Comparative Study of Iron Porphyrin Supported on Mesoporous Al-MCM-41 and Poly(methacrylic acid) (PMAA) : Characterization and Their Catalytic Activities

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Abstract

Mesoporous molecular sieve Al-MCM-41 with Si/Al=20 and poly(methacrylic acid) (PMAA) were used as supports for the immobilization of bulky iron (III)-5,10,15,20-tetra-(4-pyridyl) porphyrin, (Fe-TPyP). Metalloporphyrin of Fe(III) was encapsulated inside the mesopores of crystalline samples of Al-MCM-41 by a process of sequential synthesis of Fe-TPyP by treatment of FeCl\(_3\) with 5,10,15,20-tetra-(4-pyridyl) porphyrin (TPyP), followed by encapsulation of Fe-TPyP. Fe-TPyP complexes were also successfully encapsulated into the pore of PMAA by polymerizing a monomer (MAA) with a cross-linker around the Fe-TPyP complexes. The materials obtained were identified using, XRD, DR-UV/vis and FT-IR spectroscopies. The powder XRD data confirmed that the crystallinity of mesoporous Al-MCM-41 was maintained after encapsulation process. With mesoporous molecular sieve (Al-MCM-41) and the polymer (PMAA) as supports, the encapsulated iron-porphyrin systems have demonstrated excellent activity for the one-step oxidation of benzene to phenol under mild reaction conditions.

Keywords : Encapsulation; Iron-porphyrin; Al-MCM-41; PMAA.

Introduction

Selective oxidation of hydrocarbons under mild conditions is of academic interest and industrial importance [1]. In recent years, as a result of increasing environmental constraints, “clean” oxidants such as dioxygen (or air), hydrogen peroxide, and alkyl hydroperoxides, which are inexpensive, is becoming more important both in industry and academia, and chemical processes based on cleaner technologies are expected to increase significantly in the next few years.

In this research, the only focus was on the catalytic heterogeneous oxidation. A well-known monoxygenase, iron porphyrin-based cytochrome P-450, has been the subject of intensive study [2] largely because of their ability to catalyze a wide variety of oxidation transformations, e.g. alkenes epoxidation, alkanes hydroxylation, etc. with molecular oxygen. In the last two decades, therefore, increasing attention in catalytic oxidation has been focused on the use of biomimetic systems based on Fe(II), Ru(II) and Mn(II) [3-5]. Fig. 1 shows a unique metalloporphyrin structure containing alternately perpendicular porphyrin molecules that give rise to an unprecedented two-dimensional paddle-wheel-like pattern (4\(^4\) topology).

Synthetic metalloporphyrins are widely used as homogeneous catalysts for hydrocarbon oxidation, as well as model for cytochrome P-450 [6,7]. Metalloporphyrin complexes of iron [8] are known to be active catalysts for alkenes epoxidation. There are, however, several disadvantages in using metalloporphyrins as catalysts in homogeneous oxidation processes. The difficulty in separating the catalysts from the product substantially increases the cost of using homogeneous catalysis in commercial processes. Heterogeneous catalysts, on the contrary, can be easily separated from the reaction products simply by filtration. Yet most heterogeneous catalysts are less selective in complex reactions.

Therefore, it is highly desirable to develop new classes of catalysts which possess both the high selectivity of homogeneous catalysts and the convenience of heterogeneous catalysts.
One approach to achieve this goal is to immobilize homogeneous catalysts on porous solid supports, which simultaneously has the advantages of turning the liquid phase oxidation from homogeneous into heterogeneous.

Microporous materials with regular arrays of internal channels and uniform pores such as zeolite [9] have been extensively studied as inorganic support. Moreover, metallocoporphyrin complex such as cis-Mn(bppy)$_3$ [10] encapsulated in zeolite Y have been reported to be active catalysts towards cyclohexene oxidation. Supporting metallocoporphyrins on porous solid supports also provides a physical separation of active sites, thus minimizing catalyst self-destruction and dimerization of unhindered metallocoporphyrins [11].

