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Immobilized metalloporphyrins in mesoporous MCM-48 as efficient and selective heterogeneous catalysts for oxidation of cyclohexene

Nafiseh Rahmani Khalili · Rahmatollah Rahimi · Mahboubeh Rabbani

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Abstract Three metalloporphyrins, Mn(III)TClPPCl, Fe(III)TClPPCl, and Co(II)TClPP (TClPP = 5,10,15,20tetrakis(4-chlorophenyl)porphyrin), were synthesized and immobilized in MCM-48 channels. The designed heterogeneous catalysts were characterized by XRD, ICP, UV-Vis, FT-IR, N₂ adsorption-desorption, and scanning electron microscopy. These investigations showed that successful encapsulation occurred and the framework of mesoporous MCM-48 was retained without any change after incorporation of the metalloporphyrins. The effect of the support on the resistance to pore blocking was studied by comparing MCM-48 with MCM-41. The catalytic activities of the newly synthesized catalysts were examined in the oxidation of cyclohexene with *t*-butyl hydroperoxide as oxidant. All results confirmed that the supported catalysts presented interesting advantages such as high selectivity to the allylic products and more resistance to pore blocking. The heterogeneous catalysts were reused for several times without significant loss of their catalytic activity.

Keywords Metalloporphyrins · MCM-48 · Heterogeneous catalysts · Cyclohexene oxidation

Introduction

From the point of view of green chemistry and chemical industry, one of the challenging goals is the selective catalytic oxidation of organic compounds using environmentally friendly and cheap oxidants and a heterogeneous,

N. R. Khalili · R. Rahimi (⊠) · M. Rabbani Department of Chemistry, Iran University of Science and Technology, Narmak, 16846-13114 Tehran, Iran e-mail: rahimi_rah@iust.ac.ir easily recyclable catalyst [1–4]. Metalloporphyrins are able to imitate the activity of cytochrome P-450 and to catalyze selective oxidation processes with a diversity of oxygen donors [5-8]. The allylic oxidation of olefins, especially cyclohexene and its derivatives into α,β -unsaturated ketones, is an important process because allylic ketones are valuable intermediates for the synthesis of medicines and pesticides [9-11]. However, metalloporphyrins as homogeneous catalysts have several problems, for instance their oxidative self-destruction in the oxidizing media; furthermore, they are not able to be simply recovered for reuse at the end of the reaction. One of the suggested ways to solve these problems is to immobilize homogeneous catalysts on a solid matrix. It is expected that some advantages like promoting catalytic activity, stability, product selectivity, and easy reusability will be achieved by immobilization [12–18].

Since the invention of M41S researchers have given considerable attention to them, because these materials possess larger pores in contrast with microporous molecular sieves, which allow faster diffusion and processing of bulky molecules [19–22], so they have high potential use as adsorbents, heterogeneous catalysts, catalytic supports, and hosts for inclusion compounds [23, 24]. Most studies have concentrated on investigating the properties of mesoporous MCM-41 as supports for heterogenization of metalloporphyrins and other complexes [25-30]. In comparison with MCM-41, which has a unidirectional pore system, MCM-48 has more advantages, such as narrow pore size distribution and its interwoven as well as branched, regular, and cubic pore structure, that bring more favorable mass transfer kinetics in catalytic and separation technologies. Therefore it is a more beneficial candidate for application; moreover, its three-dimensional channels allow faster diffusion and are more resistant to pore blocking [31-36].



$$M = Fe, Mn, Co$$

 $X = Cl, OAc$

Scheme 1

However, despite these advantages less attention has been paid to MCM-48. Up to now, only one relevant paper, by Zhang and co-workers [37], has been reported on immobilizing chiral ruthenium porphyrin [$Ru(D_4-Por^*)CO$] in modified MCM-48 as catalysts for asymmetric epoxidation by 2,6-dichloropyridine *N*-oxide, so this encouraged us to examine the application of MCM-48 as a catalyst support in different conditions with other metalloporphyrins.

In the present work, Fe(III), Mn(III), and Co(II) complexes of *meso*-tetrakis(4-chlorophenyl)porphyrin were immobilized in mesoporous MCM-48 molecular sieves and the catalytic activities of these heterogeneous materials were then investigated in the oxidation of cyclohexene with *t*-butyl hydroperoxide (TBHP) as oxidant (Scheme 1).

