

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

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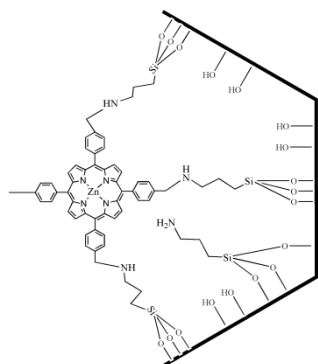
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Graphical abstract



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 NH₂-SBA-15. The metalloporphyrin, [meso-tetrakis-(p-chlorophenyl)porphyrinato]Zn(II) (ZnTCIPP) was synthesized from the reaction of meso-tetrakis-(p-chlorophenyl) porphyrin (H₂TCIPP) using zinc acetate dihydrate as a metal source and then immobilized on SBA-15 surface. The material, NH₂-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 H₂O₂ / 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 tetraetilortosilikat dengan kehadiran surfaktan kopolimer poli(etilena glikol)-blok-poli(propilena glikol)-blok-poli(etilena glikol) dan pengfungsian dengan (3-aminopropil) trietoksilsilan (APTES) melalui tindak balas sol-gel untuk menghasilkan NH₂-SBA-15. Logam porfirin, [meso-tetrakis-(p-klorofenil)porfirinato]Zn(II) (ZnTCIPP) telah disintesis daripada tindak balas meso-tetrakis-(p-klorofenil) porfirin (H₂TCIPP) dengan zink asetat dihidrat sebagai sumber logam dan seterusnya dipegunkan ke atas permukaan SBA-15. Bahan yang terhasil iaitu, NH₂-SBA-15-ZnP telah dicirikan dengan kajian SAXS, FESEM dan BET menghasilkan satu corak yang sama dengan SBA-15 dan menunjukkan bahawa struktur heksagon mesoliang SBA-15 masih lagi dikekalkan. Seterusnya, bahan tersebut telah diaplikasi untuk membolehkan tindak balas pengepoksidaan limonena menggunakan H₂O₂ / ammonium asetat dengan pelbagai suhu dan keadaan. Semua produk yang terhasil dari tindak balas pengepoksidaan telah dianalisiskan menggunakan GC-FID dan GC-MS.

Kata kunci: SBA-15; APTES; logam porfirin; pengepoksidaan; 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 terpenoid 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) (ZnTCIPP) immobilized on SBA-15 mesoporous silica modified with (3-aminopropyl) triethoxysilane (APTES) groups for epoxidation of limonene with hydrogen peroxide (H_2O_2) 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 NH_2 -SBA-15.

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

The free base porphyrin of meso-Tetrakis-(p-chlorophenyl)porphyrin (H_2TCIPP) was prepared by some modification of Alder-Longo method [11]. Afterwards, ZnTCIPP was prepared by refluxing H_2TCIPP (1 mmol) and zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) (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 ZnTCIPP 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 Kα 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 $a_0 = 2d_{100} / \sqrt{3}$, 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-ZnP (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-ZnP (200). The *d*-spacing value of the intense (100) peak have been calculated by using Bragg's law ($\lambda = 2d \sin \theta$). The *d*-spacing and unit cell parameters of all materials are shown in Table 1.

