

A Comparative Study of Catalytic Activity of Fe, Mn and Cu Porphyrins Immobilized on Mesoporous MCM-41 in Oxidation of Sulfides

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Fe, Mn, and Cu porphyrin complexes have been immobilized on mesoporous MCM-41 nanocavities. The formation and integrity of the prepared complexes have been studied using FT-IR, UV-Vis, SEM and atomic absorption spectroscopy. Also a comparative study of catalytic activity of the heterogeneous catalysts was carried out for oxidation of sulfides with urea hydrogen peroxide. It was found that the best results were obtained using Mn-porphyrin supported on MCM-41 as an efficient catalyst.

Keywords: Metalloporphyrin, mesopores MCM-41, catalytic oxidation, urea hydrogen peroxide (UHP).

Сравнительное исследование каталитической активности порфиринов Fe, Mn и Cu, иммобилизованных на мезопористом МСМ-41, в реакциях окисления сульфидов

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Fe, Mn и Cu-порфириновые комплексы были закреплены в мезопористых нанополостях МСМ-41. Для подтверждения результатов синтеза и закрепления полученных комплексов использовались методы FT-IR, UV-Vis, SEM и атомно-абсорбционной спектроскопии. Также было проведено сравнительное исследование каталитической активности гетерогенных катализаторов на примере реакции окисления сульфидов гидроперитом. Было установлено, что в качестве катализатора наиболее эффективен Mn-порфириновый комплекс, закрепленный на МСМ-41.

Ключевые слова: Металлопорфирин, мезопористый МСМ-41, каталитическое окисление, гидроперит.

Introduction

Organic sulfoxides are important intermediates, both from the laboratory and industry points of view, and oxidation of organic sulfides to the corresponding sulfoxides has attracted much attention in the last two decades.^[1–3]

Many macrocyclic complexes such as metallophthalocyanines (MPc) or metalloporphyrins (MP) are widely em-

ployed in the elimination of different organic contaminants such as sulfides. In order to improve the catalytic performance of the MPc or metalloporphyrin, numerous support materials have been employed.^[4–8] Metalloporphyrins have been investigated extensively for biomimetic oxidation of organic compounds as models of cytochrome P450s due to their innate properties, and also because of existence in many natural and fundamental products.^[9–12] These metallo-complexes are

able to catalyze selective oxidation processes with a variety of oxygen donors.^[13–15] Unfortunately, metalloporphyrins as homogeneous catalysts encountered with some drawbacks, i.e., they may easily be destroyed during the reaction and has little stability toward oxidative degradation and they cannot be easily recovered after the reaction. Also high cost of the synthetic porphyrins makes their recovery compulsory. In order to achieve more stabilized and active systems, immobilization of expensive metalloporphyrin catalysts on insoluble organic and inorganic supports, such as alumina,^[16] silica,^[17,18] zeolites,^[19–21] clays,^[22] polymers^[23,24] and resins could be an efficient method and have been widely used.

The inner pore size of the zeolites is in the range 0.7–1.3 nm which is not suitable for big complexes.^[25] Compared with zeolites, Mobil Composition of Mater (MCM) family with a large and tunable pore size, very large specific surface area (approximately 1000 m²·g^{−1}) and high capacity of adsorption are known as a very attractive candidate to host large molecules such as metalloporphyrins.^[26] On the other hand, great interest on using clean procedures for oxidation reactions catalyzed by metalloporphyrins has attracted much attention during the last two decades.^[27–29] In this regard, hydrogen peroxide and its derivatives such as urea hydrogen peroxide (UHP) as cheap and green (environmentally friendly) oxidants which only produce water and oxygen as side products are considerable oxidants for oxidation of organic compounds.^[29–32]

The research reported here presents the results of preparation, characterization and catalytic application of three metalloporphyrin catalysts (Fe(TPP)Cl, Mn(TPP)OAc and Cu(TPP)), where anchored on MCM-41 in the oxidation of methyl phenyl sulfide with urea hydrogen peroxide.