Results and discussion

Characterization of catalysts

After Soxhlet extractions of supported catalysts, a dark brown and green powder was obtained, showing that the encapsulation of metalloporphyrins into the MCM-48 was successful. Low-angle X-ray diffraction (XRD) patterns of calcined MCM-48 and encapsulated metalloporphyrins (MnTClPP-MCM48, FeTCIPP–MCM48, and CoTCIPP–MCM48; TCIPP = 5,10,15,20-tetrakis(4-chlorophenyl)porphyrin) are given in Fig. 1. All samples show two distinct peaks, (211) and (220), and several other peaks which can be indexed to highly ordered three-dimensional cubic structures [40]. Powder diffraction patterns of encapsulated catalysts (Fig. 1b-d) show no peaks due to porphyrin and the two basal peaks are still detectable. This indicates that the MCM-48 framework is still maintained when porphyrin is incorporated. The observed slight decrease in the peak intensities confirms loading of complexes into the support.

Figure 2 shows the FT-IR spectra of MnTClPP–MCM48, FeTClPP–MCM48, CoTClPP–MCM48, and the pure support. The broad band in the range of $3,700-3,000 \text{ cm}^{-1}$ can be assigned to the stretching vibration mode of the Si–OH group. Another band between 450 and $1,200 \text{ cm}^{-1}$ is



Fig. 1 XRD patterns of MCM-48 (*a*), MnTCIPP–MCM48 (*b*), FeTCIPP–MCM48 (*c*), and CoTCIPP–MCM-48 (*d*)



Fig. 2 FT-IR spectra of calcined MCM-48 (*a*), FeTCIPP–MCM48 (*b*), MnTCIPP–MCM48 (*c*), and CoTCIPP–MCM-48 (*d*)

attributed to the symmetric and asymmetric stretching vibrations for the tetrahedral SiO_4 structure units. Also an absorption band at around 960 cm⁻¹ is due to Si–OH stretching vibrations in the calcined state. In the supported



Fig. 3 N2 adsorption of calcined MCM-48 and FeTClPP-MCM48

catalysts' spectra, some new bands appearing between 1,200 and 1,600 cm⁻¹ corresponding to the phenyl C=C and pyrrole C=N stretching modes also prove the presence of metalloporphyrins inside the channels of MCM-48.

The textural properties of the MCM-48 and encapsulated catalysts were determined by a nitrogen adsorption experiment at 77 K. The adsorption–desorption isotherms of all samples show that the materials possess the typical type IV adsorption isotherms, characteristic of mesoporous solids (Fig. 3). The BET surface area and average pore size of MCM-48 are $1,323 \text{ m}^2 \text{ g}^{-1}$ and 26 Å, respectively. After incorporation of metalloporphyrins inside the pores of MCM-48, decreases in the BET surface area and average pore size were observed. For example, for FeTCIPP– MCM48 1,087 m² g⁻¹ and 24.8 Å were obtained. These results show that greater amounts of metalloporphyrins were immobilized inside the channels of the support.

Inductively coupled plasma (ICP) spectroscopy was used to estimate the loadings of metalloporphyrins in these heterogeneous catalysts. The results indicate that metalloporphyrin contents are as follows: 10.65 wt% in MnTCIPP–MCM48, 17.6 wt% in FeTCIPP–MCM48, and 13.48 wt% in CoTCIPP–MCM48. Dramatically higher loadings were obtained, because of the three-dimensional pore structure of MCM-48 in comparison with the one-dimensional MCM-41 [8, 16, 37, 41].

The typical morphology of MCM-48 and MnTCIPP– MCM48 was investigated by scanning electron microscopy (SEM). As can be seen in Fig. 4, the MnTCIPP–MCM48 sample shows that similar morphology and crystalline structure to pure MCM-48. As a result, the solid support is structurally unchanged and metalloporphyrins should be diffused molecularly within the channels.





