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Manganese porphyrin immobilized on montmorillonite: a highly efficient and reusable catalyst for the aerobic epoxidation of olefins under ambient conditions

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> **ABSTRACT:** Highly efficient aerobic epoxidation of olefins catalyzed by cationic *meso*-tetrakis-(1methyl-4-pyridyl) (TM4PyP) metalloporphyrins immobilized into montmorillonite (MT) interlayer was achieved. The heterogeneous catalysts were characterized by diffuse reflectance UV spectra, infrared, X-ray diffraction, nitrogen adsorption isotherm and scanning electron microscopy. Manganese porphyrin (MnTM4PyP-MT) showed excellent activity and selectivity for the aerobic epoxidation of olefins under ambient conditions, in which more 90% yields of epoxides were obtained. The clay basal spacing played significant role in the catalytic efficiency and selectivity for different olefins. The catalyst could be reused consecutively five times without significant loss of activity.

KEYWORDS: metalloporphyrins, montmorillonite, epoxidation, supported catalyst.

INTRODUCTION

Catalytic epoxidation of olefins has attracted much attention both in industry and in organic synthesis. for epoxides are among the most useful synthetic intermediates [1]. Synthetic metalloporphyrins have been used as cytochrome P-450 models and have been found to be a highly efficient homogeneous catalyst for alkene epoxidation in combination with various oxidants e.g. iodosylbenzene [2], and hydrogen peroxide [3]. However, decomposing easily during the epoxidation and difficulty of recovery is the main weakness of homogeneous catalysts. Great efforts have been made to immobilize metalloporphyrins onto supports to promote stability [4]. Metalloporphyrins could be immobilized on a variety of supports, such as organic polymer materials [5], chemically modified silica surfaces [6], mesoporous molecular sieves [7], SBA-15 [8], chitosan [9].

Due to the large specific surface area, chemical and mechanical stability, layered structure and high cation exchange capacity, montmorillonite is preferable to be used as the support for immobilizing metalloporphyrins [10]. The montmorillonite-supported cationic metalloporphyrins have been applied in the oxidation of alkanes and 2-mercaptoethanol, in which metalloporphyrins were immobilized in the clay by electrostatic bond [11]. Kameyama ever reported the aerobic epoxidation of cyclohexene catalyzed by different cationic montmorillonite-supported cobalt porphyrins, in which 66% yield of epoxide was obtained in a reaction time of 9 h [12]. The catalytic inefficiency of cobalt porphyrins could be attributed the uneasily accessible of high-valence species which is considered as the active species in the epoxidation, which is different from the cases of manganese and iron porphyrins. To our knowledge, the application of montmorillonte-supported cationic manganese porphyrins in the epoxidation of alkenes is still unknown.

We ever reported the aerobic epoxidation of olefins catalyzed by homogeneous mono- and μ -oxo dimeric manganese or iron porphyrins [13], in which the efficiency could be comparable to enzyme catalysis. In continuation of our ongoing research on the metalloporphyrins-based epoxidations, we report herein the efficient aerobic epoxidation of

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various alkenes catalyzed by montmorillonite-supported manganese porphyrins catalyst under ambient conditions, in which more 90% yields of epoxides were obtained. The heterogeneous catalyst showed excellent activity and could be reused consecutively five times without significant loss of activity.

RESULTS AND DISCUSSION

Supported catalyst characterization

In this work, montmorillonite was used for the immobilization of cationic metalloporphyrins because it is easily commercially available clay with interlayer surface. It is also easily exchanged with solute ions by varying the cationic composition of the solution. In the adsorption process, pyridyl ions of metalloporphyrins are bound to the clay surface by sharing one or several ligands with adsorbent cations as isolated complexes. Consequently, meso-tetrakis-(1-methyl-4pyridyl)metalloporphyrins can be firmly anchored onto its surface. In all immobilization procedures nearly all metalloporphyrins were transferred to the solids and low quantities were spectrometrically detected in solution by atomic absorption analyses. Thus, the loaded amounts of the MnTM4PyP, CoTM4PyP and FeTM4PyP was 4.7×10^{-5} mol/g, 3.8×10^{-5} mol/g and 3.5×10^{-5} mol/g, respectively. The concentration of metalloporphyrins immobilized in montmorillonite is 10 times more than that of immobilized in silica and polystyrene based resin [14, 15].

