

Synthesis and Characterization of Manganese (III) tetra (4-methoxyphenyl) porphyrin encapsulated in zeolite –X: as efficient catalyst for the hydroxylation of Thymol

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Abstract

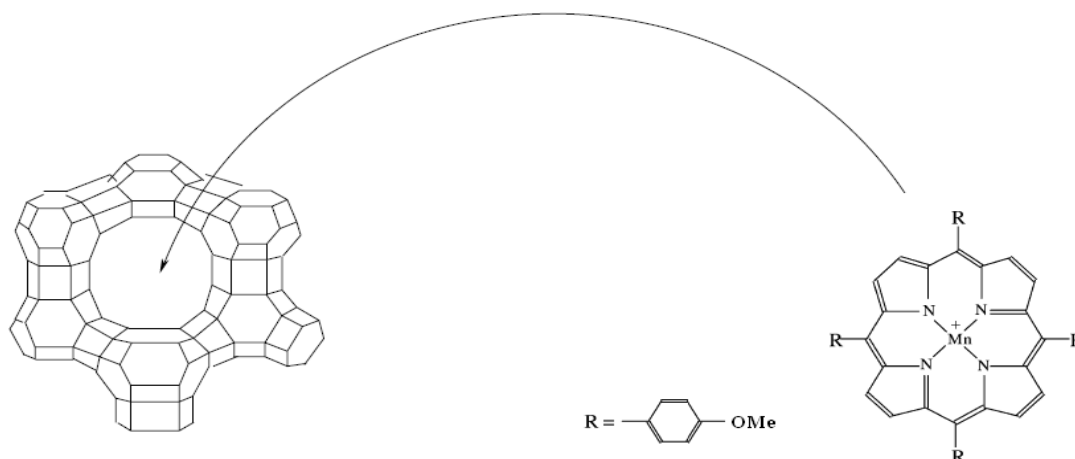
Mn(III) tetra (4- methoxyphenyl) porphyrin (MnTMePP) was synthesized inside the nanocages of zeolite-X according to “ship- in-bottle ” model. MnTMePP was impregnated (MnP-NaX imp) and encapsulated (MnP-NaX) in the zeolite matrix and had been used as an active heterogeneous catalyst for thymol hydroxylation. The oxidation results were improved by immobilization of metalloporphyrin inside zeolitic faujasite in comparison with homogeneous catalyst (MnTMePP). The hydroxylation reaction was performed at 25 °C and atmosphere pressure by using H₂O₂ / Ammonium acetate. All catalysts were characterized by X-ray diffraction (XRD) and Scanning electron microscopy (SEM) Ultraviolet-Visible (UV-Vis) spectroscopy analyses.

1. Introduction

In biomimic system, synthetic metalloporphyrins (MeP) have been used as attractive building blocks for the molecular engineering with designed chemical, Physical, or catalytic properties [1]. The immobilization of homogeneous catalyst systems is an attractive challenge because it opens access to the preparation of new, environmentally friendly means of chemical synthesis. Although homogeneous catalysts show remarkable performance for large variety of reactions, problem such as

separation, recovery and recyclization of the soluble catalysts create the demand for heterogeneous catalysts with comparable performance [2]. Thermally stable large pore molecular sieves are much in demand for applications in e.g. catalysis and have been sought for several decades. In the recent literature, there have been detailed reports of the use of organic molecules, such as crown ethers [3-6] or transition metal complexes [7-9], as structure directing agents (SDAs) in the synthesis of these systems.

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Scheme. 1. M(+n) 5,10,15,20- tetra (4-methoxyphenyl) porphyrin (MTMePP) encapsulated into zeolite nanocages.

Unfortunately, homogeneous catalysts are unstable in the oxidation processes and it is difficult to recover them. One way to overcome these problems is to immobilize the metalloporphyrins on solid supports. Such immobilization can provide selective and active heterogeneous catalyst because of support environment. Zeolites are very good host molecules because of the molecular size of the channels and pores in three dimensional networks with a well crystalline structures, providing shape and size selectivity for entranced guest molecules (Schem. 1). Zeolites are formed through a self assembly mechanism of aluminate and silicate ions around the structure-directing agent [10]. In the case of cationic metalloporphyrins because of their ideal water solubility and stability under hydrothermal and molecular synthesis, they have been studied extensively as template in the synthesis of molecular sieves, such as aluminosilicates, aluminophosphates and gallophosphates. In contrast, none- water soluble metalloporphyrins have been synthesized in presence of supports such as zeolites according ship-in-bottle model. In this paper, we describe the preparation and characterization and catalytical applications of NaX encapsulated and impregnated Mn (III) Porphyrin in the hydroxylation of Thymol.

