonding degree of HPP increase rapidly with time, but after 8 h the variation of the bonding degree of HPP turns gently. This is caused by the steric hindrance of the formed crosslinking bridges as described above, (2) within the same time, the bonding degree of HPP increases continuously with the increase of the used amount of TEA. As the used amount of TEA is greater, the catalytic action of the catalyst is stronger, and the ring-opening reaction between the epoxy groups of the grafted PGMA and THPP is accelerated more rapidly, resulting in the higher bonding degree of HPP. In this study, by varying the used amount of TEA with a fixed reaction time of 8 h, the bonded

particles HPP-PGMA/SiO₂ with the different bonding degrees of HPP were prepared.

Determination of optimal coordination reaction time of manganese salt and HPP-PGMA/SiO₂

In the published literatures about immobilizing metalloporphyrins, most adopted methods are that first metalloporphyrins are prepared via coordination reaction between porphyrins and metal salts and then metalloporphyrins are immobilized on supports. In this study, the other way is adopted. First porphyrin is immobilized on the support, namely, THPP is first bound on the grafted particles PGMA/SiO₂ as described above, and then the metallation is realized via the coordination reaction between immobilized porphyrin and metal salt, namely, the metallation of the immobilized porphyrin is realized via the coordination reaction between particles HPP-PGMA/SiO₂ and manganese salt, finally forming the catalyst MnP-PGMA/SiO₂. This route as shown in Scheme 1 has an obvious advantage of a simplified procedure.

For the coordination reaction between HPP-PGMA/SiO₂ and manganese salt, the effect of reaction time on the coordination reaction was examined, and the reaction progress was monitored by determining the manganese content with atomic absorption spectroscopy. The experimental result showed that as manganese salt was in excess, after 6 h, the manganese content turned to nearly not changing. Here, the coordination extent of the ligands, immobilized porphyrins, was estimated to be about 92%, and it was probably affected by the steric hindrance of the crosslinked matrix. Thus, in this work, 6 h was taken as a suitable time of the coordination reaction. The catalyst loadings of MnP-PGMA/SiO₂ were calculated from the manganese content (μmol/g). By using the bonded particles HPP-PGMA/SiO₂ with different bonding degree of HPP, the supported catalysts MnP-PGMA/SiO₂ with different catalyst loadings were obtained.

Besides, because the valence state of Mn in MnP-PGMA/SiO₂ is closely related to the catalytic oxidation mechanism, the valence state of Mn was examined. The coordination between small THPP and MnCl₂ was conducted under the basically same condition as that in this study, and the electronic absorption spectroscopy of the obtained small manganese porphyrin in acetone solution was determined. During the metallation process, the oxidation of Mn (II) took place and the manganese (III)porphyrin was obtained. The UV-Vis spectrum observed for the manganese porphyrin in acetone presented the Soret band at 477 nm. The Soret band adsorption of manganese(II)porphyrin and manganese(III)porphyrin are at 452 nm and at 477 nm, respectively.²¹ Obviously, in

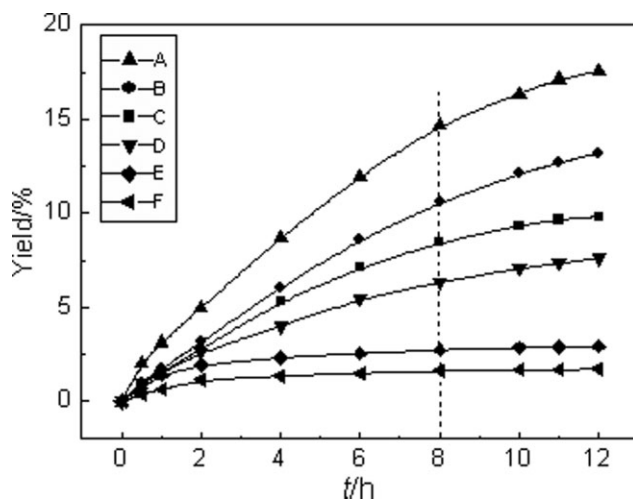


Figure 4 Variation of acetophenone yield with time with different amounts of catalyst MnP. Reaction temperature: 95°C; Ethyl benzene: 20 mL; Amount of MnP and added amount of MnP-PGMA/SiO₂: (A) 20.93 μmol/0.70g; (B) 10.76 μmol/0.36g; (C) 6.28 μmol/0.21 g; (D) 29.90 μmol/1.00 g; (E) 40.66 μmol/1.36 g; (F) 79.83 μmol/2.67 g.