The immobilization process could also be characterized by the color change of the clays. Such as MnTM4PyP, the change was from light green to brown, with a final color of dark brown in the case of the dry solid. The UV-visible spectra of metalloporphyrins were recorded on a Shimadzu UV-2450 UV-vis spectrophotometer in the 200 to 700 nm-range, using water as solvent. The presence of metalloporphyrins in the solid clay was determined by the diffuse reflectance ultraviolet-visible spectra (DRS-UV-vis) as shown in Fig. 1 (MnTM4PyP as an example). And all the results were summarized in Table 1.

Compared with those of MnTM4PyP in the region of 400–700 nm, the Soret peak and Q peak for the MnTM4PyP/MT appeared at 494 nm and at 588 nm, having been red-shifted 31 nm and 27 nm, respectively. The presence of the red-shifted Soret peak indicates that there was a coordination bond between MnTM4PyP and montmorillonite. The red shift could be interpreted as the result of a π -interaction by the metalloporphyrins aromatic ring and the surface of the clay. A similar red shift was observed for FeTM4PyP and CoTM4PyP immobilized in montmorillonite.

IR spectra of these metalloporphyrins-MT clays further provide some information about the presence



Fig. 1. The UV-vis spectra of MnTM4PyP and MnTM4PyP-MT

of metalloporphyrins in the clays. Fourier transform infrared (FT-IR) spectra of the samples were recorded in the range of 4000–400 cm⁻¹ on a FT-IR spectrometer (Bruker, VERTEX 70) using KBr pellet technique. The results of FT-IR spectroscopic measurements for cationic metalloporphyrins, montmorillonite and metalloporphyrins immobilized in the clay (CoTM4PyP as an example) were shown in Fig. 2.

For montmorillonite, a broad band at 3400 cm⁻¹ is the primary O-H stretching of hydroxyl functional group. Another broad brand between 1032 and 1300 cm⁻¹ can be attributed to the stretching vibration of Si-O bond. The strong absorption at 1609 cm⁻¹ is ascribed to the bending vibration of O-H bond. After CoTM4PyP was immobilized on the clay, the basic characteristic peaks for montmorillonite hardly changed. The characteristic peak of CoTM4PyP at 1009 cm⁻¹ disappeared. And some new bands between 1300–1600 cm⁻¹ were clearly observed, which attributed to the pyrrole C=N stretching of the skeleton of metalloporphyrins. In addition, the broad peak at 1609 cm⁻¹ is sharpened, coupling with a blue shift of 34 cm⁻¹. These changes indicated the presence of metalloporphyrins immobilized onto montmorillonite.

X-ray diffraction measurement was performed on a D-MAX diffractometer with Cu K α source and operated

Table 1. The UV-vis data of metalloporphyrins andmetalloporphyrins/MT

Compound	Solvent	λ_{max} , nm	
		Soret band	Q-band
MnTM4PyP	water	463	561
MnTM4PyP/MT		494	588
CoTM4PyP	water	428	540
CoTM4PyP/MT	_	446	571
FeTM4PyP	water	404	512
FeTM4PyP/MT	_	427	534



Fig. 2. FT-IR spectra of CoTM4PyP, MT and CoTM4PyP/MT



Fig. 3. XRD patterns of CoTM4PyP-MT (a) and MT (b)

at 40 kV and 30 mA, to determine the influence of metalloporphyrins on the structure of the clay. The diffraction patterns were recorded in the 20 value range of $1-80^{\circ}$ with a scanning rate of 8 o/min. The XRD curves of MT and CoTM4PyP-MT were presented in Fig. 3. It could be known that the struture of metalloporphyrins-immobilized clay are similar to those observed for the montmorillonite, indicating that they possess the same morphology and crystalline strutures and the solid support is structurally unchanged and the cationic metalloporphyrins should be dispersed on the interlayer.

