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Synthesis and characterization of mangenese(III) porphyrin supported on imidazole modified chloromethylated MIL-101(Cr): A heterogeneous and reusable catalyst for oxidation of hydrocarbons with sodium periodate

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Abstract- In the present work, chloromethylated MIL-101(Cr) modified with imidazole, Im-MIL-101, was applied as a support for immobilizing of tetraphenylporphyrinatomangenese(III) chloride. The imidazole-bound MIL-101, Im-MIL-101, not only used as support for immobilization of manganese porphyrin but also applied as a heterogeneous axial base. The Mn(TPP)Cl@Im-MIL-101 catalyst was characterized by UV-Vis, FT-IR, X-ray diffraction (XRD), N₂ adsorption, field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray (EDX), elemental analysis and inductively coupled plasma (ICP) methods. The catalytic activity of this new catalytic system was investigated in the alkene epoxidation and alkane hydroxylation using NaIO₄ as an oxidant in CH₃CN/H₂O at room temperature. This heterogeneous catalyst is highly efficient, stable and reusable in the oxidation of hydrocarbons.

Keywords: Metal-organic framework; Manganese porphyrin; MIL-101(Cr); Axial ligand; Oxidation.

1. Introduction

The cytochrome P-450 is a natural monooxygenase enzyme which catalyzes a wide variety of reactions in the body. The active site of this enzymeis an iron porphyrin surrounded by special proteins which can be imitated by synthetic metalloporphyrins [1, 2]. These metalloporphyrins are highly efficient homogeneous catalysts for oxidation of wide range of substrates in the presence of some single oxygen

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atom donors such as PhIO, ClO⁻, KHSO₅, H₂O₂, ROOH or IO₄⁻ [3-5]. Among the metalloporphyrins, manganese porphyrins have been used as good catalysts for oxidation of hydrocarbons [6-8]. Unfortunately, irreversible dimerization, oxidative self-destruction in an intermolecular process and impossible recovery of the catalyst at the end of reaction, are three major drawbacks which limit the usage of metalloporphyrins. One way to overcome these problems is to anchor them onto solid supports [9-15]. This leads to catalysts which are easier to handle, more cost-effective and simple to recover. On the other hands, steric and electronic effects provided by solid supports can mimic the vestige of protein matrix of hemoprotein. One of the main approaches for immobilization of metalloporphyrins is coordinative binding between support and the porphyrin metal center [16, 17].

Metal-organic frameworks (MOFs) are a subfamily of porous coordination polymers (PCPs) which have outstanding potential for a wide range of applications in gas separation/storage [18-20], sensing [21-23], magnetism [24, 25], drug delivery systems [26] and catalysis [27-30]. The use of MOFs for heterogeneous catalysis is nearly a new methodology which deserves more investigations. They have prominent properties such as high surface area, large and accessible cages, tunable pores and facile functionalizing possibility which make them suitable supports for immobilization of active catalytic species such as metal nanoparticles [31-35] or molecular complex species [36-40]. But low thermal and chemical stability of MOFs are limiting factors for their practical applications. In 2005, Ferey et al. [41] reported a 3D hybrid material, MIL-101(Cr) [(Cr₃X(H₂O)₂O(bdc)₃; X=F, OH; bdc=benzene-1,4dicarboxylate)] which possesses high chemical, thermal and hydrothermal stability. Also, MIL-101(Cr) has large cavities which can be functionalized by two main methods, the first one is grafting electron rich ligands onto the unsaturated Cr(III) sites [42] and the second one is direct reaction of aromatic rings of linker, benzene-1,4-dicarboxylate, in MIL-101 with strong reagents [43]. Recently, Goesten et al. [44] reported attachment of chloromethyl functional group into MIL-101(Cr) by post synthetic modification of aromatic rings of MIL-101(Cr) using methoxyacetyl chloride. The chlorine atom in the

structure of chloromethylated MIL-101(Cr), CM-MIL-101(Cr), can be substituted with any nucleophile.

In continuation our previous work in the oxidation of hydrocarbons catalyzed by MOF supported metalloporphyrins [45], here; we report the preparation of modified MIL-101 by substitution of chlorine atom of CM-MIL-101(Cr) with imidazole. This Im-MIL-101 was used as a support for immobilization of Mn(TPP)Cl. The catalytic activity of Mn(TPP)Cl@Im-MIL-101 was investigated in the alkene epoxidation and alkane hydroxylation as a recyclable and sustainable catalyst (Scheme 1).