the structure of MnP-PGMA/SiO₂ prepared in this investigation, the manganese should be in trivalence state, as shown in Scheme 1.

Catalytic characteristics of MnP-PGMA/SiO₂ in catalytic oxidation of ethyl benzene with O₂

Catalytic activity and selectivity

The heterogeneous catalyst MnP-PGMA/SiO₂ was used in the catalytic oxidation of ethyl benzene with molecular oxygen under ordinary pressure at 95°C, and the reaction product was identified and assayed. The experimental results showed that the main product was acetophenone. The yield of acetophenone as a function of the reaction time is displayed in Figure 4. As no MnP-PGMA/SiO₂ was added into the reaction system, nearly no acetophenone is produced at 95°C as shown by curve F in Figure 4, whereas when a little catalyst MnP-PGMA/SiO₂ was added, a certain amount of acetophenone was produced, as shown by curve C in Figure 4 (only 0.21 g of MnP-PGMA/SiO₂ was added and 6.28 μmol of manganoporphyrin was contained in the reaction system); moreover, the yield of acetophenone increases rapidly with the reaction time. Obviously, the supported catalyst MnP-PGMA/SiO₂ can effectively activate the molecular oxygen, and makes ether benzene to be oxidated by molecular oxygen under the mild condition (under ordinary pressure and at 95°C) into acetophenone, displaying its catalytic activity. The nature of the catalytic action of MnP-PGMA/SiO₂ in the oxidation reaction of ethyl benzene with dioxygen as oxidant is based on the transfer of the activated dioxygen from the center

metallic ion with a higher valence state to the substrate molecule like as other metalloporphyrine catalysts. The result of GC indicated that acetophenone holds 98% in the product mixture, whereas the content of another product, α-methyl benzalcohol, is very low, indicating the fine catalytic selectivity of MnP-PGMA/SiO₂ for conforming ethyl benzene to acetophenone.

Effect of catalyst amount on catalytic oxidation of ethyl benzene

Fixed other reaction conditions (ethyl benzene: 20 mL; temperature: 95°C; catalyst loading of MnP-PGMA/SiO₂: 29.9 μmol/g), the catalytic oxidations were performed with different amounts of manganoporphyrin (MnP) by varying the added amount of the solid MnP-PGMA/SiO₂, so as to examine the effect of the catalyst amount on the catalytic oxidation. Figure 4 displays the yield of acetophenone as a function of the reaction time under the conditions of the different amounts of MnP.

From Figure 4, a special effect of the used amount of the catalyst MnP on the catalytic oxidation reaction can be roughly found: there is an optimal amount of the catalyst MnP. To more clearly display the phenomenon, the yield data at 8 h are taken from Figure 4, and the relationship curve between the yield of acetophenone and the used amount of the catalyst MnP is plotted, as shown in Figure 5. The following facts can be seen clearly from Figure 5: the yield of acetophenone increases rapidly with the catalyst MnP amount as the catalyst amount is smaller, and this is similar to the common catalytic reaction systems; when the catalyst MnP amount is enhanced to a certain amount, a maximum yield of acetophenone appears; subsequently,