Fig. 4 SEM images of MCM-48 (a) and MnTClPP-MCM48 (b)

The presence of metalloporphyrins in the channels of MCM-48 was also confirmed by solid-state UV–Vis spectroscopy (Fig. 5a–d). In the UV–Vis spectrum of MCM-48 (Fig. 5a), no absorption band is observed, whereas after immobilization of metalloporphyrins in MCM-48 channels, the Q and Soret bands appear. The position of the Soret bands of Fe(III), Mn(III), and Co(II) porphyrins dissolved in dichloromethane (non-supported) and immobilized in MCM-48 (supported) are given in Table 1.

The supported catalysts, Mn(III), Fe(III), and Co(II) (TCIPP–MCM48), show Soret bands at 464, 412, and 428 nm, respectively, which are similar to those of the corresponding non-supported metalloporphyrins; this observation further indicates that no chemical changes have occurred to the complexes during the anchoring processes. However, the solid-state UV–Vis spectra of the complexes show a red shift in Q and Soret bands in comparison with their non-supported counterparts, which can



Fig. 5 UV–Vis spectra of MCM-48 (a), MnTClPP–MCM48 (b), FeTClPP–MCM48 (c), and CoTClPP–MCM48 (d)

 Table 1
 Wavelength of the Soret band maxima of supported and non-supported catalysts

Catalyst	Soret band/nm		
	Supported	Non-supported in dichloromethane	
MnTClPP-MCM48	464	462	
FeTClPP-MCM48	412	408	
CoTClPP-MCM48	428	426	

be attributed to the distortion of the porphyrin rings usually observed when metalloporphyrins are immobilized on solid supports [15, 42].

Catalytic activity

Effect of the support on resistance to pore blocking The catalytic properties of heterogeneous catalysts in the oxidation of cyclohexene by TBHP as oxygen transfer agent were investigated. One of the problems of using MCM-41 as a support is that with increasing porphyrin loading the catalytic activity decreases, because pore blocking and limited diffusion of the reactants take place [8, 17, 43–45]. Since MCM-48 has three-dimensional channels, it is expected to provide more favorable mass transfer kinetics, better diffusion, and resistance to pore blocking. In order to investigate this assertion, FeTClPP-MCM48 catalysts containing 0.2, 5.8, 10.2, and 17.6 wt% of FeTCIPP were prepared. The results of cyclohexene oxidation with TBHP in the presence of these heterogeneous catalysts with different amounts of Fe(III) porphyrins demonstrated that increasing amounts of metalloporphyrin loading led to an

 Table 2
 Effect of porphyrin content on cyclohexene oxidation with TBHP catalyzed by FeTCIPP–MCM48

Entry	Catalyst	Porphyrin content ^a /wt%	Conversion ^b /%		
1	FeTClPP-MCM48	0.2	11.7		
2	FeTClPP-MCM48	5.8	32.0		
3	FeTClPP-MCM48	10.2	48.3		
4	FeTClPP-MCM48	17.6	80.2		

Conditions: TBHP (15 mmol), cyclohexene (10 mmol), 5 $\rm cm^3$ acetonitrile, 60 $^{\rm o}\rm C$

^a Determined by ICP spectroscopy

^b Disappearance of cyclohexene using GC

increase in catalytic activity (Table 2). This is due to the unique nature and properties of mesoporous MCM-48.

Effect of reaction time

The effect of reaction time on the oxidation of cyclohexene in the presence of the FeTCIPP–MCM48 catalyst was studied. As can be seen in Fig. 6, the conversion of substrate to products was optimal after 6 h. With increasing reaction time up to 24 h, no significant change was observed in the conversion of substrate or product selectivity, and allylic oxidation products were the major components.

Effect of catalyst amount and reaction temperature

Table 3 shows the influence of catalyst amount on the cyclohexene oxidation reaction in the presence of the supported iron porphyrin catalyst. When the catalyst amount was increased, the conversion and the yield of 2-cyclohexene-1-one as the main product improved. The best overall result was obtained with 0.02 g of catalyst (entry 3). Furthermore, the temperature effect on the progress of oxidation was studied. It was found that the oxidation reaction at room temperature was slow (entry 5) and the conversion was increased with raising temperature to 60 °C. Therefore, the yield of the reaction depends considerably on temperature.

Oxidation of cyclohexene

The results of oxidation of cyclohexene using TBHP as oxidant and acetonitrile as solvent in the presence of the resultant catalysts are summarized in Table 4.

