SAXS, FESEM AND BET STUDIES OF MESOPOROUS CATALYST SBA-15 CONTAINING ZINC PORPHYRIN FOR EPOXIDATION OF LIMONENE

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Abstract

SBA-15 nanoporous silica was prepared by cooperative self-assembly of tetraethylorthosilicate precursor in the presence of poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) copolymer surfactant and functionalized with (3-aminopropyl)triethoxysilane (APTES) via sol-gel reaction to obtain NH\textsubscript{2}-SBA-15. The metalloporphyrin, [meso-tetrakis-(p-chlorophenyl)porphyrinato]Zn(II) ([ZnTClPP]) was synthesized from the reaction of meso-tetrakis-(p-chlorophenyl)porphyrin ([ZnTClPP]) using zinc acetate dihydrate as a metal source and then immobilized on SBA-15 surface. The material, NH\textsubscript{2}-SBA-15-ZnP was characterized by SAXS, FESEM and BET studies and showed a similar pattern as SBA-15 indicating that the mesoporous hexagonal structure of SBA-15 was still retained. Then, the material was applied to catalyze the epoxidation of limonene, using H\textsubscript{2}O\textsubscript{2} / ammonium acetate at various temperatures and conditions. All the products formed from the epoxidation reaction were analyzed using GC-FID and GC-MS.

Keywords: SBA-15; APTES; metalloporphyrin; epoxidation; limonene

Abstrak

Silika berliang nano SBA-15 telah disediakan melalui himpunan sendiri bersama dengan bahan pemula tetraethylortosilikat dengan kehadiran surfaktan kopolimer poli(etilena glikol)-blok-polil(etilena glikol)-blok-polil(etilena glikol) dan pengfungsian dengan (3-aminopropil) trietoksilan (APTES) melalui tindak balas sol-gel untuk menghasilkan NH\textsubscript{2}-SBA-15. Logam porfirin, [meso-tetrakis-(p-klorofenil)porfirinato]Zn(II) ([ZnTClPP]) telah disintesis daripada tindak balas meso-tetrakis-(p-klorofenil) porfirin ([ZnTClPP]) dengan zink asetat dihidrat sebagai sumber logam dan seterusnya dipegunkan ke atas permukaan SBA-15. Bahan yang terhasil laitu, NH\textsubscript{2}-SBA-15-ZnP telah dicirikan dengan kajian SAXS, FESEM dan BET menghasilkan satu corak yang sama dengan SBA-15 dan menunjukkan halawa struktur heksagon mesoliang SBA-15 masih lagi dikekalkan. Seterusnya, bahan tersebut telah diaplikasi untuk memangkinkan tindak balas pengepoksidan limonena menggunakan H\textsubscript{2}O\textsubscript{2} / ammonium asetat dengan pelbagai suhu dan keadaan. Semua produk yang terhasil dari tindak balas pengepoksidan telah dianalisisikan menggunakan GC-FID dan GC-MS.

Kata kunci: SBA-15; APTES; logam porfirin; pengepoksidan; limonena

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1.0 INTRODUCTION

Cytochrome P-450 enzymes can be defined as a member of the mono-oxygenase family of heme enzyme and catalyze a wide range of oxidation reactions by transfer of an oxygen atom [1]. In this context, synthetic metalloporphyrins are investigated to mimic of Cytochrome P-450 which able to catalyze selective oxidation reactions of alcohols, sulfides, epoxidation of alkenes and hydroxylation of alkanes with high selectivity and efficiency.

Due to instability of natural metalloporphyrins under oxidizing conditions and poor water solubility, a great deal of effort has been devoted to the development of synthetic metalloporphyrins that will be more resistant to degradative oxidation and active in aqueous media. These problems have been overcome by adding electron-withdrawing groups in the meso positions of metalloporphyrins [2].