Moreover, a slight shift of the basal spacing d001 (the characteristic reflection) to the lower angle with the corresponding increase in the d spacing was observed after the incorporation of CoTM4PyP into the clay. According to the Scherrer formula, the basal spacing of CoTM4PyP-MT was 1.373 nm, which agrees well with the results reported by Kameyama [12]. Similarly, the basal spacing of MnTM4PyP-MT, FeTM4PyP-MT was 1.396 nm and 1.389 nm, respectively. The metalloporphyrins plane in montmorillonite was estimated to orient

Table 2. The BET surface area and pore volume of MT and metalloporphyrins-MT

Entry	Sample	BET surface area, m ² /g	Pore volume, cm ³ /g
1	MT	34	0.043
2	MnTM4PyP-MT	83	0.085
3	CoTM4PyP-MT	67	0.059
4	FeTM4PyP-MT	66	0.056

parallel to lamella in this clay. Since the thickness of a montmorillonite crystal layer is about 0.96 nm, the thickness of the intercalated CoTM4PyP is estimated at 0.413 nm. And the size of CoTM4PyP is estimated at about 0.67 nm. The size of this cationic metalloporphyrins in the axial direction changes depending on the angle of pyridyl groups existing at the *meso*-position. Therefore, the CoTM4PyP is inserted into the clearance space of 0.413 nm, indicating that the pyridine rings incline to an angle of about 300 against the porphyrin plane.

For the montmorillonite before and after being immobilized with metalloporphyrins, the BET surface area and pore volume determined from nitrogen adsorption-desorption isotherms (Micromeritics ASAP-2010) are presented in Table 2. The BET surface area of montmorillonite is $34 \text{ m}^2/\text{g}$, which is much lower than that of metalloporphyrins-immobilized montmorillonite. Metalloporphyrins complex intercalated between the montmorillonite layers could give rise to the formation of new pores and the increase in surface area.

The morphology of the samples was examined by scanning electron microscope (SEM). Figure 4(a) shows the typical surface of montmorillonite, in which some aggregates could be observed clearly. The SEM micrograph of metalloporphyrins-immobilized montmorillonite was shown in Fig. 4(b). It could be known that particles of the supported catalyst were dispersed well, with the average diameter of about 20 μ m.

Catalytic performance for the aerobic epoxidation of olefins

With cyclohexene as model compound, the effects of reaction conditions on the epoxidation in the presence of montmorillonite-supported metalloporphyrins with molecular oxygen as oxidant and isobutyraldehyde as co-reductant have been investigated. Epoxide is the main product for the oxidation, coupling with a little amount of 2-cyclohexen-1-one and 2-cyclohexen-ol.

Catalytic performance of the various supported metalloporphyrins. Iron, manganese and cobalt were the most frequently used metals in oxidation reactions and those metals were chosen to synthesize the cationic metalloporphyrins. The catalytic activity and selectivity of different metalloporphyrins for cyclohexene



Fig. 4. SEM image of MT (a) and CoTM4PyP-MT (b)



Fig. 5. The aerobic epoxidation of cyclohexene catalyzed by various montmorillonite-supported metalloporphyrins. Cyclohexene (2 mmol), acetonitrile (4 mL), isobutylaldehyde (6 mmol), catalyst (0.02 g), O₂ bubbling, 3.0 h, room temperature

epoxidation by molecular oxygen were investigated and the results were presented in Fig. 5.

As shown in Fig. 5, the catalytic activity of the metalloporphyrins appears to be dependent on the nature of their central ions. The present results clearly show that manganese porphyrins is considerably more selective than cobalt and iron porphyrins catalysts for the aerobic epoxidation of olefins. The catalytic activity of different metalloporphyrins is probably influenced by their electric potential and the stability of different valences of metal atoms. In addition, comparing with cobalt and iron porphyirns, MnTM4PyP-MT has the higher BET surface area as shown in Table 2. The catalytic performance for this heterogeneous catalyst is positive related with surface area.

