Efficient catalytic oxidation of cyclohexane by metalloporphyrins encapsulated mesoporous MCM-48

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Abstract:

Catalytic oxidation of cyclohexane by two metalloporphyrins {manganese and iron 5, 10, 15, 20-meso-tetrakis-(p-chlorophenyl) porhyrin}immobilized in mesoporous MCM-48 with TBHP in acetonitril was investigated. It was found that immobilization significantly enhances catalytic activity as compared to the homogenous system.

Keywords: cyclohexane oxidation, metalloporphyrins, MCM-48.

1. Introduction:

The selective catalytic oxidation of organic compounds using environmentally friendly and cheap oxidants, and a heterogenous, easily recyclable catalysts is a challenging goal in chemical industries and catalytic researchers [1]. Cytochrome P450 are a class of heme-containing monooxygenase that transfer an oxygen atom from molecular oxygen to a wide range of organic substrate [2]. In an attempt to mimic the reactivity of heme proteins, many researchers have used metalloporphyrins to catalyst selective oxidation processes with a variety of oxygen donors. Metalloporphyrins are well known for their ability to catalyse selective oxidation process with a variety of oxygen donors. Heterogenous catalysis, in comparison to homogeneous catalysis, show advantages such as facilitated product separation, easy catalyst recovery, and enhanced stability of the catalytic species [3].

Among the various solid supports, the mesoporous silica materials, a member of M41s has attracted much attention due to their high surface area and well-defined array of uniform mesopores. However, due to its narrow pore size distribution and it's interwoven and branched, regular, cubic pore structure, which provides more favorable mass transfer kinetics in catalytic technologies, MCM-48 seems to be a more interesting candidate for applications than MCM-41 [4].

In this study, MCM-48 was found to serve as a novel efficient support in heterogenization of metalloporphyrins. The catalytic efficiency of metalloporphyrins with different metal centers (Fe, Mn) encapsulated MCM-48 was tested in the oxidation of cyclohexane using TBHP (80% di-tert-butylhydroperoxide) as oxygen donor. The results indicate that oxidation of cyclohexane with TBHP were successfully carried out under mild conditions in the presence of Mn//Fe TClPP-MCM-48 as catalyst.

2. Results and discussion:

2.1 characterization of the catalysts:

The DRUV-vis spectra of MnTClPP/MCM-48 and FeTClPP/MCM-48 are shown in Fig. 1. The UV-vis spectra confirm that the mesopores contain porphyrin species. There is no significant change in the position of soret band maxima with respect to the values observed in solutions of the respective metalloporphyrins.(Table 1).

Table 1:Values for unsupported porphyrins dissolved in dichloromethane

Porphyrin	Soret band (nm)
MnTClPP	456
FeTClPP	402

This result confirm the successful encapsulations of metalloporphyrins into the supports, and also be considered as a proof, that no chemical changes have occurred to metalloporphyrins during the immobilization. Broadening of the Soret bands is due to the interaction with the support, which is more significant for FeTClPP/MCM48.

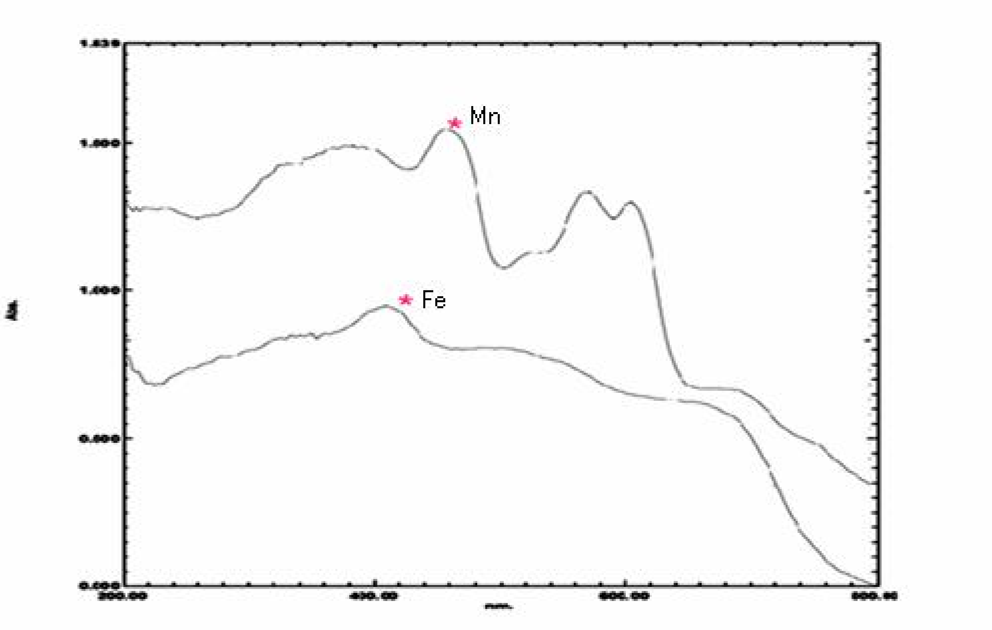

Fig1. UV-Vis spectra of MeTClPP/MCM48 catalysts (Me = Mn, Fe)

Fig.2 showes the SEM images of supported (MnTClPP/MCM-48) and unsupported (MCM-48). The SEM images of supported and unsupportedare similar to each other that explain the encapsulated materials possess the some morphology and that the solid supports were structurally unchanged upon immobilization.