However, unsupported metalloporphyrins as catalysts have several drawbacks, for instance their oxidative self-destruction in the oxidizing media and difficulties in work-out procedures due to the synthesis of metalloporphyrin that produce low yield. In addition, they are not conveniently recovered for further reuse which limits the practical application of metalloporphyrin in actual industrial processes [3].

To overcome these limitations of homogeneous catalysis, immobilization of metalloporphyrins onto supports can be achieved via different mechanism such as coordination, electrostatic interactions, covalent binding and encapsulation techniques [4]. A heterogenised homogeneous catalyst on a solid support is an ideal strategy that combines both the advantages of homogeneous and heterogeneous catalyst such as promoting catalytic activity, catalyst stability, product selectivity, enhance the possibility for reuse and easy product separation [5].

Among the different type of solid supports, mesoporous silica materials is one of the most attractive inorganic support due to their high surface area, well-defined array of uniform mesoporous, nontoxicity, high stability, good accessibility and low cost. SBA-15 materials exhibit the high ordered channel structures of pore diameter in the range between 1.5 to 30 nm, high internal surface areas, high number of silanol groups, good thermal stability and thick walls [6]. Therefore, SBA-15 silica is chosen due to their large pores size so that the high molecular mass molecules can permit an efficient diffusion of products and reactants. SBA-15 can improve the catalytic applications because of its uniform hexagonally arrayed channels with narrow pore size distribution. The thicker amorphous silica walls of SBA-15 provide higher hydrothermal stability than those of the thinner-walled MCM-41 materials. However, SBA-15 showed very limited catalytic activities because the lack of lattice defect, redox properties and low acidic strength. Thus, the framework of mesoporous SBA-15 can be modified by the introduction of different groups (metals, metal oxides, acidic groups, and organic functionalities), to increase the active sites and thus improve the catalytic activity [7]. These features make SBA-15 materials are promising candidates to be used as suitable and efficient supports for functionalization of metalloporphyrins.

Epoxidation of limonene produces the oxygenated derivatives compounds derived from terpene and natural terpenoids that have a great potential for fragrance, flavours and pharmaceutical industries [8]. 1,2-limonene oxide (1,2-epoxylimonene) is a key raw material for perfume industry and as bio-renewable monomer in the formation of biodegradable polymer [9].

In this work, we present a study of biomimetic activity of [meso-tetrakis-(p-chlorophenyl) porphyrinato]Zn(II) (ZnTClPP) immobilized on SBA-15 mesoporous silica modified with (3-aminopropyl) triethoxysilane (APTES) groups for epoxidation of limonene with hydrogen peroxide (H₂O₂) as oxidant.

2.0 EXPERIMENTAL

2.1 Preparation of SBA-15 Mesoporous Silica

SBA-15 was prepared according to the procedure reported by Zhao, D. [10] using tetraethyl orthosilicate (TEOS) as silica source and poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) copolymer (Pluronic P123) as surfactant. The resulting gel was aged at 80 °C overnight without stirring. The solid product was recovered, washed, and dried. The as-synthesized SBA-15 was calcined at 550 °C for 6 hours.

2.2 Preparation of APTES Functionalized SBA-15

The aminopropyl functionalization of SBA-15 was carried out using (3-aminopropyl) triethoxysilane (APTES) as silylation reagent. In a typical preparation, about 1.0 g of calcined SBA-15, 0.01 mol of APTES and 100 mL of toluene was added in a 250 mL flask and refluxed at 85 °C. After 24 hours, the resulting mixture was filtrated, washed repetitively with toluene and diethyl ether and then dried at ambient temperature in a desiccator. The solid was denoted as NH₂-SBA-15.