Effect of catalyst amount on the aerobic epoxidation. Figure 6 shows the influence of MnTM4PyP-MT catalyst



Fig. 6. Conversion rates profile of cyclohexene with different amounts of MnTM4PyP-MT. (\blacksquare): without catalyst, (\square): 0.005 g, (\bullet): 0.01 g, (\odot): 0.015 g, (\blacktriangle): 0.02 g, (Δ): 0.025 g. Cyclohexene (2 mmol), acetonitrile (4 mL), isobutylaldehyde (6 mmol), O₂ bubbling, 3.0 h, room temperature

amount on the aerobic epoxidation of cyclohexene in the presence of molecular oxygen and isobutyraldehyde.

As shown in Fig. 6, only 7% cyclohexene was converted in blank experiment of catalyst when the reaction was conducted for 3 h. The conversion of cyclohexene is considerably enhanced when the manganese porphyrin catalyst was used. As depicted clearly in Fig. 6, the reaction rate increases with increasing catalyst contents. Cyclohexene could be almost converted completely when the amount of catalyst was 0.02 g (MnTM4PyP: 0.94 × 10^{-3} mmol), in which the selectivity of epoxide was up to 95%. Therefore, the optimal amount of MnTM4PyP-MT for the aerobic cyclohexene epoxidation was 0.02 g.

Effect of the solvent on the aerobic epoxidation. It is well-known that the solvent plays an important and

Entry	Solvent	Dielectric constant	Conv., %	Yield, %	Selectivity, %
1	Cyclohexane	2.0	53	42	79
2	Toluene	2.4	57	45	79
3	Dichloromethane	9.1	73	72	99
4	2-Propanol	18.3	75	71	94
5	Methanol	32.6	81	77	95
6	Acetonitrile	37.5	96	91	95

Table 3. Effect of solvent on the epoxidation of cyclohexene catalyzed by MnTM4PyP-MT $^{\rm a}$

^aCyclohexene (2 mmol), isobutylaldehyde (6 mmol), catalyst (0.02 g), solvent (4 mL), O₂ bubbling, 3.0 h, rt.

sometimes decisive role in the catalytic behavior of a catalyst. Therefore, the effect of solvents on reactivity and selectivity was studied in the current catalytic system.

As shown in Table 3, the dielectric constant of solvent is closely related with the efficiency for the aerobic epoxidation catalyzed by montmorillonite-supported manganese porphyrins. The conversion of cyclohexene increased with the increasing dielectric constant of solvent in direct proportion. Among the used solvents, acetonitrile was more favorable for olefins epoxidation in the catalytic system (entry 6). When the reaction was conducted in the media with low dielectric constant such as cyclohexane and toluene, the selectivity of epoxide is much lower than that of reaction media with higher dielectric constant. It seems that non-polar solvent could promote the oxidation of α -H of the double bond, resulting in generating more by-products such as 2-cyclohexen-1one. Although cyclohexane is a commonly used model substrate for metalloporphyrin catalyzed oxidations [16], no oxidized products such as cyclohexanone, cyclohexanol or adipic acid from cyclohexane were determined in this catalytic system. Moderate conversion of cyclohexene (73%) but excellent selectivity of epoxide was obtained in the dichloromethane media (entry 3). The highly selective epoxidation with dichloromethane as solvent consists well with the homogeneous epoxidation catalyzed manganese porphyrins [13].

Aerobic epoxidation of various olefins catalyzed by MnTM4PyP-MT catalyst. To evaluate the scope of the catalytic system, various alkenes were subjected to the reaction system using only 0.02 g of montmorillonitesupported manganese porphyrins (Table 4). As shown in Table 4, most substrates could be smoothly converted to the corresponding epoxides with high conversion rate and excellent selectivity.