Transition metal complexes and organometallic compounds can be immobilized onto the mesoporous MCM-41 supports by physical adsorption or covalent linkage. More recently, much effort was focused on the immobilization of metallocoporphyrins onto the silica MCM-41 surface. Che and co-workers [12] have immobilized a ruthenium porphyrin on modified MCM-41.

In this project, iron porphyrin has been immobilized within ordered mesoporous Al-MCM-41. Supported catalysts are also often plagued by leaching of the metal into solution. Our approach to these problems is to radically change the nature of the support. The even distribution of large, regular pores and extremely high surface area that characterizes mesoporous molecular sieve MCM-41 make them ideal supports.

The key feature of the MCM-41 support which separates it from currently used supports is its extreme porosity. However, the MCM-41, an inorganic material, is hydrophilic and rigid. In this research, we also propose a procedure to immobilize iron porphyrin on the polymer support, namely poly (methacrylic acid) (PMAA). One expects that the flexibility and hydrophobicity of the polymer as support give the advantages in oxidation of organic compounds. To the best of our knowledge, there is no report of iron porphyrin supported on PMAA in the literature.

Phenol is produced globally on scale of 17 billion pounds/year and is expected to maintain an annual growth rate of 4 % through the year 2002 due to demand for bisphenol A (polycarbonate resins), phenolic resins, and caprolactam (nylon 6). The one-step production of phenol by direct insertion of oxygen into the benzene ring is an attractive and challenging method, not only from a practical point of view but also from a synthetic chemical point of view, because the direct oxygenation of the energetically stable benzene to produce phenol has been one of the most difficult oxidation reactions [13].

The gas-phase oxidations of benzene to phenol by nitrous oxide have been widely studied over Fe-ZSM-5 [14]. Othani et al. [15] have investigated the liquid-phase oxidation of benzene to phenol catalyzed by the Cu catalysts supported on zeolites, and MCM-41 [16].

![Figure 1. Iron (III)-Tetra-(4-Pyridyl)-Porphyrin (TPyP).](image)
An attractive alternative is the direct oxidation of benzene to phenol using molecular oxygen and a suitable catalyst. A one step process such as this would require less energy and generate zero waste, while producing only phenol.

Recently, the best catalysts for this reaction are Fe-ZSM-5 [14] and Cu-ZSM-5 zeolites which provide nearly 100% benzene selectivity, but low conversion of benzene. The remarkable catalytic performance of this zeolite was shown to be related to the presence of iron and upon high temperature treatment. In these systems, the reaction only occurs in the gas phase (ca. 300°C) and there is no published report on single step liquid phase oxidation of benzene to phenol. For these reasons, in this research, the single step liquid phase oxidation of benzene to phenol over iron porphyrin supported on Al-MCM-41 and PMMA has been chosen as the model reaction.

**Materials and Methods**

**Materials and equipment**

Unless otherwise stated, all reagents were of commercial reagent grade and used without further purification. TPyP (5,10,15,20-Tetra (4-Pyridyl) Porphyrin) was purchased from Fluka (97 %). FeCl₃ anhydrous was purchased from Merck. Methacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA), α,α’-azoisobutyronitrile (AIBN) were purchased from Fluka.

The samples were characterized by X-ray diffraction (XRD) analysis using Bruker D8 Advance diffractometer with a scanning range of 2θ scale of 1.5 to 10° using Cu Kα radiation (λ = 1.5418 A, kV = 40, mA = 40) as the source of radiation. Infrared spectra were recorded on Shimadzu Fourier Transformed infrared (FTIR) 8300 spectrometer. Diffuse reflectance ultraviolet visible (DRUV-Vis) spectra were recorded on Lambda 900 spectrometer.

**Direct synthesis of mesoporous molecular sieve Al-MCM-41**

The basic mole composition of MCM-41 synthesis was following the procedure as found in literature [17]: 6 SiO₂ : CTABr : 1.5 Na₂O : 0.15 (NH₄)₂O : 250 H₂O.