2.3 Preparation of [meso-tetrakis-(p-chlorophenyl) porphyrinato]Zn(II) (ZnTClPP)

The free base porphyrin of meso-Tetrakis-(p-chlorophenyl)porphyrin (ZnTClPP) was prepared by some modification of Alder-Longo method [11]. Afterwards, ZnTClPP was prepared by refluxing H₂TClPP (1 mmol) and zinc acetate dihydrate (Zn(CH₃COO)₂.2H₂O) (1 mmol) in dichloromethane (DCM) at 100 °C in an oil bath for 1 hour. Then, the solution was filtered while it was still hot, washed with water and dried at room temperature.
2.4 Immobilization of ZnTCIPP on APTES Functionalized SBA-15

The immobilized porphyrin NH₂-SBA-15-ZnP was prepared according to the procedure reported by Adam et al. [12]. At first, ZnTCIPP was added to a suspension of NH₂-SBA-15 in dry toluene and triethylamine. Then, the mixture was refluxed at 110 °C in an oil bath for 24 hours. The solid product was collected by filtration and washed with toluene, dichloromethane and distilled water. The NH₂-SBA-15-ZnP was dried in the oven and grounded into fine powder. There are two concentration of ZnTClPP immobilized into solid silica which are 100 µmol and 200 µmol while other parameters kept constant. These two samples were then labeled as NH₂-SBA-15-ZnP (100) and NH₂-SBA-15-ZnP (200).

2.5 Characterizations

The materials were characterized by small angle X-ray scattering (SAXS) using Bruker AXS Nanostar instrument with a scanning range 2θ scale of 0-6° using Cu Ka radiation (λ = 1.5406 Å, generator at 35 kV and 40 mA) as the source of radiation. The sample-detector distance was 0.52 m. The hexagonal a₀ cell parameter was calculated as a₀ = 2d₁₀₀/√3, where d₁₀₀ is the interplanar spacing for the (100) reflection. The morphology of the materials was analyzed using JEOL JSM-6701F Field Emission Scanning Electron Microscope. The observation of the samples begins from 5,000 to 100,000 magnifications. The N₂ adsorption-desorption isotherms analysis of materials were analyzed at 77K using Micromeritics ASAP 2010.

2.6 Catalytic Test

The catalytic testing of the prepared materials was performed on epoxidation of limonene to limonene oxide. Typically, substrate (2 mmol), solvent (5 mL of acetonitrile), catalyst (20 mg), co-catalyst (0.23 mmol of ammonium acetate) and oxidant (30% of H₂O₂) were placed into a round-bottom flask. The mixture was stirred at 80°C for 24 hours. All the products were analyzed with Agilent Gas chromatography model 6890N equipped with flame ion detector (FID) using ThermoFinnigan, HP-5m x 0.32mm 0.25µm column.

3.0 RESULTS AND DISCUSSION

3.1 Characterization Of Materials

Small angle X-ray scattering (SAXS) patterns of pure SBA-15, NH₂-SBA-15, NH₂-SBA-15-ZnP (100) and NH₂-SBA-15-Zn (200) are shown in Figure 1. Figure 1 (a) shows the SAXS patterns of the pure SBA-15, which is in agreement with the typical patterns reported in the literature [13]. This pattern displayed an intense diffraction peak of (100) reflection at about 2θ = 0.85°, which is characteristic of a mesostructure. Moreover, there are two weak peaks were due to the (110) and (200) reflections of hexagonal structure with p6mm symmetry. A similar SAXS pattern of NH₂-SBA-15 can be seen in Figure 1 (b). No significant changes of SBA-15 functionalized with APTES were observed. However, the intensity of dominant peak around 2θ = 0.9 which attributed to the (100) diffraction peak was decreased and shifted slightly to the right. This is due to the difference in the scattering contrast of the silica pores and the walls after modifications. Moreover, Figure 1 (c) and (d) also exhibit the same SAXS patterns as pure SBA-15 indicating that well-ordered hexagonal mesoporous channels of SBA-15 are remained intact after the immobilization of zinc porphyrin. It can be seen that the peak intensity of (100) plane of all the materials decreased significantly in the order of SBA-15 > NH₂-SBA-15 > NH₂-SBA-15-ZnP (100) > NH₂-SBA-15-Zn (200). The d-spacing value of the intense (100) peak have been calculated by using Bragg’s law (λ=2d sin θ). The -d-spacing and unit cell parameters of all materials are shown in Table 1.