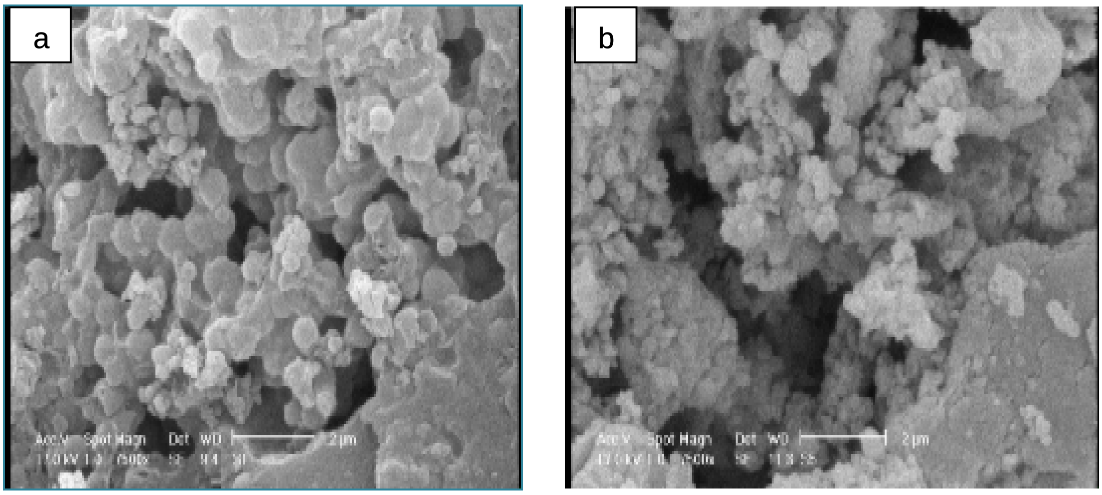

Fig2. SEM images of (a) MCM48 (b) MnTClPP-MCM48

2.2. Oxidation of cyclohexane:

The activities of the supported MnTClPP and FeTClPP porphyrins are lower than those of the unsupported compounds. The amounts of MnTClPP and FeTClPP was determined by elemental analysis (ICP), which showed values of 10.58 % and 20.2 % respectively. The amounts of encapsulated metalloporphyrins in MCM-48 were stringly higher than MCM-41. Catalytic oxidation data of cyclohexane with TBHP is shown in Table 2.

Table 2. catalytic oxidation of cyclohexane with TBHP by supported metalloporphyrins

Ctalysts	Cyclohexanon (%)	Cyclohexanone (%)
MnTClPP/MCM48	76	19
FeTClPP/MCM48	82	14

All studied catalysts showed a remarkable activity on cyclohexane oxidation reactions. Products were obtained with fair to excellent turnover numbers. Enhanced selectivity to cyclohexanone is attributed stereoselectivity effects of mesoporous silica supports.

3. Conclusion:

In conclusion, MCM-48 was found to serve as a novel efficient support in heterogenization of metalloporphyrins. The catalytic activity of these heterogenous catalysts were also compared with a heterogenous catalysts supported in MCM-41 nanoporous. The results indicate that highly active also selective, simple, safe to operate.

4. Experimental

4.1. Synthesis of metalloporphyrins

Meso –tetrakis (4-chlorophenyl)porphyrin (TClPP) was synthesized according to Adler's method [5]. An equivalent quantity of distilled pyrrole and reagent grade 4-chlorobenzaldehyde were refluxed in prpionic acid for 2 hr. the mixture was cooled to 298 k and the precipitate was filtered and washed thoroughly with water. It was dried in vaccum to get purple colored TClPP ligand. The metallation procedure was followed the method of Adler [6]. The purified TClPP was allowed to reflux, with an exceess of metal chloride in 45 ml of dimethylformamide. After 5 h reflux and 1 h ice bath , 50 ml of cooled water was added and an immediate precipitation of the solid was occurred.

4.2 *.Synthesis of MCM-48 :*

MCM-48 was prepared according to the synthesis procedure described by Shao [7]. In a representative synthesis, MCM-48 molecular sieves were prepared as follows:
10 g of TEOS were mixed with 50 g of deionized water and the mixture was vigorously stirred at 35 C for 40 min, then required amount of NaOH was added into the mixture, at the same time, the required amount of NaF was also added into the mixture. After another 60 min of vigorous stirring at 35 C , 10.61 g of CTAB were added to the mixture and the stirring continued at 35 C for 60 min. The molar composition of the final mixture was 1.0SiO2 : 0.65CTAB : 0.5NaOH :62H2O:0.1NaF. Finally, the mixture was heated for 24h at 120 C in an autoclave under a static condition; the resulting MCM-48 product was filtered, washed with distilled water and dried at 100 C. The as-synthesized sample was designated as as-MCM-48. The as-MCM-48 sample was then calcined for 4 h at 550 C, after increasing the temperature to 550 Cat 1 C/min of heating rate and designated as cal. MCM-48.