2. Experimental

We synthesized NaX zeolite according to the modified procedure of Khan and Hriljac [11] under hydrothermal conditions. The synthetic procedure was as follows:

2.1. Na X synthesis

Sodium aluminate (2.16 g) was dissolved in 10 ml of distilled water in a plastic beaker. Sodium metasilicate (6.10 g) was dissolved in 10 ml of distilled water. These solutions were heated to reach complete dissolution and were mixed slowly with rapid stirring. The gel was mixed thoroughly until it was smooth and homogenous. Then transferred into a screw cap polyethylene jar and the reaction vessel were tightly capped. The jar was placed in the oven at 100 °C for 4.5 h. Then cooled at room temperature and isolated via filtration and washed thoroughly with

several portions of distilled water. The samples were dried overnight at 100 °C. The resultant solid was white in color.

2.2. Ion-exchanged zeolite

The Mn^{II} cationic metal was incorporated into the NaX zeolite through ion exchange procedure [12].

For the cationic exchanges of NaX zeolite with Mn^{II}, concentration of salt was obtained nearly 2.5% of magnesium cations (W/W) in NaX zeolite after the exchanging reactions. In this stage cationic exchanged zeolite were prepared in a coprecipitation impregnation method [13] as follows: In a two neck bottom round flask an aqueous solution of 4 g of Mn(acetate)₂·4H₂O in 100 ml of deionized (DI) water was dropped with Na₂CO₃ solution at the same time into a solution of 8 g of Zeolite- X in 300 ml of DI water at 60 °C, under vigorously stirring (6 h). The pH value of the slurry was controlled at 7.0-8.0 during the coprecipitation. Then the slurry was washed and filtered several times with DI water and after that dried at 160 °C and calcinated in air at 200 °C for 8 h.

2.3. Metalloporphyrin synthesis

TMePP synthesis: We synthesized meso-tetra methoxyphenyl porphyrin (TMePP) according to the method described by Adler et al. [14]. A three neck round bottomed flask was set-up with two condensers and an overhead stirrer. The flask was charged with 100 ml of propionic acid as solvent and was heated until propionic acid began boiling (Boiling Point of propionic acid is 141 °C). Then a solution of 4-Methoxy benzaldehyde (1 mmol) dissolved in 5 ml of propionic acid was added very slowly to the hot propionic acid. Pyrrole (1 mmol) was dissolved in 5 ml of propionic acid and added slowly reaction mixture. The mixture was heated to reflux for 4 h and then cooled while still stirring. After transferring into a large container, according to Khan and Hriljac procedure [13], sodium acetate trihydrate (16 g) was dissolved in water (100 ml) and added to the reaction mixture and stirred to bring the pH to approximately 3.0, then the mixture was left overnight. The light purple was collected by Buchner filtration and washed with dichloromethane and methanol several times until the supernatant was pale yellow. The precipitate was then washed with hot DI water and dried at 100 °C. For more purification the precipitate was Soxhlet with methanol, dichloromethane and DMF for 72 h (24 h for each). Magnesium insertions into TMePP was achieved by heating the free-base porphyrin and Mn(acetate)₂·4H₂O at reflux condition in DMF for 24 h. At the end of the reaction, the mixture was transferred into a larger container and placed into an ice bath and 100 ml of cool DI water was then added into mixture. After that the mixture was cooled overnight and the solid metalloporphyrin was isolated by Buchner filtration.

2.4. Preparation of catalysts applying immobilization methods

2.4.1. Impregnation method

First, the zeolite-X was synthesized, and then a sample was prepared by impregnation of proportional amounts of MnTMePP on NaX (NaX-MnTMePP_{imp}) at reflux condition in dichloromethane for 24 h. The reaction mixture was cooled and followed by evaporation of solvent at room temperature.

2.4.2. Template synthesis method (ship-in-bottle)

In a tree neck round-bottomed flask, a mixture was prepared with (2) g of MnNaX, 100 ml of distilled propionic acid, 1 mmol of freshly distilled pyrrole and 1mmol of 4-methoxybenzaldehyde. The suspension was stirred under reflux conditions for 24 h using an oil bath at 140 °C. The color of suspension changed to dark purple nearly 15 min after reaction beginning. After that, the dark solid obtained was collected and filtered with Buchner and washed with dichloromethane, chloroform and DI water, respectively to remove the adsorbed compounds from external surface of the MnNaX.

The solid was dried and washed by Soxhlet extraction with dichloromethane for 72 h. The solid was named MnX-TMePP.