The blank experiment with pure support (MCM-48) did not show any oxidation products. This obviously indicates that metalloporphyrin complexes encapsulated in MCM-48 play the main role in the catalytic activity. All applied catalysts displayed significant activity in cyclohexene oxidation reactions. The data in Table 2 highlight the high selectivity of the process: allylic oxidation is favored over epoxidation and 2-cyclohexene-1-one appears as the main



Fig. 6 Changes of cyclohexene conversion with reaction time. Reaction conditions: TBHP (15 mmol), cyclohexene (10 mmol), 0.63 mol% FeTCIPP–MCM48, 5 cm³ acetonitrile, 60 °C

product. This is a remarkable and multifaceted substance with various applications in the synthesis of a variety of chemical products like pharmaceuticals and perfumes. The selectivity pattern indicates that attack at the activated C–H bond is more preferable than at the C=C bond under our reaction conditions. Also, on the basis of reported literature [46], it shows that the metalloporphyrin species are almost entirely immobilized in the internal pore wall surface of MCM-48.

The cubic three-dimensional pore openings of MCM-48 provide easy access for the reactants into the active sites of the metalloporphyrins in mesoporous channels. This remarkably enhances the catalytic ability and selectivity of the porphyrin complexes, because it increases the probability of interaction between reactants and catalytic active sites; these properties imply that MCM-48 is a good solid support. From a general point of view, the obtained results are in agreement with those of Zhang et al. [37], i.e., the cubic three-dimensional MCM-48 has more advantages as a catalyst support than the one-dimensional MCM-41.

The dependence between the catalytic activity and the nature of the central metal of porphyrin ligand is obvious. Comparison of the catalytic activity of these heterogeneous catalysts under similar conditions shows that FeTCIPP–MCM48 is better than both MnTCIPP–MCM48 and CoT-CIPP–MCM48 in the oxidation of cyclohexene. The noticed trend of catalytic activity is FeTCIPP–MCM 48 > MnTCIPP–MCM48.

Catalyst recycling and leaching

The reuse and stability of these heterogeneous catalysts were studied for several times. After finishing the oxidation

Entry	Amount of catalyst/g	Time/h	Temperature/°C	Conversion ^a /%	Yield ^b /%
1	0.05	6	60	35	29.2
2	0.01	6	60	61	47.0
3	0.02	6	60	80.2	72.0
4	0.05	6	60	82	72.2
5	0.02	6	25	32	28.1

Table 3 Effect of catalyst amount and temperature on oxidation of cyclohexene in the presence of FeTCIPP-MCM48

Conditions: TBHP (15 mmol), cyclohexene (10 mmol), 5 cm³ acetonitrile

^a Disappearance of cyclohexene using GC

^b Yield of 2-cyclohexene-1-one obtained by GC

Table 4 Catalytic oxidation of cyclohexene by TBHP in the presence of supported metalloporphyrin catalysts

Catalyst	Cyclohexene conversion ^b /%	Epoxide selectivity/%	Ketone selectivity/%	Alcohol selectivity/%	TON ^c	TOF ^d /h ⁻¹
Si-MCM48 ^a	-	-	-	-	_	_
MnTClPP-MCM48	65	11.4	85.2	3.4	144.6	24.1
FeTClPP-MCM48	80	3.9	95.0	1.1	114.2	19.0
CoTClPP-MCM48	54	9.3	88.4	2.3	105.0	17.5

Conditions: TBHP (15 mmol), cyclohexene (10 mmol), 0.38 mol% MnTClPP-MCM48, 0.63 mol% FeTClPP-MCM48, and 0.45 mol% CoT-ClPP-MCM48, 5 cm³acetonitrile, 6 h, 60 °C

^a Conditions: MCM-48 (0.02 g), TBHP (15 mmol), cyclohexene (10 mmol), 5 cm³ acetonitrile

^b Disappearance of cyclohexene using GC

^c Turnover number: mole of product per mole of catalyst

^d Turnover frequency: mole of product per mole of catalyst per hour

reaction, the catalysts were separated by filtration, washed with acetonitrile followed by methanol, and dried at 80 °C for 12 h before using in the subsequent run. The recycled catalysts were used in fresh reaction mixture under the same oxidation reaction conditions. The experiment showed that all solid catalysts were reused for four times, and no significant change was observed in catalytic activity and pattern selectivity of products. The leaching of the metal complexes from the solid support into the reaction medium was also checked. The absence of any absorption peaks associated with porphyrins in the UV–Vis spectra of the reaction solution indicated that during the oxidation reactions, leaching of metalloporphyrins does not take place.