**Synthesis of Iron-porphyrin (Fe-TPyP)**

Iron insertion into TPyP by heating (at 100°C) TPyP (250 mg, 0.404 mmol) and FeCl₃ anhydrous (100 mg, 0.606 mmol) at reflux in ethanol (30 mL) using oil bath, for 1 h. The hot solution was filtered, washed with water and dried under vacuum. The Fe-TPyP obtained was characterized by FTIR, DRUV-Vis.

**Synthesis of Fe-TPyP-Al-MCM-41**

Fe-TPyP-Al-MCM-41 was synthesized via a modification of the method of Li et al. [11]. A suspension of Al-MCM-41 (250 mg) in methanol containing Fe-TPyP (0.24 mmol) was stirred for 24 hours at 20°C. The resulting materials was filtered and washed with CH₂Cl₂ and acetonitrile until the filtrate becomes colorless. The solid obtained was dried at 100°C for 4 hours which afforded Fe-TPyP. The material was characterized by FTIR, DRUV-Vis, XRD.

**Synthesis of Fe-TPyP-PMAA**

Fe-TPyP-PMAA was prepared using the method of Tamayo et al. [18]. Fe-TPyP (1 mmol), toluene (12 mL) and MAA (4 mmol) were placed into a 25 mL glass tube and the mixture was left in contact for 10 minutes. Subsequently, EGDMA (20 mmol) and AIBN (30 mg) were added. The glass tube was sealed and thermostated at 60°C in an oil bath to start the polymerization process. After 24 hours, the obtained micro-spheres were air dried and weighted. Characterization of samples was done using FTIR, DRUV-Vis.

**Catalytic Testing**

Benzene was used without further purification. A typical oxidation procedure is as follows: 2 mL of benzene (22.5 mmol), 50 mg of catalysts, hydrogen peroxide (1 mL), and 2 mL of methanol were mixed. The benzene oxidation was performed using a magnetic stirrer at 70°C in an oil bath. After propane-2-ol, as an internal standard was added to the reaction solution and the solid catalysts were separated by centrifugation, the product was analyzed by a Hewlett Packard 5890 Series II GC.
Results and Discussion

Preparation of iron porphyrin

Iron (III)-Tetra (4-Pyridyl) Porphyrin (Fe-TPyP) has been successfully prepared. Uniform dark-purple powders were obtained in all cases and the material was characterized by various techniques such as FTIR and DRUV-Vis spectroscopy.

The FTIR spectra of the TPyP (commercial) and Fe-TPyP are shown in Fig. 2. In the FT-IR spectra of TPyP, the broad peak at 3431.1 cm⁻¹ is related to the stretching vibrations of the N-H bonds of the aromatic. Another characteristic peak in the IR spectra is the –C=H stretching vibration of the aromatic which was observed at 3100 - 2900 cm⁻¹. The strong peaks at wavenumber 1595.0 cm⁻¹ are due to the C=C conjugation of the aromatic; the C=N and C=C stretching vibrations are assigned at 1631.7 cm⁻¹ and 1467.7 cm⁻¹, respectively, and peaks at 1000 – 700 cm⁻¹ show the C-H bonds of the aromatic. We did not observe any appreciable changes in the frequencies of the Fe-TPyP complexes after iron insertion into the porphyrin.

The strong peak at 1595.0 cm⁻¹ of the IR spectrum of TPyP shows the C=C conjugation of aromatic, but in the IR spectrum of Fe-TPyP, the C=C peak is assigned at 1592.1 cm⁻¹. Appearance of the absorption band at 1650.0 cm⁻¹ (C=N bond) in the FTIR spectrum of Fe-Porphyrin is indicative of the incorporation of iron into the porphyrin.

The purple-dark colours of the samples are indicative that iron (III) has been included in porphyrin, and this was confirmed by diffused reflectance ultraviolet visible (DR-UV-Vis) spectroscopy. The DR-UV-Vis spectra of TPyP and Fe-TPyP are given in Fig. 3. The three peaks present in the region of 500 – 700 nm (bands at 513, 556 and 587 nm) are typical of high-spin Fe³⁺ porphyrins. The iron porphyrin complexes also present absorption bands at 410 and 645 nm. These bonds shows that Fe-N bond formations.
Preparation of Fe-TpyP-Al-MCM-41

Preparation of Fe-TpyP-Al-MCM-41 was carried out in two steps: synthesis of the parent Al-MCM-41, and synthesis of Al-MCM-41 encapsulated Fe-TpyP complex. First step, Al-MCM-41 has been prepared. The mesoporous materials obtained has been characterized by XRD and FTIR spectroscopy.