Scheme 1.

2. Experimental

2.1. Reagents and methods

All materials were commercial reagent grade. Alkenes, alkanes and alkylaromatic compounds were obtained from Merck or Fluka chemical companies. All of these compounds were passed through a column containing active alumina to remove peroxidic impurities. Tetraphenylporphyrin was prepared and metallated according to a literature procedure [46].

The diffuse reflectance UV–vis spectra were recorded by a JASCO V-670 UV–vis spectrophotometer. Diffuse reflectance FT-IR spectra were obtained with potassium bromide pellets in the range of 400–4000 cm⁻¹ with a JASCO 6300 spectrophotometer. The XRD patterns were recorded using a Bruker D8 ADVANCE X-ray diffractometer equipped with nickel monochromatized Cu K_a radiation ($\lambda = 1.5406$ Å). The scanning electron micrographs were taken on a Hitachi S-4700 field emission-scanning electron microscope (FE-SEM). Specific surface area was measured by adsorption–desorption of N₂ gas at 77 K with ASAP 2000 Micromeritics instrument. The ICP analyses were carried out by a Jarrell-Ash 1100 spectrometer. Elemental analysis was performed on a LECO, CHNS-932 analyzer. Gas chromatography experiments (GC) were performed with a Shimadzu GC-16A instrument using a 2 m

column packed with silicon DC-200 or Carbowax 20M. In the GC experiments, *n*-decane was used as the internal standard.

2.2. Preparation of the catalyst

MIL-101(Cr) and chloromethylated MIL-101were synthesized based on the procedure reported by Férey et al. [41] and Goesten et al. [44], respectively. The resulting CM-MIL-101(Cr) was modified with imidazole through the same method described by Alvarez-Builla et al. [47]. In a typical procedure, imidazole (0.68 g) and NaI (0.01 g) were added to a mixture of CM-MIL-101 (1 g) in CH₃CN (20 ml) and refluxed for 48 h. Then, the solid was filtered off, washed with CH₃CN, K₂CO₃/H₂O, methanol/H₂O and methanol/diethyl ether and dried in vacuum for several hours. The prepared Im-MIL-101was used as support for immobilization of Mn(TPP)Cl *via* axial ligation. For this purpose, to a solution of 0.25 g (0.32 mmol) manganese(III) tetraphenylporphyrin in toluene (25 mL), Im-MIL-101 (2 g) was added and the mixture was vigorously stirred at 80°C for 48 h. After cooling, the dark green powder was collected by filtration, washed thoroughly with toluene, dichloromethane and acetone, respectively, and dried at room temperature. The manganese content of the heterogenized catalyst was determined by ICP.

2.4. Catalytic experiments

All of the reactions were carried out at room temperature with magnetic stirring. To a mixture of alkene or alkane (1 mmol), Mn(TPP)Cl@Im-MIL-101(100 mg) in CH₃CN (10 mL), a solution of NaIO₄ (2 mmol) in H₂O (10 mL) was added. The reaction mixture was stirred at room temperature. The progress of the reaction was monitored by GC. At the end of the reaction, the mixture was diluted with Et₂O (20 ml) and filtered. The catalyst was thoroughly washed with Et₂O and the combined washings and filtrates were purified on a silica gel plates or a silica gel column to afford the product.

The reusability of the Mn(TPP)Cl@Im-MIL-101 was investigated in the multiple sequential epoxidation of cyclooctene as described above. At the end of each reaction, the catalyst was separated

from the reaction mixture by filtration, washed with acetonitrile and Et_2O and dried before reusing. The catalyst was consecutively reused four times without a detectable catalyst leaching or a significant loss of its activity. The catalyst stability was followed by XRD, FT-IR and solid state UV-vis.