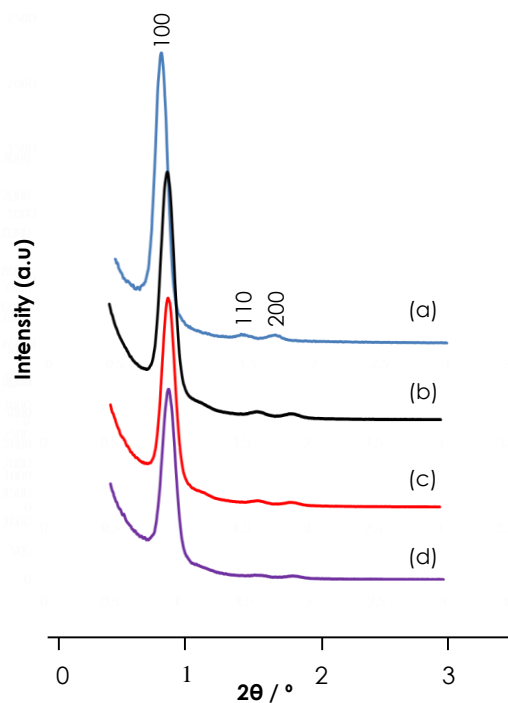


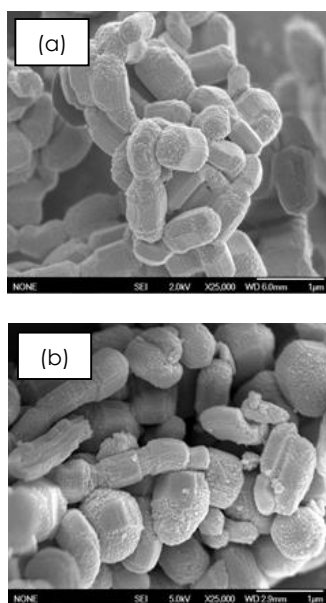
Figure 1 SAXS patterns of (a) pure SBA-15, (b) NH₂-SBA-15, (c) NH₂-SBA-15-ZnP (100) and (d) NH₂-SBA-15-ZnP (200)

From the Table 1, it can be seen that the intensity (100) peak of pure SBA-15 reflects *d*-spacing, *d*₁₀₀ 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.

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

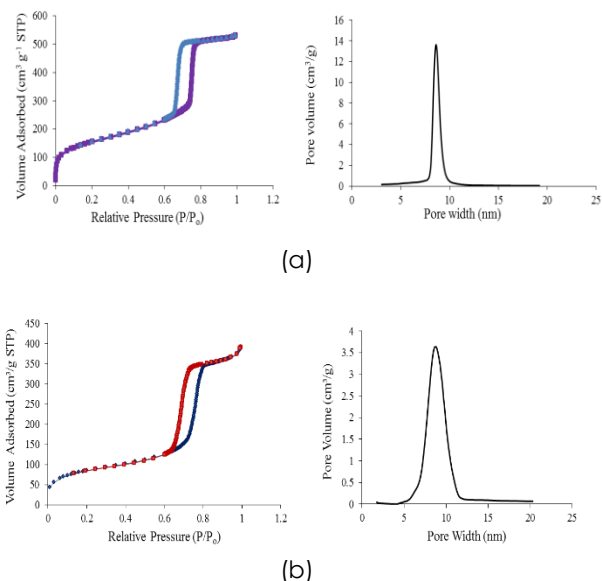
Samples	d_{100} (nm)	2θ	a_0 (nm)
SBA-15	10.35	0.850	11.95
NH ₂ -SBA-15	9.39	0.940	10.84
NH ₂ -SBA-15-ZnP (100)	9.44	0.935	10.90
NH ₂ -SBA-15-ZnP (200)	9.44	0.935	10.90

The morphology of the pure SBA-15 and immobilization of zinc porphyrin on functionalized SBA-15 material, NH₂-SBA-15-ZnP (100) were investigated by field emission scanning electron microscopy. Figure 2 represent the FESEM micrographs of these materials at 25 K magnification. The wheat-like hexagonal particles shown in Figure 2 (a) refers to the SBA-15. Upon the immobilization of metalloporphyrin, ZnTCIPP, Figure 2 (b) showed that the morphology and the hexagonal shape of SBA-15 remain the same. Moreover, there are fine agglomerated sphere particles appeared which probably due to the excess ZnTCIPP that cannot be loaded into the SBA-15 pores and they adsorb on the outer surface.

**Figure 2** FESEM micrographs of (a) pure SBA-15 and (b) NH₂-SBA-15-ZnP (100) at 25 K magnification

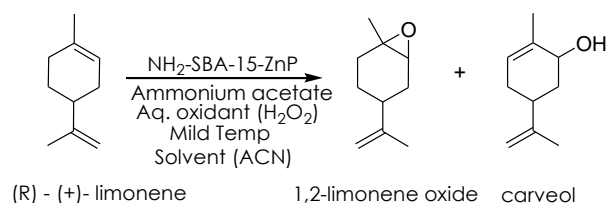
The surface area and pore size of the pure SBA-15 and NH₂-SBA-15-ZnP (100) was investigated by N₂ adsorption/desorption. The isotherms and pore distribution curves are presented in Figure 3. As we can see from the figure, it clearly showed that both samples exhibit typical type IV isotherms with characteristic 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 m²g⁻¹. After

immobilization of zinc porphyrin on functionalized SBA-15, the total surface area (S_{BET}) of NH₂-SBA-15-ZnP (100) decreases to 301 m²g⁻¹. These results indicate that the decrease in the surface area of SBA-15 can be due to the immobilization of ZnTCIPP.