2.5. Catalyst characterization

X-ray powder diffraction patterns were obtained on a Philips PW1800 diffract meter using CuK α radiation (40 kV, 30 mA) selected by a graphite monochromatic in the diffracted beam. Scanning electron microscopy (SEM) and Energy dispersive x-ray microanalysis (EDX) were carried out using a Philips XL30 microscope equipped with EDS system, while the metallization were made with gold in Bal-TecSDC 005 instrument. UV-Vis spectroscopy was performed on shimadzu 1700 double beam spectrophotometer using quartz cells of 1 cm optical path. The IR spectra were recorded on a Shimadzu-8400S spectrometer using KBr pellets. Gas chromatographic analyses were performed on a Perkin-elmer- 8420 equipped with a FID detector. The oxidation products were characterized by using HP 5970 GC-MS

2.6. Catalysts Reaction

The oxidation of Thymol was carried out at 25 °C and atmospheric pressure using hydrogen peroxide as the oxygen-atom donor:

Method A. 0.1 mmol H₂O₂ was added each 30 min (until a total of 1 mol) to the reaction mixture composed of 1 mmol Thymol, 250 μ l acetonitrile as solvent, 0.13 mmol ammonium acetate, 20 mg supported or 0.01 mg free metalloporphyrin.

Method B. 0.5 mmol hydrogen peroxide each 15 min until a total of 4 mmol.

3. Result and discussion

3.1. Catalyst characterization

The SEM image and XRD pattern of MnP-NaX presented in Figs. 1 and 2, respectively. Both of these figures are similar to those for NaX that confirm same morphology and crystalline Structures, i.e., framework around the guest molecule MnTMePP is the faujasite X. The same figure is observed for MnTMePP-NaX_{imp}, indicating that the solid support is structurally unchanged and the Mn (III) porphyrin is adsorbed on the external surface of the NaX. The Si/ Al ratio of three samples is nearly 1.2 that calculated by EDS.