It seems that the efficiency of the epoxidation in this catalytic system is not closely related with the steric conformation of substrates. For instance, 1-methylcyclohexene could be converted completely with less reaction time than cyclohexene (entries 1–2). This phenomenon could further be demonstrated from the oxidation of trans-stilbene (entry 4). In addition, the steric hindrance of cyclohexene derivatives is more favorable for the selectivity of epoxide (entries 2–3). It maybe that the suitable space of the montmorillonite interlayer make the α -position active site be free risk of attacking from the metal high-valent species.

Similarly, in the epoxidation of other cycloolefin *e.g.* cyclooctene, the reaction system exhibits high catalytic performance and excellent selectivity of epoxide (entry 6). However, slow oxidation occurred and an unsatisfactory selectivity could be obtained for the simple linear olefins such as 1-octene, 1-hexene and trans-2-octene, even including styrene (entries 6–9). The results were contrary to the homogeneous epoxidation of olefins with Mn porphyrins as catalyst [13]. Another salient feature of the present epoxidation is its high regioselectivity. When (+)-limonene was subjected to the epoxidation, the monoepoxide with the epoxide group on the ring almost was the only product and its selectivity was 98% (entry 10).

Catalyst reuse and stability. The stability of the MnTM4PyP-MT catalyst was monitored using multiple sequential aerobic epoxidation of cyclohexene in the presence of isobutyraldehyde. The catalyst was recovered by centrifugation, filtration, washed with acetonitrile and dried before using it in the subsequent run. The results are presented in Fig. 7.

From Fig. 7, the catalyst was consecutively reused five times without a significant loss of its activity. The leaching of the metalloporphyrins from the support to the reaction medium was checked by taking UV-vis spectra of the solution at the end of the reaction. No presence of manganese porphyrins, characterized by the Soret band was observed, indicating that the metalloporphyrins remain tightly bound to the support during the oxidation reaction. The results clearly showed that the supported catalyst was active in the epoxidation and could be reused without significant decrease in the catalytic activity and with almost similar selectivity.

Plausible mechanism of the aerobic epoxidation. As reported previously, the homogeneous epoxidation catalyzed by metalloporphyrin complexes plus aldehyde is considered to involve a radical and high-valent metal

Entry	Substrate	Product	Reaction time, h	Conv., %	Yield, %
1	\bigcirc	0	3	96	91
2	\bigcup	6	2.5	>99	98
3	Ph	Ph	3	96	94
4			2	>99	98
5			4	87	86
6 ^b		°,	4	93	82
7	$\frown \frown \frown \frown$	$\sim \sim $	5	87	80
8		$\sim \sim $	5	93	82
9			4	91	84
10			3	90	88

Table 4. Aerobic epoxidation of various olefins catalyzed by MnTM4PyP-MT^a

^aCyclohexene (2 mmol), isobutylaldehyde (6 mmol), catalyst (0.02 g), acetonitrile (4 mL), O₂ bubbling, rt. ^bThe by-product is benzaldehyde.



Fig. 7. The stability and reuse of MnTM4PyP-MT catalyst in the aerobic epoxidation of cyclohexene, (I): conversion of cyclohexene, (III): selectivity of epoxide

intermediate mechanism. The feature of radical-involved reaction could be informed from the profile of oxidation of cyclohexene as shown in Fig. 6, in which the reaction occurred first with induction period and then followed by sharp acceleration till completion. Moreover, the oxidation could be subsequently quenched in the presence of a free radical inhibitor.

High-valent porphyrin intermediate is generally accepted as the active species for the oxidations catalyzed by metalloporphyrins [17]. The epoxidation of olefins is assumed to occur *via* reactive high-valent metal oxo intermediates that are produced by the reaction of peroxyacid with the metal catalysts from this mechanism [18]. Therefore, in the aerobic epoxidation of olefins catalyzed by montmorillonite-supported manganese porphyrins system, the high-valent Mn porphyrins intermediate is generated through at first. Then the epoxide is produced by the reaction of carbon–carbon double bond with the active high-valent Mn porphyrin intermediate.