Fig. 4. shows the X-ray powder diffractograms of Al-MCM-41 sample before and after calcination at 550°C. The as-synthesized sample exhibits a very strong peak at 41.1 Å and weak peaks at 23.8 Å, and 20.8 Å, corresponding to the (100), (110) and (200) reflections, respectively [19].

The presence of a single intense $d_{100}$ Bragg reflection at 41.1 Å indicates that the material possesses regular mesopores. The sample after the calcination reveals a $d_{100}$ value of about 39.5 Å, which for a hexagonal lattice gives $a_0 = 45.6$ Å. The intensity of this peak increases significantly after calcination owing to the removal of the organic surfactant molecule. In the second step of the preparation, Al-MCM-41 encapsulated Fe-TpyP complexes have been prepared using the procedure of Li, Z. et al. [11]. The solid obtained has been characterized by FTIR, XRD and DRUV-Vis.

Fig. 5 (a, b and c) shows the IR spectra of the pure Al-MCM-41 and the encapsulated Fe-TpyP complex. Comparison of the signals at 1461.0 and 1636.5 cm$^{-1}$ (C=C bond) and 1594.1 cm$^{-1}$ (C=N bond) in the spectrum of the pure Al-MCM-41 sample with those of Fe-TpyP, clearly indicate that Fe-complexes were successfully encapsulated onto the channels of Al-MCM-41 [11]. The IR bands of encapsulated complexes are weaker due to their low concentration in the molecular sieve. The presence of TpyP is obvious, because there is no band observed in the region 1700 – 1300 cm$^{-1}$ in the spectrum of the pure Al-MCM-41.

X-ray powder diffraction (XRD) patterns of Al-MCM-41 and the encapsulated Fe-TpyP (fig. 4), which are in excellent agreement with the XRD pattern for unloaded molecular sieve without any peaks arisen from Fe-TpyP. This suggests that that crystalline molecular sieve Al-MCM-41 can still be obtained during the encapsulation of Fe-TpyP complexes. This means also that the solid support is structurally unchanged and the iron-porphyrin species should be monodispersed within the MCM-41 channels. The results show that anchoring the catalyst inside the mesoporous molecular sieve has prevented Fe-TpyP aggregation or degradation through bimolecular interaction [11].

A typical XRD pattern after encapsulation of the Fe-TpyP complex showed weak peaks of (110), (200) and (210) in the $2\theta$ range 3.5 – 6.0 indicating that the long range order of the inorganic host, Al-MCM-41 has decreased after the encapsulation, but fundamentally the mesostructure of the host materials is still maintained.

The Fe-TpyP encapsulated in molecular sieve Al-MCM-41 has also been characterized by diffuse reflectance UV-Vis spectroscopy and the typical DRUV-Vis spectra are given in fig. 6. The similarity of bands of FeTpyP and encapsulated FeTpyP means the porphyrins are really present in the aluminosilicate framework and their properties have been retained. The Fe-porphyrin complexes present absorption bands at 410 nm. Fe-porphyrin presents a broad single band at 418 nm and three typical bands attributed to high spin Fe(III)porphyrin species in the region of 500 – 700 nm (bands at 516, 557 and 648 nm) [19].
Fig. 4. XRD of Al-MCM-41 samples before and after calcination at 550°C and Fe-TPyP-Al-MCM-41.

**Figure 5.** FTIR spectra of (a) free Fe-TPyP, (b) encapsulated Fe-TpyP, (c) Al-MCM-41, (d) Poly(methacrylic acid) (PMAA) and (e) Fe-TPyP-PMAA.