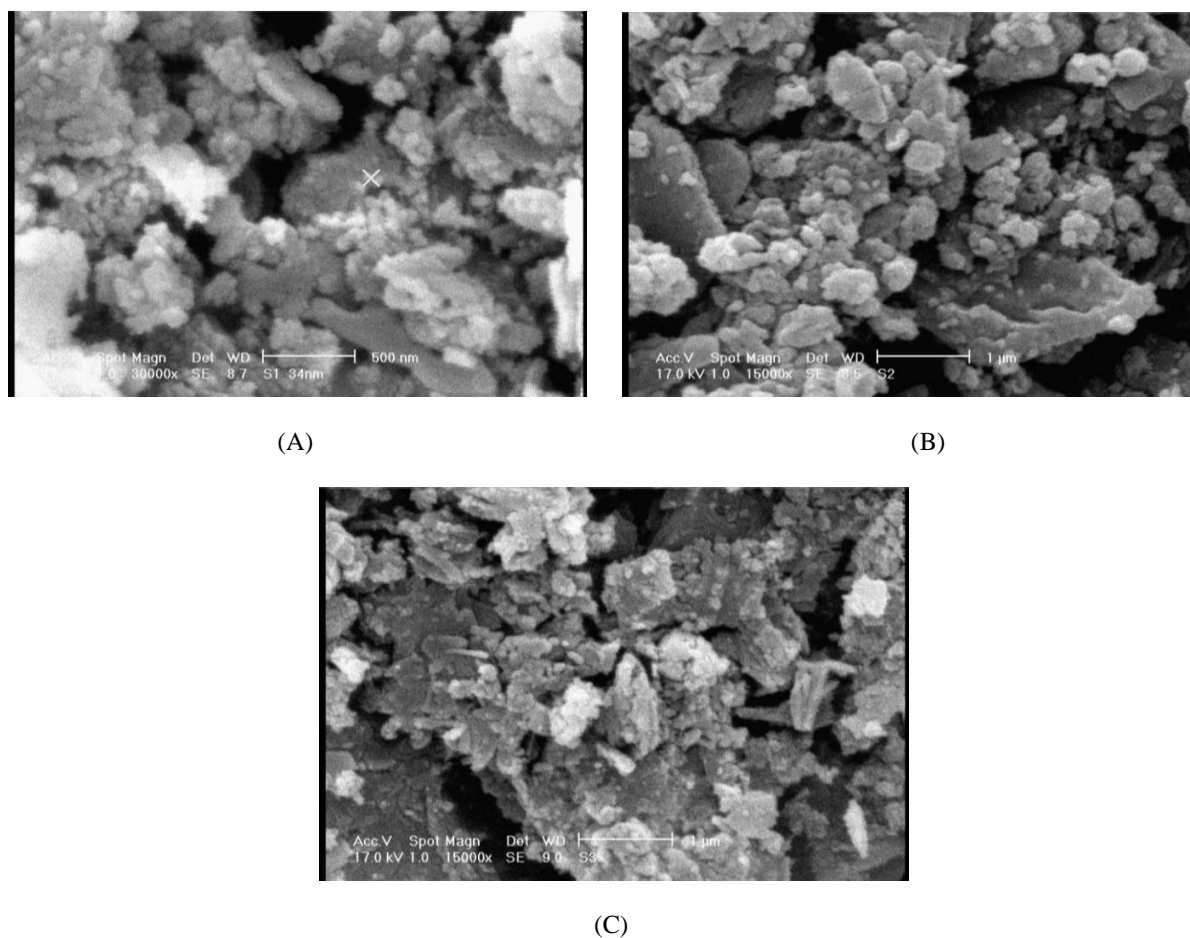


Fig.1. SEM images of MnX (A), TMePP (B), MnTMePP-NaX (C)

The comparison of UV-Vis spectrum of TMePP complex and the diffuse reflectance spectra of MnNaX and TMePP encapsulated in zeolite X (Fig. 3) confirmed the incorporation of metalloporphyrin into the supercages of zeolite. The same band is present in the UV-Vis spectra of MnTMePP-NaX but the maxima have been shifted to lower wavelength. Such blue shift of the absorption band in comparison with the free metalloporphyrin indicates that the immobilization of the complex modifies the electronic and spectral properties of encapsulated metalloporphyrins.