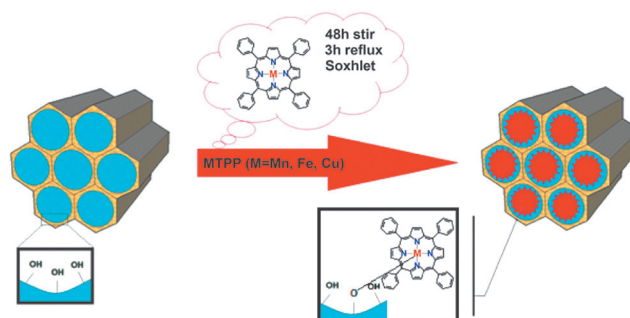
Experimental

Electronic absorption spectra were recorded on a single beam spectrophotometer (Camspect, UV-M330) in CH₂Cl₂. FT-IR spectra was recorded on an ABB Bomem: FTLA 2000–100 in the range of 400–4000 cm^{−1} using spectral-grade potassium bromide. Gas chromatography experiments (GC) were performed with a Shimadzu GC-14B equipped with a flame ionization detector (FID) with a SAB-5 capillary column (phenyl methyl siloxane 30 m×320 mm×0.25 mm). All reagents and solvents were purchased from Merck or Fluka chemical companies and were employed without further purification. *meso*-Tetraphenylporphyrin and metalloporphyrins were prepared according to the literature.^[33,34]

***meso*-Tetraphenylporphyrin.** Dark violet solid; m.p. >300 °C: ¹H NMR (CDCl₃, 500 MHz) δ ppm: 8.85 (s, 8H, β pyrrole); 8.20–8.24 (d, 8, *o*-phenyl); 7.73–7.75 (d, 8H, *m*-phenyl); −2.77 (s, 2H, NH). FT-IR (KBr) cm^{−1}: 1349 (ν C–N), 1445 (ν C=N); 1484 (ν C=C_{Pyrro}); 1591 (ν C=C_{Pyrro}); 3425 (ν N–H). UV-Vis (CH₂Cl₂) λ_{max} nm: 418; 515; 551; 593; 650.

Preparation of MCM-41. MCM-41 mesoporous silica was synthesized according to the literature^[35] using the following procedure: 7.48 g tetradecyl (trimethyl) ammonium bromide was dissolved in 80.0 g water. Then, an aqueous solution of sodium silicate (9.9 g in 30.0 g water) was added dropwise under vigorous magnetic stirring. After 30 min, the pH was adjusted to 10 using 2 M sulfuric acid solution. This mixture was transferred into a Teflon lined autoclave and heated statically at 100 °C for 2 days. The obtained solid material was filtered, washed with water and dried at 60 °C. The sample was then calcined in flowing nitrogen at 550 °C (2 °C/min), then in air at the same temperature for 5 h.

Preparation of the heterogeneous catalysts. The heterogeneous catalysts were prepared according to literature.^[34] Briefly, 0.05 g of metalloporphyrin (Fe(TPP)Cl, Mn(TPP)OAc or Cu(TPP)) was added to 0.2 g of MCM-41 in dichloromethane (20 mL). The mixture was allowed to stir at room temperature for 48 h, and then under reflux conditions for 3 h. The solid product was then washed in a Soxhlet apparatus with 200 mL of dichloromethane for 10 h. Finally, the solids were dried in air at room temperature (Scheme 1).



Scheme 1. Preparation of heterogeneous catalysts.

General oxidation reaction. Catalytic experiments were carried out in a 5 mL test tube. In a typical procedure, 0.16 mmol of urea hydrogen peroxide (UHP) and 0.16 mmol of acetic anhydride as an activator were added to a mixture of sulfide (0.08 mmol), imidazole as an axial base (0.4 mmol) and catalyst (0.004 mmol) in solvent (1 mL) and the mixture was stirred for 30 min. Eventually, the products were characterized by GC.

Results and Discussion

Characterization of Heterogeneous Catalysts

UV-Vis spectra of metalloporphyrins show typical bands of metalloporphyrins (Soret and Q) and the results are listed in Table 1. These data are clearly in agreement with the literature.^[33] The metalloporphyrins encapsulated in molecular sieve have been characterized by UV-Vis spectroscopy. The spectra of encapsulated metalloporphyrins clearly show the Soret bands with a slight red shift which were almost the same as that in the spectra of the free metallocomplexes.