**Figure 3** N₂ adsorption-desorption isotherm and pore size distribution curve of (a) pure SBA-15 and (b) NH₂-SBA-15-ZnP (100)

3.2 Catalytic Studies

ZnTCIPP immobilized on APTES functionalized SBA-15 catalyst (NH₂-SBA-15-ZnP) was investigated in the epoxidation of limonene to limonene oxide as shown in Scheme 1.

**Scheme 1** Catalytic epoxidation of limonene to limonene oxide over NH₂-SBA-15-ZnP

The catalytic activity of NH₂-SBA-15-ZnP were tested in the epoxidation of limonene with aqueous hydrogen peroxide (H₂O₂) 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 (H₂O₂) as oxidant require the ammonium acetate which were

shown to act both as axial ligand and co-catalyst used to promote the desired heterolytic cleavage of O-O bond of H_2O_2 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 $Zn(II)=O$ from the reaction of $Zn(II)$ porphyrin with H_2O_2 . 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 NH_2 -SBA-15-ZnP as catalyst. Based on the results, the heterogeneous catalyst NH_2 -SBA-15-ZnP gave a percentage conversion of limonene and selectivity of product comparable to that obtained from unsupported ZnTCIPP. However, the NH_2 -SBA-15-ZnP catalyst had lower percentage selectivity in the formation of limonene oxide than the unsupported ZnTCIPP. The NH_2 -SBA-15-ZnP (200) catalyst showed a higher percentage conversion of limonene when compared to the NH_2 -SBA-15-ZnP (100) catalyst. It is obvious that the percentage conversion of limonene using NH_2 -SBA-15-ZnP increase with the increasing of concentration of ZnTCIPP immobilized into solid silica.

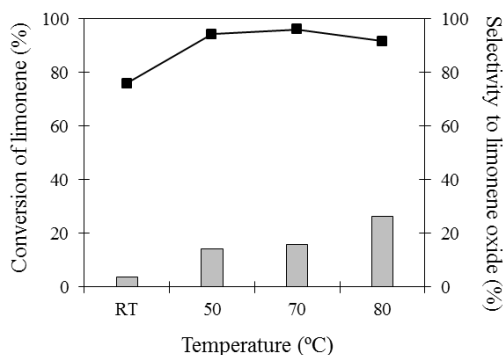
On the other hand, the maximum conversion of the NH_2 -SBA-15-ZnP (200) catalyst is lower compared to previous studies that up to 81% conversion, but higher selectivity of the product [18]. Therefore, it can be concluded that the catalysts are active for the epoxidation of limonene reaction.

Table 2 Catalytic epoxidation of limonene by H_2O_2 in the presence of supported metalloporphyrin catalysts

Catalyst	Conversion of limonene (%)	Selectivity (%)
ZnTCIPP	34.7	95.2
NH_2 -SBA-15-ZnP (100)	23.8	93.0
NH_2 -SBA-15-ZnP (200)	26.2	91.6

Reaction conditions: 20 mg of catalyst; $T = 80^\circ C$, $t = 24$ hours; oxidant; aqueous H_2O_2 ; solvent, acetonitrile (ACN)

(a)



(b)

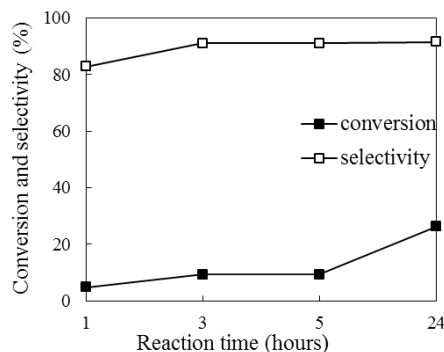


Figure 4 Effect of (a) reaction temperature and (b) reaction time on the catalytic epoxidation of limonene to limonene oxide over NH_2 -SBA-15-ZnP (200) catalyst