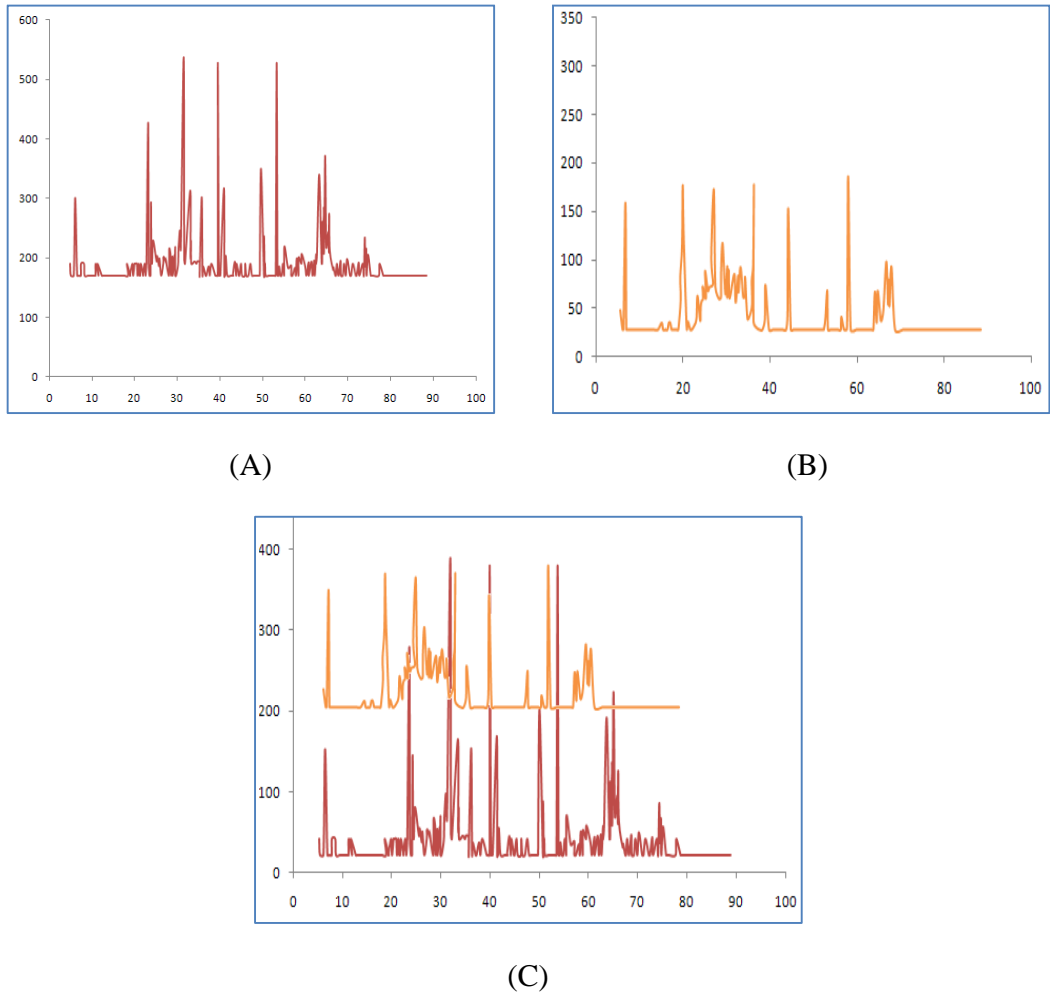


Fig. 2. XRD patterns of (A) MnX, (B) TMePP and (C) MnTMePP-NaX

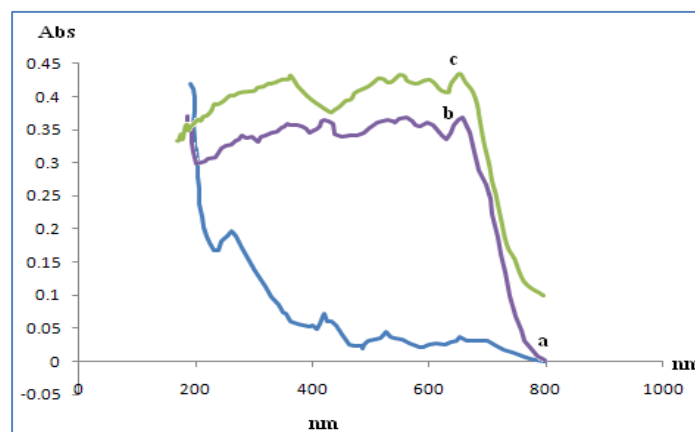
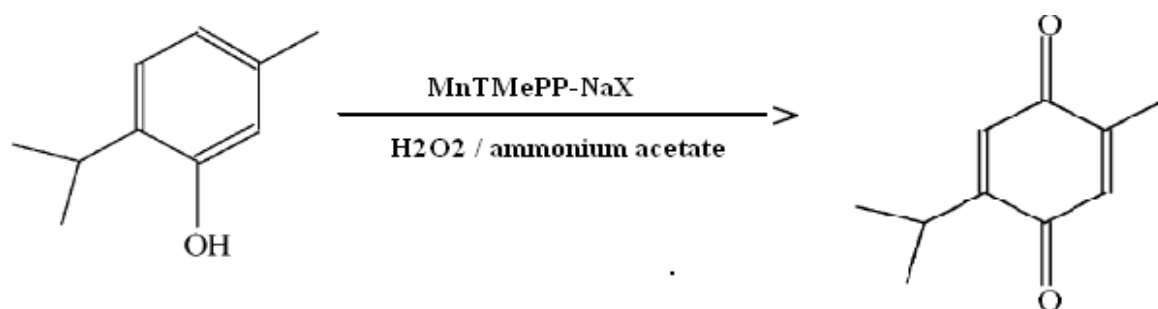


Fig. 3. Solide state UV-Vis of (a) MnX, (b) MnTMePP-NaX and (C)TMePP

3.2. Hydroxylation of Thymol

The catalytic performance of MnTMePP-NaX was studied for the hydroxylation of Thymol using $\text{H}_2\text{O}_2/\text{NH}_4\text{CH}_3\text{COO}$, acetonitrile as solvent, at 25°C and atmosphere pressure (Schem. 2). The catalytic results are compared with the homogeneous system. Control experiments showed that NaX zeolite is inactive, under the operating conditions. Both heterogeneous and homogeneous catalysts are active in the oxidation of monoterpenes. The oxidation result were compiled in table (1).



Scheme. 2. Hydroxylation of thymol using $\text{H}_2\text{O}_2/\text{NH}_4\text{CH}_3\text{COO}$ by MnTMePP-NaX

Table. 1

Catalytic activity of MnTMePP, MnTMePP-NaX and MnTMePP-NaX imp catalysts in the hydroxylation of the thymol

Catalyst	Time (h)	Conversion (%)
MnTMePP	12	25
	24	31
	72	35
MnTMePP-NaX	12	65
	24	67
	72	73
MnTMePP-NaX _{imp}	12	45
	24	47
	72	53

4. conclusion

The present study showed that the ship-in-a-bottle synthesis of metalloporphyrins inside the zeolites and impregnation of them on external zeolitic surface were extensively increased the catalytic activity and stability and recovery in comparison with homogeneous system. The result of characterization of the mentioned catalyst using UV-Vis and XRD confirmed that the capsulation and impregnation process were performed successfully. The SEM analysis showed that the support structure was remained without any destruction after immobilization of metalloporphyrin inside the zeolite. Finally, to complete the study, oxidation reactions were performed and both of the heterogeneous and homogeneous catalysts were compared with each other in the hydroxylation of thymol at different times.

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