The steric constraints of the support which caused a modification of the metalloporphyrin can be an explanation for the red shift of the Soret bands (Figure 1). This result

Table 1. Experimental values for Soret and Q bands obtained by UV-Vis analysis.

Entry	Catalyst	Soret band, nm	Q band, nm
1	Mn(TPP)OAc	474	578, 615
2	Mn(TPP)OAc/MCM-41	477	–
3	Fe(TPP)Cl	419	480, 511, 665
4	Fe(TPP)Cl/MCM-41	426	–
5	Cu(TPP)	418	450
6	Cu(TPP)/MCM-41	420	–

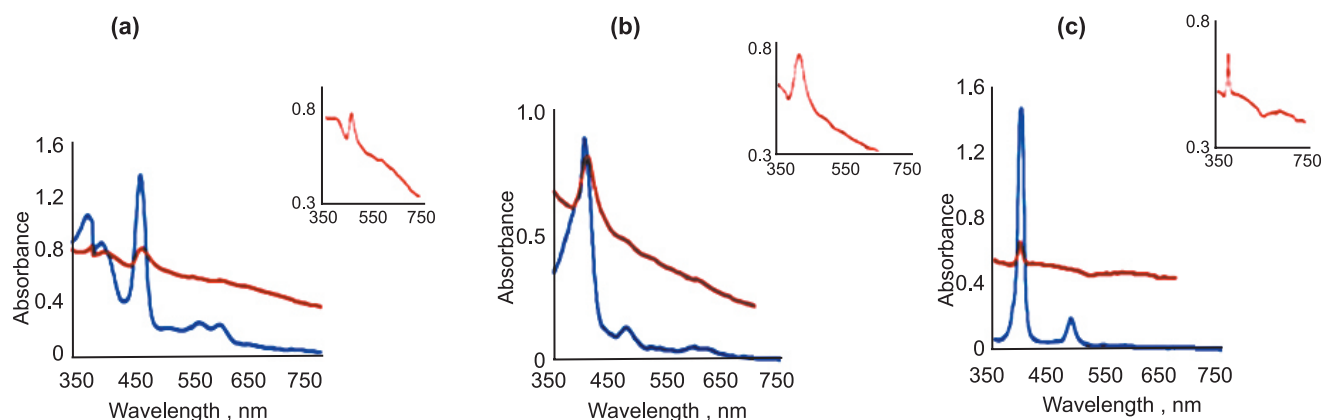


Figure 1. UV-Vis spectra of homogeneous and heterogeneous (a) Mn-porphyrin, (b) Fe-porphyrin and (c) Cu-porphyrin.

indicates that the successful anchoring of metalloporphyrins into the solid support was achieved.

The amount of metalloporphyrin immobilized on the solid support was determined by atomic absorption spectroscopy (AAS) and the results are presented in Table 2.

Table 2. AAS results for the metals after metalloporphyrins immobilization.

Entry	Catalyst	Amount of metal (%)
1	Mn-Porphyrin/MCM-41	1.39
2	Fe-Porphyrin/MCM-41	0.64
3	Cu-Porphyrin/MCM-41	0.16

The SEM image of the Mn(TPP)OAc/MCM-41 are shown in Figure 2. This result presents irregular plate morphology with smooth surface and some hollow network structure for the heterogeneous catalyst.

FT-IR spectra were obtained to observe the interactions between silanol groups on the surface support (MCM-41) and metalloporphyrins (Figure 3). The bands observed at 470, 804, 961 and 1093 cm^{-1} , which are related to $\nu(\text{Si-O-Si})$, $\nu_s(\text{Si-O-Si})$, $\nu(\text{Si-OH})$ and $\nu_{as}(\text{Si-O-Si})$, respectively, are the

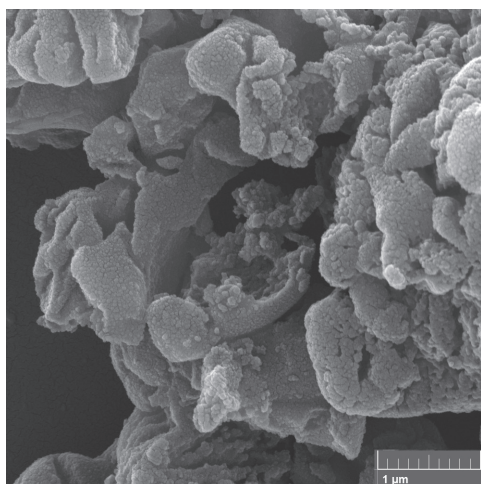


Figure 2. SEM image of the Mn(TPP)OAc/MCM-41.