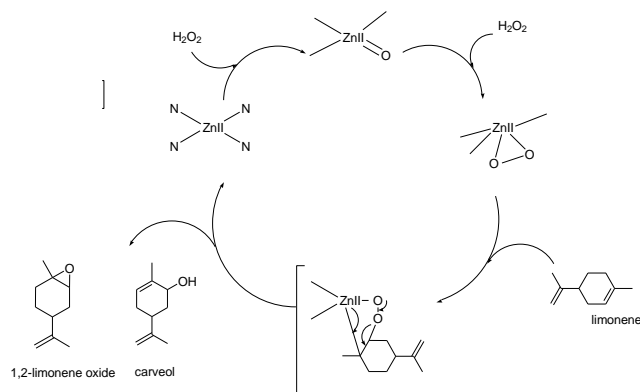
The effect of reaction parameters, such as different temperature and time towards the epoxidation of limonene was further investigated. The effect of reaction temperature on the catalytic activity was studied at room temperature, $50^\circ C$, $70^\circ C$ and $80^\circ C$. Figure 4 (a) shows a gradual increase in the conversion of limonene and selectivity of limonene oxide from room temperature to $80^\circ C$. However, the reaction mixture was decomposed when at temperature higher than $80^\circ C$ and thus the reaction cannot proceed. Therefore, it can be concluded that the highest conversion of limonene was obtained at $80^\circ C$ 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 NH_2 -SBA-15-ZnP (200) catalyst at $80^\circ C$ 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 NH_2 -SBA-15-ZnP (200) was increased with the increase in the reaction time up to 24 hours.

Table 3 presents the catalytic reusability of NH_2 -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 NH_2 -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 ZnTCIPP 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.

Table 3 Catalytic epoxidation of limonene by H₂O₂ of reused catalyst, NH₂-SBA-15-ZnP (200)

Entry	Catalyst	Conversion (%)
1	NH ₂ -SBA-15-ZnP (200) (fresh)	26.2
2	NH ₂ -SBA-15-ZnP (200) (2nd run)	25.6
3	NH ₂ -SBA-15-ZnP (200) (3rd run)	35.9
4	NH ₂ -SBA-15-ZnP (200) (4th run)	27.6

**Scheme 2** Proposed mechanism for epoxidation of limonene over zinc(II) porphyrin using H₂O₂

The proposed catalytic mechanism of epoxidation of limonene with H₂O₂ over zinc(II) porphyrin is depicted in Scheme 2. Firstly, zinc(II) porphyrin is coordinated with H₂O₂ to form complex comprising a higher valence transition metal-oxo complex. Then, zinc complex transform from Zn^{IV}-oxo to Zn^{IV}-peroxo under H₂O₂. Limonene is bound with the one of the metal-peroxo bonds to produce the peroxometalocycle. Finally, the peroxometalocycle is broken/break down and 1,2-limonene oxide and carveol are formed and the zinc(II) porphyrin is generated.

4.0 CONCLUSION

NH₂-SBA-15-ZnP catalysts was successfully synthesized by immobilizing the metalloporphyrin complex, ZnTCIPP onto the APTES functionalized SBA-15 as silica support. SAXS and FESEM data proved that NH₂-SBA-15-ZnP have a hexagonal crystal structure and the framework of mesoporous SBA-15 was preserved after functionalization with APTES and immobilization of ZnTCIPP. BET studies showed that the surface area of SBA-15 was decreased after immobilization of ZnTCIPP. In the catalytic reaction, ZnTCIPP and NH₂-SBA-15-ZnP catalysts were tested in the epoxidation of limonene using aqueous hydrogen peroxide as oxidant. Homogeneous catalyst, ZnTCIPP gave higher catalytic conversion of limonene and selectivity of limonene oxide than heterogeneous catalysts, NH₂-SBA-15-ZnP. The effect of reaction temperature and time of the

NH₂-SBA-15-ZnP in catalytic activity also have been investigated.