As discussed above, in investigating the catalytic efficiency for various substrates, it is interesting to find that the catalytic system is highly efficient for the substrates with larger molecule bulk (entries 2–5, Table 4), while poor selectivity of epoxides and the necessary longer reaction time were observed for the simple linear olefins (entries 6–9, Table 4). It indicates

that the clay basal spacing plays significant role in the catalytic efficiency and selectivity for different olefins. The substrates with small molecule size can pass through the interlayers easily. It decreases the opportunities of molecules collision between substrates and the anchored metal-oxo intermediate, which results in the low reaction rates. Meanwhile, the attack opportunities to the α -position site of olefins by the metal-oxo intermediate could increase, which leads to the low selectivity for the epoxide during the oxidation.

EXPERIMENTAL

Olefins were of analytical grade and purchased from Alfa Aesar or Aldrich without further purification unless indicated. Pyrrole and isobutyraldehyde were redistilled before use. Other solvents were all of analytical grade. The montmorillonite was purchased from Aladdin Reagents.

Synthesis of *meso*-tetrakis-(1-methyl-4-pyridyl) metalloporphyrin

Pyrrole (20 mL) and 4-pyridinecarbaldehyde (20 mL) were refluxed in propionic acid (200 mL) for 60 min to produce *meso*-tetrakis(4-pyridyl) porphyrin (T4PyP) with the yield of 24%. Next, T4PyP (0.25 g) and manganese acetate (1 g) were refluxed in dimethylformamide (35 mL) for 6 h under nitrogen atmosphere to form *meso*-tetrakis-(4-pyridyl)manganese porphyrin (MnT4PyP) with the yield of 88%.

In the following step, MnT4PyP (0.2 g) and methyl p-toluenesulfonate (12 g) were added to 100 mL dimethylformamide solution. The mixture was stirred for 12 h at 90 °C, and the solution was cooled to room temperature. Ethyl ether (20 mL) was added in the mixture and was kept overnight. After filtration, the filter cake was washed thoroughly with ethyl ether and was purified by recrystallization with water/acetone (1:2) to obtain meso-tetrakis-(1-methyl-4-pyridyl)manganese porphyrin (MnTM4PyP) with 80% yield. The other metalloporphyrins could be synthesized with similar procedures by replacing other metal ions. The spectral and analysis data of metalloporphyrins catalysts were listed as following. [MnTM4PyP]4+. EI-MS: m/z 731. UV-vis (H₂O): λ_{max} , nm (log ε) 464 (2.48), 559 (1.25). IR (KBr): v, cm⁻¹ 1640, 1009. Anal. calcd. for $C_{44}H_{28}N_8Mn$: C, 72.22; H, 4.96; N, 15.31. Found: C, 71.79; H, 4.92; N, 15.16. [CoTM4PyP]⁴⁺. EI-MS: *m/z* 735. UV-vis (H₂O): $λ_{max}$, nm (log ε) 418 (2.47), 539 (0.93). IR (KBr): ν, cm⁻¹ 1640, 1005. Anal. calcd. for C₄₄H₂₈N₈Co: C, 71.83; H, 4.93; N, 15.23. Found: C, 71.43; H, 4.72; N, 14.96. $[FeTM4PyP]^{4+}$. EI-MS: *m/z* 732. UV-vis (H₂O): λ_{max} , nm (log ε) 415 (2.84), 543 (1.23). IR (KBr): ν, cm⁻¹ 1638, 1002. Anal. calcd. for C₄₄H₂₈N₈Fe: C, 72.13; H, 4.95; N, 15.29. Found: C, 72.32; H, 4.95; N, 15.31.

Preparation procedures of montmorillonite interlayerfixed metalloporphyrins

A mixture of 100 mg *meso*-tetrakis-(1-methyl-4pyridyl)metalloporphyrin (Mn, Co, Fe) and montmorillonite (1 g) in 0.1 M nitric acid (100 mL) was submitted to reflux and stirred for 5 h. Then, the mixture was slowly cooled at room temperature. The solid was filtered, washed with water and ethanol for several times. And the solid was dried in vacuum at 80 °C. The amount of metalloporphyrins adsorbed into clay was quantified by measuring the amount of MTM4PyP (M=Mn, Co, Fe) in the nitric acid and filtrate by Atomic Absorption Spectrum (Shimadzu AA2580).