3. Results and discussion

3.1. Preparation and characterization of the catalyst, Mn(TPP)Cl@Im-MIL-101

Scheme 2 shows the preparation procedure for immobilization of Mn(TPP)Cl on imidazole modified CM-MIL-101. First, the Im-MIL-101 was prepared by the reaction of imidazole with –CH₂Cl group. In the next step, the Mn(TPP)Cl was reacted with Im-MIL-101 *via* axial ligation to obtain the catalyst. In biomimetic oxidations with NaIO₄ catalyzed Mn(III) porphyrin as catalyst, imidazole has a co-catalytic role [48-50]. In this catalytic system, the Im-MIL-101 not only used as support but also applied as a heterogeneous axial base.

Scheme 2

During the conversion of MIL-101 to Mn(TPP)Cl@Im-MIL-101, the color changed clearly from greenblue to green (Fig. 1).

Fig. 1

The synthesized hybrid catalyst was characterized by diffuse reflectance FT-IR and diffuses reflectance UV-vis spectroscopic methods, inductively coupled plasma, elemental analysis, XRD, BET and SEM methods. The nitrogen content of the support was determined by CHN analysis which showed a value of about 2.98%. According to this value, the degree of imidazole which was introduced into the CM-MIL-101 was 1.06 mmol/g of support. The Mn content of the catalyst, measured by ICP analysis, was obtained 0.098 mmol/g of Mn(TPP)Cl@Im-MIL-101.

The most prominent spectroscopic data, which confirmed the anchoring of the Mn(TPP)Cl on the Im-MIL-101, were obtained by comparison of the diffuse reflectance UV-vis spectra of Im-MIL-101 and Mn(TPP)Cl@Im-MIL-101 (Fig. 2) with the UV-vis spectrum of homogeneous Mn(TPP)Cl (Fig. 3).

The appearance of Soret and Q bands of homogeneous manganese tetraphenylporphyrin with a slight shift in the supported catalyst clearly indicated the presence of the metalloporphyrin on the support.

Fig. 2 and 3

The FT-IR spectrum (Fig. 4A) and XRD pattern (Fig. 5A) of MIL-101 match well with the literature [30, 51]. The characteristic vibrational bands of the framework, -(O-C-O)- groups, around 1550 and 1400 cm⁻¹ in the FT-IR spectra (Fig. 4) are preserved and confirm the stability of framework during modification process and attachment of the metalloporphyrin. In the FT-IR spectrum of Im-MIL-101(Fig. 4C), the C=N vibrational band of imidazole group appears in 1549 cm⁻¹ which confirmed the anchoring of imidazole to CM-MIL-101. This characteristic band showed a slight shift to 1560 cm⁻¹ after attachment of Mn(TPP)Cl to Im-MIL-101 (Fig. 4D). Comparison of this spectrum with the FT-IR spectrum of metalloporphyrin (Fig. 4F) showed the characteristic bands of pure metalloporphyrin in the supported catalyst at 1091 and 1256 cm⁻¹ which proved the coordination of Mn(TPP)Cl to the support.

Fig. 4

It is obvious from the XRD patterns (Fig. 5B and 5C) that the crystallinity of MIL-101 is maintained after chloromethylation and imidazole modification, respectively. The additional peak in Fig. 5D, corresponding to Mn(TPP)Cl (Fig. 5F), is a strong evidence for the synthesis of Mn(TPP)Cl@Im-MIL-101.

Fig. 5

The FE-SEM images of the catalyst, Im-MIL-101, CM-MIL-101 and MIL-101 are shown in Fig. 6. These images show that the morphology of MIL-101 are octahedral and maintain during modification and attachment of metalloporphyrin.

The energy dispersive X-ray (EDX) results, obtained from SEM analysis for the catalyst in Fig. 6E clearly show the presence of Mn in Mn(TPP)Cl@Im-MIL-101.

Fig. 6

6

The specific surface area of Mn(TPP)Cl@Im-MIL-101, determined using nitrogen physisorption measurements at low temperature (Fig. 7), shows a predictable decrease in pore volume compared to MIL-101. The BET surface area decreased from 2125 to $1117 \text{ m}^2\text{g}^{-1}$.

Fig. 7

The TEM images showed that the Mn(TPP)Cl was homogeneously dispersed on the MIL-101 support (Fig. 8B) and after reusing the catalyst in the epoxidation of cyclooctene, no obvious change which represent the aggregation was observed (Fig. 8C).

Fig. 8

3. 2. Catalytic experiments

At first, the catalyst amount was optimized in the epoxidation of cyclooctene (0.5 mmol) with NaIO₄ (1 mmol). The best results were obtained with 100 mg (0.0098 mmol) of the catalyst (Fig. 9).