Conclusion

In summary, we have prepared three novel heterogeneous catalysts by direct encapsulation of Fe(III), Mn(III), and Co(II) metalloporphyrins into the channels of mesoporous MCM-48. The catalytic properties of these catalysts were studied in the oxidation of cyclohexene with TBHP as oxygen source. The unique characteristics of the support have a significant effect on the catalytic efficiencies and afford some advantages including more resistance to pore blocking and high catalytic ability and selectivity to the allylic oxidation products. We anticipate that MCM-48 would be more useful and applicable for porphyrin heterogenization. These features imply that MCM-48 is an applicable support. The immobilized catalysts can be reused for four times.

Experimental

All materials were of commercial reagent grade. Pyrrole, *p*-chlorobenzaldehyde, propionic acid, methanol, dimethylformamide (DMF), metal chlorides, tetraethylortho silicate (TEOS), cetyltrimethylammonium bromide (CTAB), sodium hydroxide (NaOH), sodium fluoride (NaF), dichloromethane, cyclohexene, acetonitrile, and TBHP (70 % aqueous solution) were purchased from Merck and Aldrich chemical companies. 5,10,15,20-Tetrakis(4-chlorophenyl)porphyrin was synthesized in our laboratory, according to Adler's method [38]. The metallation procedure was carried out by the method described previously [39].

Synthesis of MCM-48

The following procedure was used for preparing of MCM-48: a mixture of 10 g TEOS and 50 g deionized water was vigorously stirred at 35 °C for 40 min, then the required

amount of NaOH and NaF was added into the mixture. After another 60 min of vigorous stirring at 35 °C, 10.61 g of CTAB was added to the mixture and the stirring continued at the same temperature for 60 min. The molar composition of the final SiO₂/CTAB/NaOH/H₂O/NaF mixture was 1.0:0.65:0.5:62:0.1. The resulting gel was transferred into an autoclave and kept at 120 °C for 24 h. The obtained MCM-48 product was filtered, washed with distilled water, and dried at 100 °C. The as-synthesized samples were calcined at 550 °C for 6 h [40].

Synthesis of supported catalysts

Supported metalloporphyrins were achieved by direct encapsulation. To encapsulate the metalloporphyrins into the channels of MCM-48, 1 g of mesopore was immersed into 5 cm³ of dichloromethane and then added to a flask containing 0.1 g of complexes (MnTCIPP, FeTCIPP, and CoTCIPP). Then, the system was vigorously stirred by magnetic stirring for 48 h. Materials were filtered and exhaustively washed in a Soxhlet system with dichloromethane and DMF for 24 h to remove any non-supported metalloporphyrin. The final products were dried for 24 h at 80 $^{\circ}$ C.

Catalytic oxidation reaction

Oxidation reactions were carried out under reflux conditions at atmospheric pressure. At first, a mixture of cyclohexene (10 mmol), 5 cm^3 acetonitrile, and 0.02 g heterogeneous catalyst was added to a flask containing a magnetic stirrer bar. After 5 min, TBHP as oxidant (15 mmol) was added. The reaction mixture was heated under stirring at the desired temperature for 6 h. The catalyst was then separated by filtration and the collected products were detected by GC and GC–MS.

Characterization of the samples

X-ray diffraction patterns were recorded with a Philips X'pert MPD using Co K α radiation. FT-IR spectra were recorded on a Shimadzu FTIR-8400 spectrophotometer. Specific surface areas were determined from nitrogen adsorption at 77 K on an ASAP 2010 apparatus. UV–Vis diffuse reflectance spectroscopy was performed on a Shimadzu 2550 spectrometer. Scanning electron microscopy images were recorded on a Philips XL30 microscope. The amount of adsorbed metalloporphyrin in the mesoporous MCM-48 was determined by means of ICP spectroscopy. The oxidation products were analyzed with a gas chromatograph (Shimadzu) equipped with an HP-5 capillary column. The reaction products were confirmed by GC–MS (Perkin-Elmer).

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