General procedures of the aerobic epoxidation

A 20 mL Schlenck flask was charged with cyclohexene (2 mmol), catalyst (0.02 g), acetonitrile (4 mL), isobutyraldehyde (6 mmol), 0.2 mmol naphthalene (inert internal standard) and then the mixture was stirred at room temperature. Dioxygen was bubbled through the solution. The consumption of the starting styrene and formation of products was monitored by GC (Shimadzu GC-2010 plus) or GC-MS (Shimadzu GCMS-QP2010).

For the recycling experiments, the catalyst was recovered by centrifugation and first washed with water (5 mL) for 5 times, and then with acetonitrile (10 mL) to remove the occluded reactants and products. After washing, the acetonitrile solution was checked for the existence of reactants/products using gas chromatography. The recycled catalysts were then dried in vacuum at 80 $^{\circ}$ C for 6 h and re-used using the same experimental conditions as described above.

CONCLUSION

In conclusion, highly efficient epoxidation of olefins by molecular oxygen in the presence of montmorillonitesupported metalloporphyrins has been reported. The cationic *meso*-tetrakis-(1-methyl-4-pyridyl) (TM4PyP) porphyrins (Co, Mn and Fe) immobilized into montmorillonite were confirmed by diffuse reflectance spectra, infrared, X-ray diffraction, nitrogen UV adsorption isotherm and scanning electron microscopy. MnTM4PyP-MT is considerably more selective than cobalt and iron porphyrins catalysts for the aerobic epoxidation of olefins. The catalytic system is highly efficient for the substrates with larger molecule bulk due to the clay basal spacing. The catalyst could be reused consecutively five times without significant loss of activity.

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REFERENCES

- a) Rubajlo VL, Maslov SA and Zaikov GE. *Liquid Phase Oxidation of Unsaturated Compounds*, Nova Science Publishers: Hauppauge, 1993. b) Xia QH, Ge HQ, Ye CP, Liu ZM and Su KX. *Chem. Rev.* 2005; **105**: 1603. c) McGarrigle EM and Gilheany DG. *Chem. Rev.* 2005; **105**: 1563. d) Wong OA and Shi Y. *Chem. Rev.* 2008; **108**: 3958.
- a) Li Z, Xia CG and Ji M. *Appl. Catal. A* 2003; 252: 17. b) Castaman ST, Nakagaki S, Ribeiro RR, Ciuffi KJ and Drechsel SM. *J. Mol. Catal. A* 2009; 300: 89. c) Murakami Y and Konishi K. *J. Am. Chem. Soc.* 2007; 129: 14401.
- a) De Paula R, Simoes MMQ, Neves MGPM and Cavaleiro JAS. *Catal. Commun.* 2008; **10**: 57. b) Stephenson NA and Bell AT. *J. Mol. Catal. A* 2007; **275**: 54. c) Stephenson NA and Bell AT. *Inorg. Chem.* 2006; **45**: 2758.
- a) Faria AL, Mac Leod TCO and Assis MD. *Catal. Today* 2008; **133**: 863. b) Moghadam M, Tangestaninejad S, Mirkhani V, Mohammadpoor-Baltork I and Moosavifar M. *J. Mol. Catal. A* **2009**; 302: 68. c) Ye YJ, Zhou XT, Huang JW, Cai JH, Wu WH, Yu HC, Ji HB and Ji LN. *J. Mol. Catal. A* 2010; **331**: 29.
- a) Tangestaninejad S, Moghadam M, Mirkhani V and Kargar H. Ultrason. Sonochem. 2006; 13: 32.
 b) Gao BJ, Wang RX and Zhang Y. J. Appl. Polym. Sci. 2009; 112: 2764. c) Ferrand Y, Daviaud R, Le Maux P and Simonneaux G. Tetrahedron-Asymmetry 2006; 17: 952. d) Burri E, Leeder SM, Severin K and Gagne MR. Adv. Synth. Catal. 2006; 348: 1640. e) Mirkhani V, Moghadam M, Tangestaninejad S and Kargar H. Appl. Catal. A 2006; 303: 221.
 f) Zhang JL, Huang JS and Che CM. Chem. Eur. J. 2006; 12: 3020.
- a) Smith JRL, Iamamoto Y and Vinhado FS. J. Mol. Catal. A 2006; 252: 23. b) Mirkhani V, Moghadam M, Tangestaninejad S, Mohammdpoor-Baltork I, Kargar H and Araghi M. Appl. Catal. A 2009; 353: 61. c) Eriksson KLE, Chow WWY, Puglia C, Backvall JE, Gothelid E and Oscarsson S. Langmuir 2010; 26: 16349. d) Ghiaci M, Molaie F, Sedaghat