The presence of the band at 589 nm in the spectra in of Al-MCM-41/Fe-TpyP (fig. 6. (b)), suggests the occurrence of axial interactions between the iron porphyrin and the Al-MCM-41 pore surfaces [20]. This result suggests that the electrostatic interaction between Fe-TPyP complex and the anionic aluminosilicate framework of Al-MCM-41 contributes to the successful incorporation of porphyrin into the framework. Further work is required to identify all the species present in the system and to determine the loading levels of Fe-TPyP in Al-MCM-41.
Preparation of Fe-TpyP-PMAA
The supported Fe-TpyP catalysts with poly(methacrylic acid) were prepared using the method of Tamayo et al. [18]. The brown solids obtained were characterized using FTIR and DRUV-Vis.

Fig. 5 (a, d and e) shows the IR spectra of Fe-TpyP complexes, pure poly(methacrylic acid) and the poly(methacrylic acid) supported Fe-TpyP complexes. The peaks at 1635.5 cm\(^{-1}\) (C=N) and at 1452.3 cm\(^{-1}\) (C-C) in the FTIR spectrum of poly(methacrylic acid) supported Fe-TpyP complexes, when compared with those of the pure poly(methacrylic acid) at 1724.2 cm\(^{-1}\) (C=O), 1159.1 cm\(^{-1}\) (C-H) clearly indicate that Fe-TpyP complexes were successfully incorporated into the polymer.

Further, the Fe-TpyP supported on PMAA have been characterized by DRUV-Vis spectroscopy and the spectra are shown in Fig. 6c. The results of the DRUV-Vis study have been shown that a broad single band at 423 nm in the spectrum is probably due to the axial coordination of the Fe-TpyP to OH-containing ligands present in PMAA. The three peaks present in the region of 500 – 700 nm (bands at 518, 555 and 592 nm) are typical of high-spin Fe\(^{III}\) porphyrins [21].

The direct oxidation of benzene to phenol
The effect of different catalyst
The excellent activities of iron-porphyrins for the direct oxidation of benzene to phenol in solution and supported in molecular sieve and polymer were demonstrated using H\(_2\)O\(_2\) as oxidant. The data are shown in Fig. 7.

Encapsulated catalysts Fe-TpyP/Al-MCM-41 and Fe-TpyP/PMAA give rise higher activity than Fe-TpyP. This efficiency possibly arises from Fe-TpyP coordination to molecular sieve/polymer, which render them more resistant to oxidative self-destruction. From the results, it is evident that Fe-TpyP/PMAA gives higher phenol yield than Fe-TpyP/Al-MCM-41. By using a Hewlett Packard 5890 Series II GC to analyze products reaction, no other products such as hydroquinone and/or catechol were detected in the reaction conditions carried out in this study.

![Figure 7](image_url)

**Figure 7.** The phenol yield of Fe-TpyP (A), Fe-TpyP/Al-MCM-41 (B) and Fe-TpyP-PMAA (C).

The effect of time reaction
Fig. 8 illustrates the dependences of the phenol yield on the reaction time using Fe-TpyP/Al-MCM-41 as catalyst and the reaction temperature of 343 K. The yield phenol almost linearly increased with the increase in the reaction time up to around 5h.
Reuse of the catalyst

The activity of encapsulated Fe-TpyP has not changed after third times of reusing. The results is given in fig. 9. This was observed for Fe-TpyP/Al-MCM-41, which presented an increased in its activity from the first to the third recycling for 5 h reaction time.

![Graph showing phenol yield vs. time](image1)

**Figure 8.** Effect of time in the oxidation of benzene to phenol with H$_2$O$_2$ catalyzed by Fe-TpyP/Al-MCM-41.

![Graph showing phenol yield vs. recycling times](image2)

**Figure 9.** Phenol yield with used Fe-TpyP/Al-MCM as catalyst after third times of reusing.

Conclusions

Initial works showed that Fe-TPyP complexes were successfully prepared by incorporating Fe-TPyP within mesoporous molecular sieve Al-MCM-41 and poly (methacrylic acid) (PMAA) as inorganic and organic supports, respectively. These catalysts will be used as catalysts in the chosen model reaction, namely, the single step liquid phase oxidation of benzene to phenol.
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References