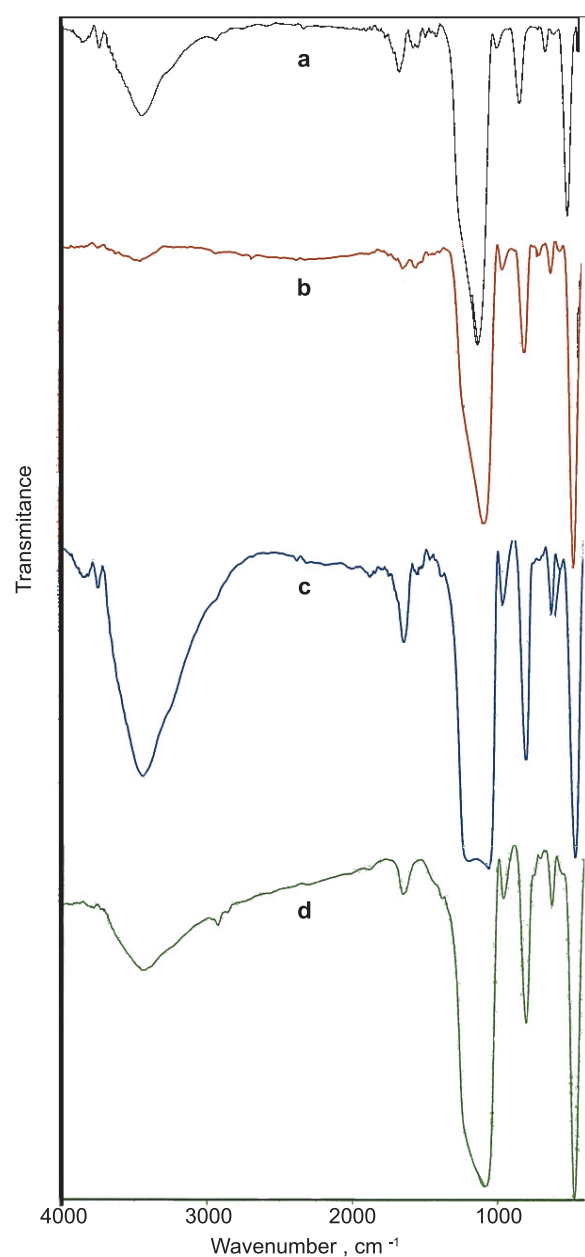


Figure 3. FT-IR spectra of synthesized catalysts at room temperature: a) MCM-41, b) Mn(TPP)OAc/MCM-41, c) Fe(TPP)Cl/MCM-41 and d) Cu(TPP)/MCM-41.

main features of MCM-41^[34,36] and wide band at 3445 cm^{-1} is related to hydroxyl group vibration in mesoporous MCM-41. Also stretching vibration for aliphatic C–H observed at 2921 cm^{-1} . Although slight changes could be observed at 1000 and 1200 cm^{-1} , the band assigned around 950 cm^{-1} is the one that indicates the presence of organic groups on the MCM-41 surface^[37] by a shift to lower wavenumbers. Due to the low amount of metalloporphyrins immobilized on the surface support, this main characteristic of the anchored complexes could not be observed. Also comparing IR spectra of support and heterogenized catalysts and not changing main peaks demonstrating that after anchoring metalloporphyrins on mesoporous MCM-41, the mesoporous host was maintained after inclusion of metalloporphyrins.

Catalytic Oxidation Reaction

Oxidation of methyl phenyl sulfide (MePhS) with UHP catalyzed by M(TPP)/MCM-41 gave methyl phenyl sulfoxide as the major product. In a search for suitable reaction conditions to achieve the maximum conversion and highest selectivity for sulfoxide, the effect of different parameters including solvent, temperature, amount of oxidant and imidazole and the presence of acetic acid (HOAc) was studied.