A blank experiment in the presence of oxidant and pure MIL-101 under the same reaction conditions was also investigated. The obtained results showed that only 8% cyclooctene oxide was detected in the reaction mixture by GC. Also in the presence of sole oxidant and in the absence of catalyst, only 5% of the desired product was produced. Recently, we reported the catalytic activity of MIL-101 in the oxidation of alkenes with H_2O_2 under reflux conditions in which the alkenes were converted directly to diacids. In those experiments, the catalytic active site is Cr [51]. But in the present work, the pure MIL-101 is inactive using NaIO₄ as oxidant, and only 8% of the cyclooctene oxide was produced in the presence of pure MIL-101. These observations prove that the catalytic active site is Mn species.

Fig. 9

The effect of different oxidants on the epoxidation of cyclooctene catalyzed by Mn(TPP)Cl@Im-MIL-101 was investigated. The results obtained at room temperature are summarized in Table 1. The results

show that $NaIO_4$ is the best oxygen source because this oxidant, which is inert in the absence of catalyst, can give good oxidation conversion in CH_3CN/H_2O mixture.

Table 1

Different alkenes and alkanes were oxidized with NaIO₄ in the presence of the prepared catalyst Mn(TPP)Cl@Im-MIL-101 at room temperature in a 1:1 mixture of acetonitrile/water as the reaction medium. The optimized reaction parameters used for the epoxidation of cyclooctene was catalyst, oxidant and substrate in a molar ratio of 0.0098: 1: 0.5 and Im-MIL-101 plays the role of support as well as co-catalytic axial ligand in this catalytic system. The Mn(TPP)Cl@Im-MIL-101 was found as an efficient catalyst for the epoxidation of alkenes with NaIO₄ (Table 2). This heterogenized catalytic system showed good activity in the oxidation of cyclooctene and afforded the cyclooctene oxide in 96%. In the case of cyclohexene, the major product was cyclohexene oxide (82%) and 2-cyclohexen-1-one was produced as a minor product (10%). Epoxidation of styrene yielded styrene oxide as the major product with only a small amount of benzaldehyde. The epoxidation of linear alkenes such as 1-octene and 1-decene was also investigated which showed high yields with 100% selectivity.

Cyclic alkenes are more reactive than linear ones. In the case of linear alkenes, upon increasing the alkene chain, its mobility toward catalyst active site decreases and therefore its reactivity reduces.

Table 2

The catalytic oxidation of alkanes is also one of the typical challenging problems in organic chemistry. For this purpose the catalytic activity of Mn(TPP)Cl@Im-MIL-101 was investigated in biomimetic oxidation of saturated hydrocarbons. This catalytic system converts different alkanes to their corresponding alcohols and ketones. Cyclooctane, cyclohexane and tetralin were oxidized in high yields to their corresponding alcohols and ketones. In contrast, ethylbenzene and propylbenzene only produced the corresponding ketones (Table 3). As mentioned before in biomimetic systems using manganese porphyrins as catalysts, addition of a π -donor base increases the stability of the metal oxo

complex and increase catalytic activity. Actually, imidazole coordinates to Mn and activates the catalyst [48, 49]. In this case, by using Im-MIL-101, it is possible to immobilize Mn(TPP)Cl and obtain a pentacoordinate Mn(III) complex which leaves a vacant position on the manganese for catalysis.

Table 3

Our research group, previously, reported the catalytic activity of Mn(TPP)Cl immobilized on silica [15], polystyrene [16] and carbon nanotubes [7] in the oxidation of hydrocarbons. Comparison of this new supported Mn(TPP)Cl catalytic system with these three systems show that Mn(TPP)Cl@Im-MIL-101 is more efficient and have higher catalytic activity than other ones (Table 4). This can be related to higher specific surface area of MIL-101 and isolation of catalytic active sites, which in turns increases the catalytic activity. NUS

Table 4

3.5. Catalyst reuse and stability

The stability and reusability of a heterogeneous catalyst is very significant for economical purposes. In this manner, for completion of our study, the reusability of Mn(TPP)Cl@Im-MIL-101 was checked in the multiple sequential epoxidation of cyclooctene with NaIO₄. As shown in Table 5, the catalyst could be reused for four consecutive times without significant loss of its catalytic activity. After each reaction, the filtrates were collected for determination of the Mn leached. The amounts of Mn leached after each run was determined by ICP. No remarkable manganese was detected in the filtrates.