ME and Dorostkar N. *Catal. Commun.* 2010; **11**: 694.

- a) Rahiman AK, Bharathi KS, Sreedaran S, Rajesh K and Narayanan V. *Inorg. Chim. Acta* 2009; 362: 1810. b) Zimowska M, Michalik-Zym A, Poltowicz J, Bazarnik M, Bahranowski K and Serwicka EM. *Catal. Today* 2007; 124: 55. c) Rahiman AK, Rajesh K, Bharathi KS, Sreedaran S and Narayanan V. *Appl. Catal. A* 2006; 314: 216.
- Espinosa M, Pacheco S, Vargas S, Estevez M, Llanos ME and Rodriguez R. *Appl. Catal. A* 2011; 401: 119.
- 9. Huang G, Luo J, Cai CC, Guo YA and Luo GW. *Catal. Commun.* 2008; **9**: 1882.
- Bhattacharyya KG and Sen Gupta S. Adv. Colloid. Interfac. 2008; 140: 114.
- a) Haber J, Matachowski L, Pamin K and Poltowicz J. *Catal. Today* 2004; **91–92**: 195. b) Machado AM, Wypych F, Drechsel SM and Nakagaki S. *J. Colloid Interf. Sci.* 2002; **254**: 158. c) Hassanein M, Gerges S, Abdo M and El Khalafy S. *J. Mol. Catal. A* 2005; **240**: 22.
- 12. Kameyama H, Narumi F, Hattori T and Kameyama H. *J. Mol. Catal. A* 2006; **258**: 172.
- a) Zhou XT, Tang QH and Ji HB. *Tetrahedron Lett.* 2009; **50**: 6601. b) Zhou XT, Ji HB, Xu HC, Pei LX, Wang LF and Yao XD. *Tetrahedron Lett.* 2007; **48**: 2691.
- 14. Cai JH, Huang JW, Zhao P, Ye YJ, Yu HC and Ji LN. *J. Sol-Gel Sci. Techn.* 2009; **50**: 430.
- Shi BL, Scobie M and Boyle RW. *Tetrahedron Lett.* 2003; 44: 5083.
- a) Fu B, Yu HC, Huang JW, Zhao P, Liu J and Ji LN. J. Mol. Catal. A 2009; 298: 74. b) Huang G, Luo ZC, Xiang F, Cao X, Guo YA and Jiang YX. J. Mol. Catal. A 2011; 340: 60. c) Ye YJ, Huang JW, Cai JW, Yu HC, Wu WH, Zhou XT, Ji HB and Ji LN. Transit. Metal. Chem. 2010; 35: 627.
- a) Meunier B, de Visser SP and Shaik S. Chem. Rev. 2004; **104**: 3947. b) Meunier B. Biomimetic Oxidations Mediated by Metal Complexes, Imperial College Press: London, 2000. c) Ji HB and Zhou XT. In Biomimetics, Learning from Nature; Biomimetic Homogeneous Oxidation Catalyzed by Metalloporphyrins with Green Oxidants; In-Tech publishing: Vienna, 2010.
- 18. Zhou XT and Ji HB. Chem. Eng. J. 2010; 156: 411.