The presence of nitrogen donors especially imidazole (ImH) has been shown to have significant effect on the catalytic activity of manganese porphyrins.^[38–40] Various molar ratios of ImH/catalyst were examined for oxidation of methyl phenyl and the 1:100 molar ratio was found to be the optimized one (Figure 4).

Further increase in the molar ratio of catalyst to ImH, beyond the 1:100, led to a dramatic decrease in the catalytic efficiency. This observation may be attributed to the formation of an inactive six coordinate species, i.e. $\text{Mn}(\text{porphyrin})(\text{ImH})_2$.^[41]

The effect of reaction temperature, sulfide/catalyst and UHP/catalyst molar ratio is shown in the Table 3.

Hydrogen peroxide as a green oxidant is a widely used oxidant with high active oxygen content compared to other stoichiometric oxidants, but it is a rather slow oxidizing agent in the absence of activators. It is shown that the latter could be largely increased by the addition of

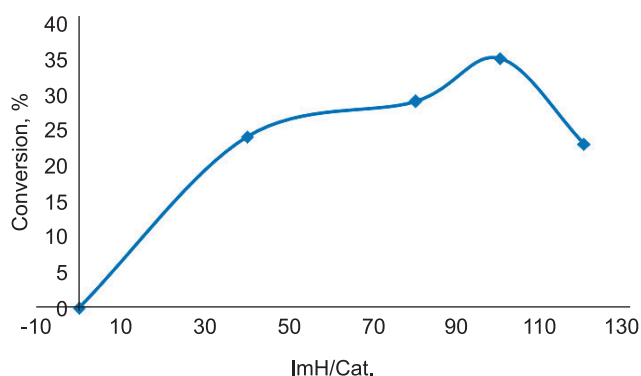


Figure 4. The effect of different amounts of ImH on oxidation of MePhS with UHP by encapsulated Mn(TPP)OAc. The molar ratios for Mn(TPP)OAc/MCM-41:ImH:MePhS:UHP are 1:X:20:55. The reaction was carried out in 0.2 ml CH_2Cl_2 :0.8 ml MeOH, room temperature, 30 min.

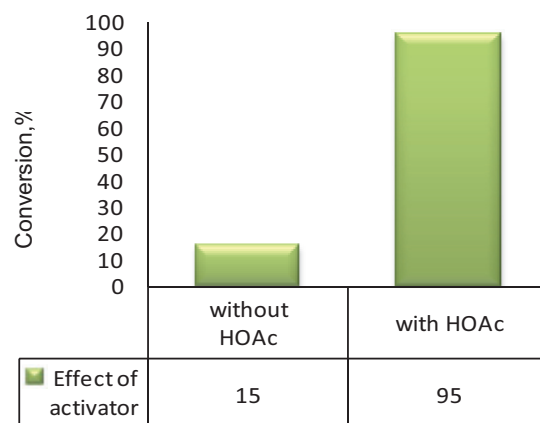


Figure 5. The effect of HOAc on the oxidation of methyl phenyl sulfide with UHP at room temperature.

different activators.^[42–44] In large-scale bleaching applications and many synthetic oxidations, activation via formation of peroxycarboxylic acids^[45–50] or with bicarbonate ion^[51] can be a favored method. The effect of HOAc as activator in the catalytic oxidation of MePhS with UHP was investigated and the results are presented in Figure 5. Based on the results, in the absence of HOAc, very low conversion was obtained, but addition of a small amount of HOAc has increased the conversion up to 95 %.

In order to investigate the effect of metal ion on the catalytic activity of catalyst in the oxidation reaction, encapsulated iron, manganese and copper metalloporphyrins were selected for catalytic oxidation of MePhS with UHP in the optimized condition and the results are described in Table 4. Based on the results, Mn(TPP)/MCM-41 shows the best efficiency for sulfide oxidation.

Table 3. Effect of various conditions on the oxidation of MePhS with UHP by encapsulated MnTPP(OAc) in the presence of ImH.