![Figure 1 SAXS patterns of (a) pure SBA-15, (b) NH₂-SBA-15, (c) NH₂-SBA-15-ZnP (100) and (d) NH₂-SBA-15-ZnP (200)](image_url)

From the Table 1, it can be seen that the intensity (100) peak of pure SBA-15 reflects d-spacing, d₁₀₀ of 10.35 nm corresponding to unit cell parameter (a₀=11.95 nm). The d-spacing and unit cell parameter of NH₂-SBA-15 tended to decrease after the functionalization with APTES. These results proved that the silica framework of SBA-15 still maintained and was not influenced during the grafting process.
immobilization of zinc porphyrin on functionalized SBA-15, the total surface area ($S_{BET}$) of NH$_2$-SBA-15-ZnP (100) decreases to 301 m$^2$g$^{-1}$. These results indicate that the decrease in the surface area of SBA-15 can be due to the immobilization of ZnTClPP.

![Figure 2](image1.png)

**Figure 2** FESEM micrographs of (a) pure SBA-15 and (b) NH$_2$-SBA-15-ZnP (100) at 25 K magnification

The surface area and pore size of the pure SBA-15 and NH$_2$-SBA-15-ZnP (100) was investigated by N$_2$ adsorption/desorption. The isotherms and pore distribution curves are presented in Figure 3. As we can see from the figure, it clearly showed that both samples exhibit typical type IV isotherms with characteristic of capillary condensation in mesoporous channels and hysteresis loops type H1 according to the IUPAC classification [14]. The total surface area ($S_{BET}$) of SBA-15 is 532 m$^2$g$^{-1}$. After

![Figure 3](image2.png)

**Figure 3** N$_2$ adsorption-desorption isotherm and pore size distribution curve of (a) pure SBA-15 and (b) NH$_2$-SBA-15-ZnP (100)

### 3.2 Catalytic Studies

ZnTClPP immobilized on APTES functionalized SBA-15 catalyst (NH$_2$-SBA-15-ZnP) was investigated in the epoxidation of limonene to limonene oxide as shown in Scheme 1.

![Scheme 1](image3.png)

**Scheme 1** Catalytic epoxidation of limonene to limonene oxide over NH$_2$-SBA-15-ZnP

The catalytic activity of NH$_2$-SBA-15-ZnP were tested in the epoxidation of limonene with aqueous hydrogen peroxide ($H_2O_2$) as an oxidant and expected to give 1,2-limonene oxide and carveol as the products. The presence/addition of ammonium acetate as co-catalyst (weak base) is necessary to incorporate hydrogen peroxide and to obtain efficient reactions that help in increase the conversion and selectivity [15]. From the previous study, reaction by metalloporphyrins with hydrogen peroxide ($H_2O_2$) as oxidant require the ammonium acetate which were

### Table 1 The d-spacing and unit cell parameter of materials

<table>
<thead>
<tr>
<th>Samples</th>
<th>d$_{100}$ (nm)</th>
<th>2θ (°)</th>
<th>a$_o$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15</td>
<td>10.35</td>
<td>0.850</td>
<td>11.95</td>
</tr>
<tr>
<td>NH$_2$-SBA-15</td>
<td>9.39</td>
<td>0.940</td>
<td>10.84</td>
</tr>
<tr>
<td>NH$_2$-SBA-15-ZnP (100)</td>
<td>9.44</td>
<td>0.935</td>
<td>10.90</td>
</tr>
<tr>
<td>NH$_2$-SBA-15-ZnP (200)</td>
<td>9.44</td>
<td>0.935</td>
<td>10.90</td>
</tr>
</tbody>
</table>
shown to act both as axial ligand and co-catalyst used to promote the desired heterolytic cleavage of O–O bond of H₂O₂ at the expense of its homolysis [16]. Moreover, the role of the co-catalyst in such system is to facilitate the formation of the active oxygen species Zn(III)=O from the reaction of Zn(III) porphyrin with H₂O₂. The report by Rebelo, S.L.H. [17] indicated the best result seems to be obtained by buffering substances (ammonium acetate, imidazole) or combination of acids and bases (pyridine plus benzoic acid) as co-catalyst in the epoxidation reactions.