4.3. Synthesis of supported catalysts:

In order to immobilize the complexes within the MCM-48, using Costa et al methods [8]. 0.2 g of metalloporphyrin (FeTClPPCl and MnTClPPCl) in dichlorometane were slowly added to 2g of MCM–48 in 50 ml of dichlorometane. The mixture was kept under magnetic stirring for 48 h, and then under reflux conditions for 1 h. The solid product was then washed in a Soxhlet apparatus for 48 h with dichlorometane, in order to remove the weakly adsorbed metallocomplexes on the mesoporous surface. Finally, the solids were dried in air at room temperature.

4.4. Oxidation reactions:

Oxidation reactions were carried out at atmospheric pressure under reflux conditions mixing 20 mmol of cyclohexane, 24 mmol of oxidizing agent (TBHP), 0.1 g of the catalyst and 3ml of acetonitrile [9].The solid was filtered after 8 h, and the solution was then submitted to chromatographic analysis.

Acknowledgment

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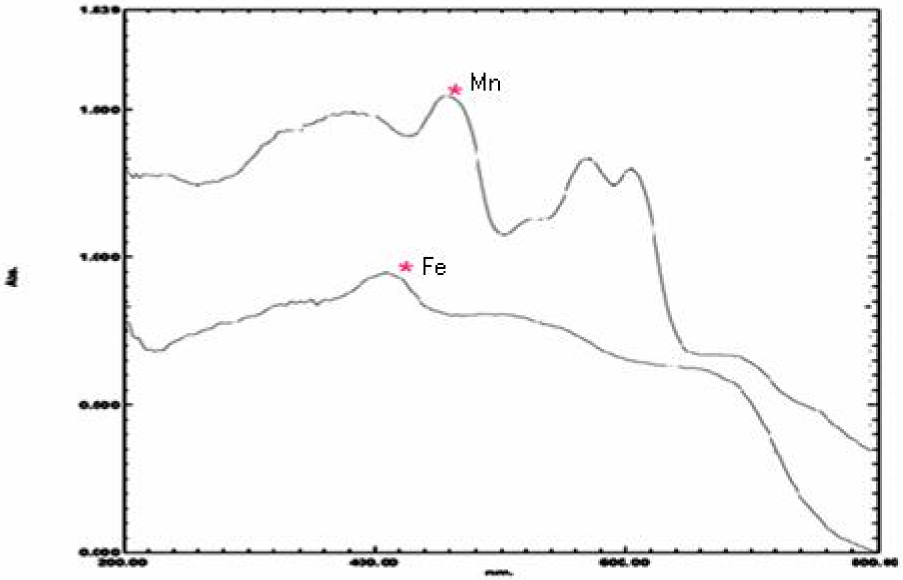

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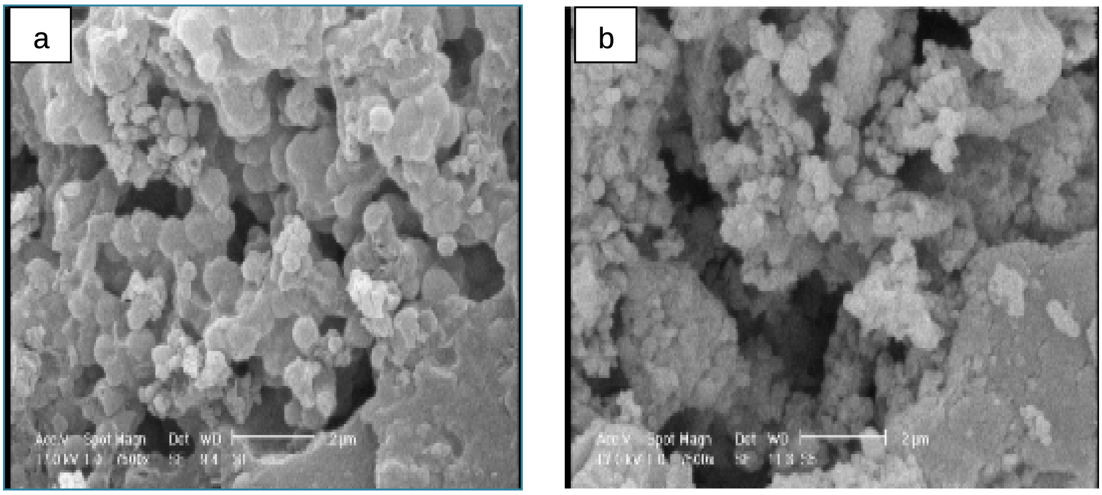

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