Entry	Temperature, °C	MePhS/Cat.	UHP/Cat.	Conversion, % ^a
1	25	40	55	15
2	25	20	55	35
3	25	20	65	34
4	35	20	55	20
5	45	20	55	28

^aThe reaction was carried out in 0.2 ml CH_2Cl_2 : 0.8 ml MeOH, reaction time: 30 min. Sulfoxide is the isolated product.

Table 4. Results of MePhS oxidation reactions catalysed by a series of immobilized metalloporphyrins with UHP.^a

Entry	Catalyst	Conversion, %
1	Mn-Porphyrin/MCM41	95
2	Fe-Porphyrin/MCM41	92
3	Cu-Porphyrin/MCM41	10

^aThe molar ratios for Cat:ImH:MePhS:UHP:HOAc are 1:100:20:40:40. The reaction was carried out in 0.2 ml CH_2Cl_2 :0.8 ml MeOH, room temperature, time: 30 min.

Catalyst Reuse and Stability

The reusability of a heterogeneous catalyst is of great importance in catalyst design. The homogeneous [M(TPP) M=(Mn, Fe, Cu)] is readily degraded within the first few minutes of reaction and cannot be recovered even once; in contrast, the mesoporous supported porphyrin catalysts can be filtered and reused several times without significant loss of its activity.^[47,48] In other words, the degradation of [M(TPP)/MCM-41 M=(Mn, Fe, Cu)] has been significantly decreased by immobilization of the metalloporphyrin on MCM-41. The enhanced efficiency of the immobilized catalysts with respect to [M(TPP) M=(Mn, Fe, Cu)] seems to be due to decreased oxidative degradation of the former relative to the latter.

The reusability of the catalysts was examined in the multiple sequential oxidations of MePhS with urea hydrogen peroxide in the presence of HOAc (Figure 6). The catalysts were isolated from the reaction mixture after each experiment by simple filtration, washed with methanol, dichloromethane and petroleum ether (three times) and dried carefully in the oven at 80 °C before being used in the subsequent run. Based on the results, in the presence of Mn(TPP)OAc/MCM-41 yield decreased gradually from the second cycle, whereas the production yield decreases fast in the presence of Fe(TPP)Cl/MCM-41 after the first cycle. It should be mentioned that the IR spectrum of the recovered catalyst almost was unchanged after it had been reused several times.

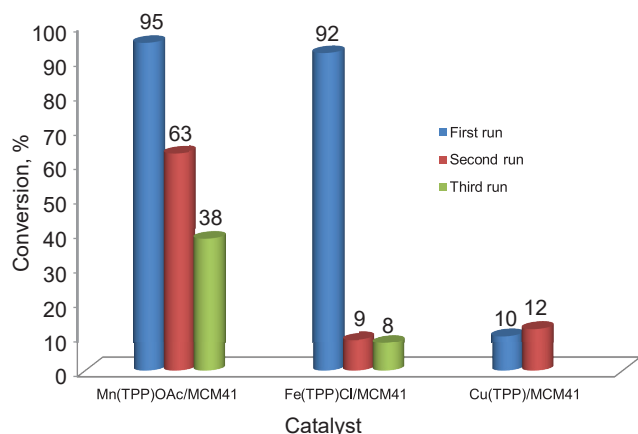


Figure 6. The catalytic activity of the recovered catalyst during the recycling experiments for oxidation of MePhS with UHP in the optimized conditions.

Oxidation of Various Sulfides

Oxidation of various sulfides with UHP was carried out in the presence of catalytic amount of Mn(TPP)OAc/MCM-41 under the optimized reaction conditions (Table 5). Excellent yield and selectivity were obtained for all cases and based on the results, it seems that Mn(TPP)OAc/MCM-41 is a very efficient catalyst for oxidation of sulfide, since it can catalyze different sulfides very well.

Table 5. Results of sulfide oxidation reactions catalysed by immobilized Mn-porphyrins with UHP.^a

Sulfide	Conversion, %	Selectivity, % (sulfoxide)
	95	78
	75	90
	90	100
	36 ^b	100

^aThe molar ratios for MnTPP(OAc)/MCM-41:ImH:MePhS:UHP are 1:100:20:40:40. The reaction was carried out in 0.2 ml CH₂Cl₂:0.8 ml MeOH, room temperature, time: 30 min.

^bThe molar ratios for MnTPP(OAc)/MCM-41:ImH:MePhS:UHP are 1:100:20:55:82.