Table 2 shows the conversion of limonene and selectivity of product using NH₂-SBA-15-ZnP as catalyst. Based on the results, the heterogeneous catalyst NH₂-SBA-15-ZnP gave a percentage conversion of limonene and selectivity of product comparable to that obtained from unsupported ZnTClPP. However, the NH₂-SBA-15-ZnP catalyst had lower percentage selectivity in the formation of limonene oxide than the unsupported ZnP. The NH₂-SBA-15-ZnP (200) catalyst showed a higher percentage conversion of limonene when compared to the NH₂-SBA-15-ZnP (100) catalyst. It is obvious that the percentage conversion of limonene using NH₂-SBA-15-ZnP increase with the increasing of concentration of ZnTClPP immobilized into solid silica.

On the other hand, the maximum conversion of the NH₂-SBA-15-ZnP (200) catalyst is lower compared to previous studies that up to 81% conversion, but higher selectivity of the product [18]. Therefore, it can be concluded that the catalysts are active for the epoxidation of limonene reaction.

**Table 2** Catalytic epoxidation of limonene by H₂O₂ in the presence of supported metalloporphyrin catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion of limonene (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnTClPP</td>
<td>34.7</td>
<td>95.2</td>
</tr>
<tr>
<td>NH₂-SBA-15-ZnP (100)</td>
<td>23.8</td>
<td>93.0</td>
</tr>
<tr>
<td>NH₂-SBA-15-ZnP (200)</td>
<td>26.2</td>
<td>91.6</td>
</tr>
</tbody>
</table>

Reaction conditions: 20 mg of catalyst; T = 80 °C; t = 24 hours; oxidant: aqueous H₂O₂; solvent: acetonitrile (ACN)

The effect of reaction parameters, such as different temperature and time towards the epoxidation of limonene was further investigated. The effect of reaction temperature on the catalytic activity was studied at room temperature, 50 °C, 70 °C and 80 °C. Figure 4 (a) shows a gradual increase in the conversion of limonene and selectivity of limonene oxide from room temperature to 80 °C. However, the reaction mixture was decomposed when at temperature higher than 80 °C and thus the reaction cannot proceed. Therefore, it can be concluded that the highest conversion of limonene was obtained at 80 °C because this temperature is the nearest to the boiling point of acetonitrile (solvent) which helps the catalyst to perform under optimal conditions.

As depicted in Figure 4 (b), epoxidation of limonene over NH₂-SBA-15-ZnP (200) catalyst at 80 °C by using acetonitrile as solvent was found to be influenced by reaction time. Based on the graph, the catalytic conversion of limonene was slowly increased for the first 5 hours. Afterwards, the catalytic conversion of limonene was continuously increased up to 24 hours. On other hand, it can be observed that the selectivity of NH₂-SBA-15-ZnP (200) was increased with the increase in the reaction time up to 24 hours.

Table 3 presents the catalytic reusability of NH₂-SBA-15-ZnP (200) catalyst for three runs under the same conditions. The used catalyst was filtered, washed thoroughly with solvent and dried before using it in the subsequent reactions. From Table 3, it can be seen that the catalytic activity NH₂-SBA-15-ZnP (200) catalyst decreased only 0.6% after the first run. This shows that the activity of catalyst was not affected after three runs. However, after three runs, the conversion of limonene decreased to 27.6% probably due to the leaching of some weakly bound or decomposition of ZnTClPP complex under the present reaction condition. Therefore, it can be concluded that the catalytic activity of prepared catalyst can be recovered and recycled up to three runs only.
NH$_2$SBA-15-ZnP in catalytic activity have also been investigated.

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