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References

- [1] Huang, G., Luo, Z.-C., Hu, Y.-D., Guo, Y.-A. and Jiang, S.-J. 2012. Preparation and Characterization of Iron Tetra (Pentafluorophenyl)-Porphyrin (TPFPP Fe) Supported on Boehmite (BM). *Chemical Engineering Journal*. 195-196: 165-172.
- [2] Khalili, N.R., Rahimi, R. and Rabbani, M. 2013. Immobilized Metalloporphyrins in Mesoporous MCM-48 as Efficient and Selective Heterogeneous Catalysts for Oxidation of Cyclohexene. *Monatsh Chem*. 144:597-603.
- [3] Pires, S.M.G., Simoes, M.M.Q., Santos, I.C.M.S., Rebelo, S.L.H., Pereira, M.M., Neves, M.G.P.M.S. and Cavaleiro, J.A.S. 2012. Biomimetic Oxidation of Organosulfur Compounds with Hydrogen Peroxide Catalyzed by Manganese Porphyrins. *Applied Catalysis A: General*. 439-440: 51-56.
- [4] Bolzon, L.B., Airoidi, H.R., Zanardi, F.B., Granada, J.G. and Yamamoto, Y. 2013. Metalloporphyrin-Functionalized Hexagonal Mesoporous Silica: Synthesis, Structural Properties and Catalytic Activity as Cytochrome P450 Model. *Microporous and Mesoporous Materials*. 168:37-45.
- [5] Kolahdoozan, M., Kalbasi, R.J. and Hossaini, M. 2013. Synthesis of Heterogeneous Copper Catalyst Based on Amino-Functionalized Triazine Rings Supported by Silica-Gel for Oxidation of Alcohols. *Journal of Chemistry*. 2013: 1-7.
- [6] Zhang, J., Zhao, G.-F., Popovic, Z., Lu, Y. and Liu, Y. 2010. Pd-Porphyrin Functionalized Ionic Liquid-Modified Mesoporous SBA-15: An Efficient and Recyclable Catalyst for Solvent-Free Heck Reaction. *Materials Research Bulletin*. 45: 1648-1653.
- [7] Xiao, F.-S. 2005. Ordered Mesoporous Materials with Improved Stability and Catalytic Activity. *Topics in Catalysis*. 35:9-24.
- [8] Trytek, M., Fiedurek, J. and Radzki, S. 2007. A Novel Porphyrin-Based Photocatalytic System for Terpenoids Production from (R)-(+)-Limonene. *Biotechnol. Prog.* 23(1):131-137.
- [9] Byrne, C.M., Allen, S.D., Lobkovsky, E.B. and Coates, G.W. 2004. Alternating Copolymerization of Limonene Oxide and Carbon Dioxide. *J. Am. Chem. Soc.* 126 (37): 11404-11405.
- [10] Zhao, D., Huo, Q., Feng, J., Chmelka, B.F. and Stucky, G.D. 1998. Nonionic Triblock and Star Diblock Copolymer and Oligomeric Surfactant Syntheses of Highly Ordered, Hydrothermally Stable, Mesoporous Silica Structures. *J. Am. Chem. Soc.* 120: 6024-6036.
- [11] Adler, A.D., Longo, F.R. and Finarelli, J.D. 1967. A Simplified Synthesis for Meso-tetraphenylporphyrin. *Journal Organic Chemistry*. 32:476.
- [12] Adam, F. and Ooi, W.-T. 2012. Selective Oxidation of Benzyl Alcohol to Benzaldehyde over Co-Metalloporphyrin Supported on Silica Nanoparticles. *Applied Catalysis A: General*. 445-446:252-260.

- [13] Zhang,Z., Yin,J., Heeres,H.J. and Melian-Cabrera, I. 2013. Thermal Detemplation of SBA-15 Mesophases. Effect of the Activation Protocol on the Framework Contraction *Microporous and Mesoporous Materials*. 176:103.
- [14] Bui, T.X., Kang,S-Y., Lee,S-H. and Choi, H. 2011. Organically Functionalized Mesoporous SBA-15 as Sorbents for Removal of Selected Pharmaceuticals from Water. *Journal of Hazardous Materials*. 193: 156-163.
- [15] Louloudi, M., Kolokytha, C. and Hadjiiladis, N. 2002. Alkene Epoxidation Catalysed by Binuclear Manganese Complexes. *Journal of Molecular Catalysis A: Chemical*. 180 (1-2):19-24.
- [16] Trytek, M., Majdan, M. and Fiedurek, J. 2011. *Biomimetic Based Applications*. InTech Europe.
- [17] Rebelo,S.L.H., Simoes, M.M.Q. and Cavaleiro, J.A.S. 2003. Oxidation of Alkylaromatics with Hydrogen Peroxide Catalysed by Manganese (III) Porphyrins in the Presence of Ammonium Acetate. *Journal of Molecular Catalysis A, Chemical*. 201(1-2):9-22.
- [18] Madadi, M. and Rahimi, R. 2012. Zeolite-Immobilized Mn(III), Fe(III) and Co(III) Complexes with 5,10,15,20-tetra (4-methoxyphenyl)porphyrin as Heterogeneous Catalysts for the Epoxidation of (R)-(+)-Limonene: Synthesis, Characterization and Catalytic Activity. *Reac. Kinet. Mech. Cat.* 107(1):215-229.