Conclusions

The present work showed the results of synthesis, characterization and application of three metalloporphyrin catalysts [Fe(TPP)Cl, Mn(TPP)OAc and Cu(TPP)] immobilized on mesoporous MCM-41, in the oxidation reaction of MePhS with urea hydrogen peroxide. A comparative study of the effect of the metal ion of the immobilized porphyrins on catalytic activity was carried out. Also, total conversion was found to be significantly influenced by the presence of acetic acid. The catalytic activity of these heterogeneous complexes in the oxidation of methyl phenyl sulfide with UHP and HOAc is in the order: Mn(TPP)OAc/MCM-41 > Fe(TPP)Cl/MCM-41 > Cu(TPP)/MCM-41.

Acknowledgements. The financial support of this work by K.N. Toosi University of Technology research council is acknowledged.

References

- Kim S.S., Rajagopal G. *Synthesis* **2003**, *16*, 2461–2463.
- Bagherzadeh M., Zare. M. *J. Sulfur Chem.* **2011**, *32*, 335–343.
- Khodaei M.M., Bahrami K., Arabi M.S. *J. Sulfur Chem.* **2010**, *31*, 83–88.
- Tarasjuk I.A., Kuzmin I.A., Marfin Y.S., Vashurin A.S., Voronina A.A., Rumyantsev E.V. *Synth. Met.* **2016**, *217*, 189–196.
- Han Z., Han X., Zhao X., Yu J., Xu H. *J. Hazard. Mater.* **2016**, *320*, 27–35.
- Fernández L., Esteves V.I., Cunha Â., Schneider R.J., Tomé J.P.C. *J. Porphyrins Phthalocyanines* **2016**, *20*, 150–166.
- Shaabani A., Keshipour S., Hamidzad M., Shaabani S. *J. Mol. Catal. A* **2014**, *395*, 494–499.
- Rezaeifard A., Jafarpour M., Naeimi A., Mohammadi K. *J. Mol. Catal. A* **2012**, *357*, 141–147.