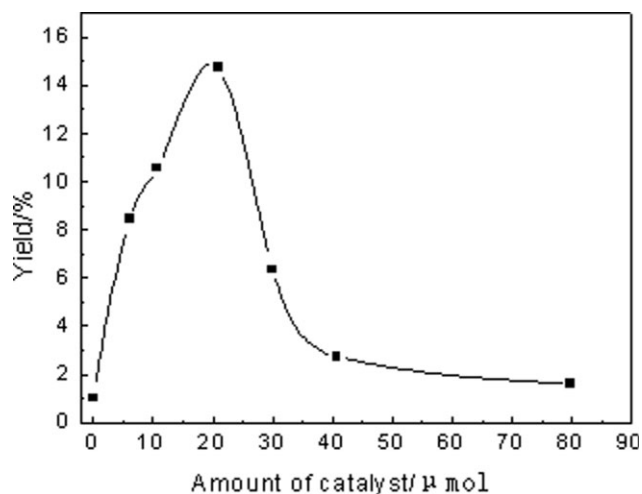


Figure 5 Effect of catalyst MnP amount on catalytic oxidation reaction Ethyl benzene: 20 mL; Reaction temperature: 95°C; Reaction time: 8 h.

the yield of acetophenone turns to decreasing with the continuative increase of the catalyst MnP amount; as the catalyst MnP amount is very great, the yield of acetophenone seems to be very low. Apparently, the excessive addition of the catalyst MnP will inhibit the catalytic activity of the catalyst. This is different from the common catalysts. This special phenomenon of biomimetic catalysts also was found by another research group,²² and the reason for this needs to be studied in depth.

Effect of immobilization density of manganoporphyrin on MnP-Pgma/SiO₂ on catalytic activity

Fixed other reaction conditions (ethyl benzene: 20 mL; temperature: 95°C; MnP amount: 14.56 μ mol), the catalytic oxidations were performed using the supported catalysts MnP-PGMA/SiO₂ with different immobilization densities of MnP, to examine the effect of the immobilization density of manganoporphyrin of MnP-PGMA/SiO₂ on the catalytic activity of the supported catalyst MnP-PGMA/SiO₂. The plots of ethyl benzene yield in the different systems with different immobilization densities of MnP are shown in Figure 6. The yield data at 8 h are taken from Figure 6, and the relationship curve between the yield of ethyl benzene and the immobilization density of MnP is given in Figure 7.

It can be found from Figures 6 and 7 that as the supported catalyst MnP-PGMA/SiO₂ on which the immobilization density of manganoporphyrin is smaller is used, the yield of acetonephenone is greater, i.e., the catalytic activity of MnP-PGMA/

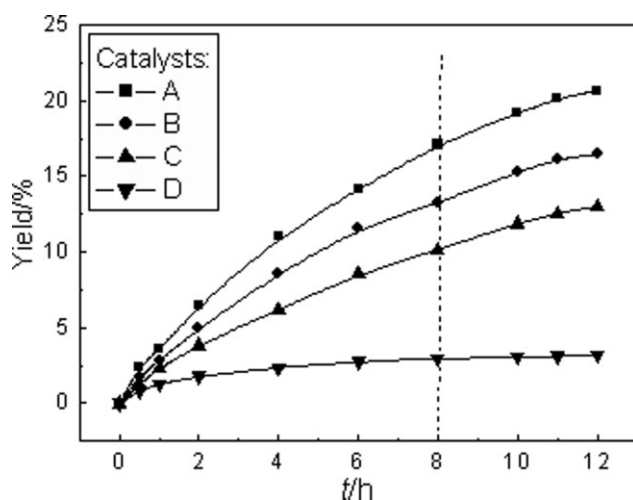


Figure 6 Variation of acetophenone yield with time using solid catalysts with different immobilization density of MnP. Reaction temperature, 95°C; Ethyl benzene, 20 mL; amount of MnP, 14.56 μ mol; Immobilized density of MnP on solid catalysts: (A) 20.8 μ mol/g; (B) 29.9 μ mol/g; (C) 45.5 μ mol/g; (D) 57.2 μ mol/g.