Table 5

4. Conclusion

In conclusion, we reported Mn(TPP)Cl@Im-MIL-101 as a highly efficient and reusable heterogeneous catalytic system in oxidation of alkenes and alkanes. This new heterogeneous catalyst was synthesized by covalent attachment of manganese(III)tetraphenylporphyrin to chloromethylated MIL-101(Cr)

modified with imidazole by elimination of chlorine atom. The catalyst showed several unique features such as excellent yields, noticeable reusability, mild reaction conditions and easy work up.

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Fig. 1. The color change during the preparation of Mn(TPP)Cl@Im-MIL-101 from MIL-101

Fig. 2. Diffuse reflectance UV–vis spectrum of: (A) Im-MIL-101, (B) Mn(TPP)Cl@Im-MIL-101 and (C) Recovered catalyst

Fig. 3. The UV–Vis spectrum of homogeneous [Mn(TPP)Cl]

Fig. 4. FT-IR spectrum of: (A) MIL-101; (B) CM-MIL-101; (C) Im-MIL-101; (D) Mn(TPP)Cl@Im-MIL-101; (E) Recovered catalyst and (F) Mn(TPP)Cl

Fig. 5. XRD pattern of: (A) MIL-101; (B) CM-MIL-101; (C) Im-MIL-101; (D) Mn(TPP)Cl@Im-MIL-101: (E) Recovered catalyst and (F) Mn(TPP)Cl

Fig. 6. FE-SEM image of: (A) MIL-101; (B) CM-MIL-101; (C) Im-MIL-101; (D) Mn(TPP)Cl@Im-MIL-101 and (E) SEM-EDX spectrum of Mn(TPP)Cl@Im-MIL-101 (Al is for sample holder)

Fig. 7. N₂ Adsorption/ desorption isotherm of: (A) MIL-101 and (B) Mn(TPP)Cl@Im-MIL-101 (■ Adsorption, □ Desorption)

Fig. 8. TEM image of: (A) MIL-101; (B) Mn(TPP)Cl@Im-MIL-101 and (C) Recovered catalyst

Fig. 9. Optimization of the catalyst amount in the epoxidation of cyclooctene with NaIO₄ at room temperature (Reaction conditions: cyclooctene (0.5 mmol), oxidant (1 mmol), catalyst, CH_3CN/H_2O (5 ml/ 5 ml).



Scheme 1. Epoxidation of alkenes and hydroxylation of alkanes with $NaIO_4$ catalyzed by

Mn(TPP)Cl@Im-MIL-101



Scheme 2. Preparation of Mn(TPP)Cl@Im-MIL-101



Fig. 1. The color change during the preparation of Mn(TPP)Cl@Im-MIL-101 from MIL-101



Fig. 2. Diffuse reflectance UV-vis spectrum of: (A) Im-MIL-101, (B) Mn(TPP)Cl@Im-MIL-101 and

(C) Recovered catalyst



Fig. 3. The UV–Vis spectrum of homogeneous [Mn(TPP)Cl]



Fig. 4. FT-IR spectrum of: (A) MIL-101; (B) CM-MIL-101; (C) Im-MIL-101; (D) Mn(TPP)Cl@Im-MIL-101; (E) Recovered catalyst and (F) Mn(TPP)Cl



Fig. 5. XRD pattern of: (A) MIL-101; (B) CM-MIL-101; (C) Im-MIL-101; (D) Mn(TPP)Cl@Im-MIL-101: (E) Recovered catalyst and (F) Mn(TPP)Cl



Fig. 6. FE-SEM image of: (A) MIL-101; (B) CM-MIL-101; (C) Im-MIL-101; (D) Mn(TPP)Cl@Im-MIL-101 and (E) SEM-EDX spectrum of Mn(TPP)Cl@Im-MIL-101 (Al is for sample holder).



Fig. 7. N₂ Adsorption/ desorption isotherm of: (A) MIL-101 and (B) Mn(TPP)Cl@Im-MIL-101 (

Adsorption,
Desorption)



Fig. 8. TEM images of: (A) MIL-101; (B) Mn(TPP)Cl@Im-MIL-101 and (C) Recovered catalyst.