9. Farzaneh F., Taghavi J., Malakooti R., Ghandi M. *J. Mol. Catal. A* **2005**, *244*, 252.
10. Meunier B. *Chem. Rev.* **1992**, *92*, 1411–1456.
11. Golubchikov O.A., Berezin B.D. *Russ. Chem. Rev.* **1986**, *55*, 768–785.
12. Borovkov V.V., Evstigneeva R.P., Strekova L.N., Filippovich E.I. *Russ. Chem. Rev.* **1989**, *58*, 602–619.
13. Collman J.P., Kodadek T., Brauman J.I. *J. Am. Chem. Soc.* **1986**, *108*, 2588–2594.
14. Mansuy D. *Coord. Chem. Rev.* **1993**, *125*, 129–141.
15. Rayati S., Nejabat F., Zakavi S. *Inorg. Chem. Commun.* **2014**, *40*, 82–86.
16. de Lima O.J., de Aguirre D.P., de Oliveira D.C., da Silva M.A., Mello C., Leite C.A.P., Sacco H.C., Ciuffi K.J. *J. Mater. Chem.* **2001**, *11*, 2476–2481.
17. Cai J.H., Huang J.W., Zhao P., Ye Y.J., Yu H.C., Ji L.N. *J. Sol-Gel Sci. Technol.* **2009**, *50*, 430–436.
18. Milaeva E.R., Gerasimova O.A., Maximov A.L., Ivanova E.A., Karachanov E.A., Hadjiliadis N., Louludi M. *Catal. Commun.* **2007**, *8*, 2069–2073.
19. Sosa R.C., Parton R.F., Neys P.E., Lardinois O., Jacobs P.A., Rouxhet P.G. *J. Mol. Catal. A* **1996**, *110*, 141–151.
20. Haber J., Pamin K., Poltowicz J. *J. Mol. Catal. A* **2004**, *224*, 153–159.
21. Viana Rosa I.L., Manso C.M.C.P., Serra O. A., Iamamoto Y. *J. Mol. Catal. A* **2000**, *160*, 199–208.
22. Carrado K.A., Winans R.E. *Chem. Mater.* **1990**, *2*, 328–335.
23. Brule E., de Miguel Y.R., Hii K.K. *Tetrahedron* **2004**, *60*, 5913–5918.
24. Oh K.C., Kim K.A., Paeng I.R., Baek D.J., Paeng K.J. *J. Electroanal. Chem.* **1999**, *468*, 98–103.
25. Norman H. *J. Coord. Chem. Soc.* **1988**, *19*, 25–38.
26. Liu C.J., Li S.G., Pang W.Q., Che C.M. *J. Chem. Soc., Chem. Commun.* **1997**, 65–66.
27. Stephenson N.A., Bell A.T. *J. Mol. Catal. A* **2007**, *272*, 108–117.
28. Nam W., Oh S.Y., Sun Y.J., Kim J., Kim W.K., Woo S.K., Shin W. *J. Org. Chem.* **2003**, *68*, 7903–7906.
29. Campestrini S., Tonellato U. *J. Mol. Catal. A* **2001**, *171*, 37–42.
30. Bagherzadeh M., Tahsini L., Latifi R. *Catal. Commun.* **2008**, *9*, 1600–1606.
31. Zhou X.T., Ji H.B., Xu H.C., Pei H.L.X., Wang L.F., Yao X.D. *Tetrahedron Lett.* **2007**, *48*, 2691–2695.
32. Zakavi S., Abasi A., Pourali A. R., Talebzadeh S. *Bull. Korean Chem. Soc.* **2012**, *33*, 35–38.
33. Adler A.D., Longo F.R., Shergalis W. *J. Am. Chem. Soc.* **1964**, *86*, 3145–3149.
34. Costa A., Ghesti G.F., de Macedo J.L., Braga V.S., Santos M.M., Dias S.C.L., Dias J. *J. Mol. Catal. A* **2008**, *282*, 149–157.
35. Kruk M., Jaroniec M., Sayari A. *Micropor. Mesopor. Mater.* **2000**, *35*, 545–553.
36. Rayati S., Zakavi S., Jafarzadeh P., Sadeghi O., Amini M.M. *J. Porphyrins Phthalocyanines* **2012**, *16*, 260–266.
37. Nassar E.J., Messaddeq Y., Ribeiro S.J.L. *Quim. Nova* **2002**, *25*, 27–31.
38. Mohajer D., Rezaeifard A. *Tetrahedron Lett.* **2002**, *43*, 1881–1884.
39. Rayati S., Zakavi S., Noroozi V. *J. Sulfur Chem.* **2010**, *31*, 89–95.
40. Rayati S., Zakavi S., Motlagh S.H., Noroozi V., Razmjoo M., Wojtczak A., Kozakiewicz A. *Polyhedron* **2008**, *27*, 2285–2290.
41. de Sousa A.N., Moreira Dai de Carvalho M.E., Idemori Y.M., *J. Mol. Catal. A* **2001**, *169*, 1–10.
42. Karimi B., Montazerzohori M., Habibi M.H. *Molecules* **2005**, *10*, 1358–1363.
43. Yao H., Richardson D.E. *J. Am. Chem. Soc.* **2000**, *122*, 3220–3221.
44. Richardson D.E., Yao H., Frank K.M., Bennett D.A. *J. Am. Chem. Soc.* **2000**, *122*, 1729–1739.
45. Pietikäinen P. *J. Mol. Catal. A* **2001**, *165*, 73–79.
46. Fujita M., Que Jr. L. *Adv. Synth. Catal.* **2004**, *346*, 190–194.
47. Mas-Balesté R. *J. Am. Chem. Soc.* **2007**, *129*, 15964–15972.
48. Serra A.C., d'A. Rocha Gonsalves A.M. *J. Mol. Catal. A* **2001**, *168*, 25–32.
49. Ankudey E.G., Olivo H.F., Peeples T.L. *Green Chem.* **2006**, *8*, 923–926.
50. Fakhraian H., Valizadeh F. *J. Mol. Catal. A* **2010**, *333*, 69–72.
51. Serwica E.M., Poltowicz J., Bahrnowski K., Olejniczak Z., Jones W. *Appl. Catal. A* **2004**, *275*, 9–14.

Received 02.01.2017

Accepted 18.02.2017