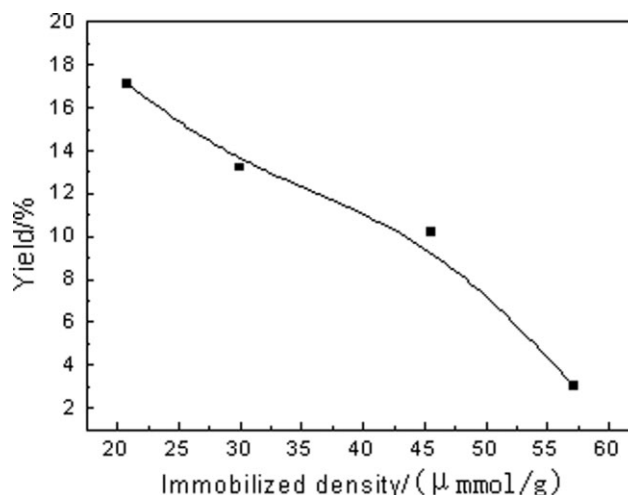


Figure 7 Effect of immobilization density of MnP of solid catalyst on catalytic oxidation reaction Ethyl benzene: 20 mL; Reaction temperature, 95°C; Amount of MnP, 14.56 μ mol; Reaction time, 8 h.

SiO₂ is higher. In contrast, as the supported catalyst MnP-PGMA/SiO₂ on which the immobilization density of manganoporphyrin is greater is used, the catalytic activity of MnP-PGMA/SiO₂ is lower. This fully displays that the polymer microenvironment is very important for the biomimetic catalysts. It is obvious that when the immobilization density of manganoporphyrin is smaller, the polymer effect of the polymeric microenvironment is more outstanding. It is possible that the fine polymeric microenvironment is not only helpful to exert the catalytic action of the catalyst, but can also effectively protect manganoporphyrin and prevent it from destruction and deactivation, resulting in high catalytic activity. The effect of the immobilization density of metalloporphyrin on polymeric supports on the catalytic activity is found for the first time, and it needs to be further investigated.

The recycle and reuse experiments for the supported metalloporphyrin catalyst MnP-PGMA/SiO₂ were performed to examine its stability. The preliminary study indicated that MnP-PGMA/SiO₂ had excellent reuse performance. During the consecutive reuse eight times, its catalytic activity enhanced tardily, and this behavior is also different from common heterogeneous catalysts. The possible reason for this is being studied, and the further study result will be reported in the future.

CONCLUSIONS

In this investigation, a novel polymeric support PGMA/SiO₂ for the immobilization of metalloporphyrin catalysts was prepared via grafting monomer glycidyl methacrylate (GMA) on the surface of silica gel particles. The support PGMA/SiO₂ combines

well the advantage of polymer supports and inorganic carriers. Meso-tetra (4-hydroxyphenyl) porphyrin (THPP) was bound on the support PGMA/SiO₂ through the ring-opening reaction of the epoxy groups of the grafted PGMA and the hydroxyl groups of THPP in the presence of basic catalysts. The suitable catalyst is triethylamine, and higher bonding amount of THPP can be obtained. The obtained supported catalyst MnP-PGMA/SiO₂ was used in the catalytic oxidation of ethyl benzene to acetophenone by molecular oxygen, and exhibited higher catalytic activity and excellent selectivity to acetophenone. In this study, some special phenomena were found. The amount of the biomimetic catalysts seems to have an optimal value in a certain reaction system, and excessive addition of the biomimetic catalysts will inhibit the catalytic activity of the catalyst. For the supported catalyst of MnP-PGMA/SiO₂, the immobilization density of metalloporphyrins has a great effect on the catalytic activity of the catalyst. The supported metalloporphyrin catalyst with a smaller immobilization density of metalloporphyrins will have higher catalytic activity. These findings are significant and important for the development of the heterogeneous metalloporphyrin catalysts. To conclude, we have developed a new efficient route to supported metalloporphyrin catalysts, and demonstrated the effectiveness of the supported catalyst MnP-PGMA/SiO₂ in the catalytic oxidations of hydrocarbons.

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