Fig. 9. Optimization of the catalyst amount in the epoxidation of cyclooctene with $NaIO_4$ at room temperature (Reaction conditions: cyclooctene (0.5 mmol), oxidant (1 mmol), catalyst, CH₃CN/H₂O (5 ml/ 5 ml).

 Table 1. The effect of oxidant on the epoxidation of cyclooctene catalyzed by [Mn(TPP)Cl@Im-MIL-101] at room temperature.^a

Entry	Oxidant	Solvent	Epoxide yield (%) ^b
1	NaIO ₄ (1 mmol)	CH ₃ CN/H ₂ O	96
2	NaIO ₄ (0.5mmol)	CH ₃ CN/H ₂ O	44
3	H_2O_2	CH ₃ CN	40
4	Urea-H ₂ O ₂ (UHP)	CH ₃ CN	29
5	tert-BuOOH	CH ₃ CN	18

^aReaction conditions: cyclooctene (0.5 mmol), oxidant (1 mmol), catalyst (100 mg), CH₃CN/ H₂O (5 ml/ 5 ml).

^bGC yield based on the starting alkene.

Entry	Alkene	Conversion (%) ^b	Epoxide yield (%) ^b	Time (h)	$TOF(h^{-1})$
1		96	96	2.5	19.6
2		92 ^c	82	2.5	16.7
3		94 ^d	83	2.5	16.9
4	1-Octene	76	76	3.5	11.1
5	1-Decene	48	48	3.5	7.0

Table 2. Epoxidation of alkenes with NaIO₄ catalyzed by Mn(TPP)/Im-MIL-101.^a

^aReaction conditions: alkene (0.5 mmol), NaIO₄ (1 mmol), catalyst (0.0098 mmol), CH₃CN/H₂O (5/5 nant ml).

^bGC yield based on the starting alkene.

^cThe by-product is allylic ketone.

^dThe by product is benzaldehyde.

Table 3. Hydroxylation of alkanes with	NaIO ₄ catalyzed by Mn(TPP)/Im-MIL-101. ^a

Entry	Alkane	Conversion (%) ^b	Ketone (%) ^b	Alcohol (%) ^b	Time (h)	TOF (h^{-1})
1		75	45	30	4	9.5
2		58	49	9	4	7.3
3		53°	53	-	4	6.8
4		50 ^d	50	-	4	6.4
5		69 ^e	48	21	4	8.8

^aReaction conditions: alkane (0.5 mmol), NaIO₄ (1 mmol), catalyst (0.0098 mmol), CH₃CN/H₂O (5/5 ml).

^bGLC yield based on the starting alkane.

^cThe product is acetophenone.

^dThe product is ethyl phenyl ketone.

 e Only the α -position was oxidized.

 Table 4. Comparison of the results obtained for the oxidation of cyclooctene with

 NaIO₄under magnetic stirring catalyzed by manganese porphyrins with those obtained

 by the recently reported catalysts.

Row	Catalyst	$TOF(h^{-1})$	Ref
1	Mn(TPP)Cl-SiIm	8.33	[15]
2	Mn(TPP)-PSI	16.2	[16]
3	Mn(TPP)Cl-APy-MWCNT	10.26	[7]
4	Mn(TPP)Cl-AP-MWCNT	7.59	[7]
5	Mn(TPP)Cl/Im-MIL-101	19.6	Present work

Accept

Table 5. Recyclability of Mn(TPP)/Im-MIL-101 in the

run	Yield (%) ^b	Mn leached (%) ^c
1	96	1.1
2	92	0.6
3	88	0
4	88	0

^aReaction conditions: cyclooctene (0.5mmol), NaIO₄ (1 mmol),

catalyst (100 mg), CH₃CN/H₂O (5/5 mL).

^bGC yield based on the starting alkene.

^cDetermined by ICP.

Graphical



MIL-101 was modified by covalent post synthetic modification **>** Mn(TPP)Cl was anchored to imidazole modified MIL-101 by covalent attachment > A heterogeneous catalyst was prepared > The catalyst was used for epoxidation of alkenes and hydroxylation of alkanes ► The catalyst was reusable