Highly Efficient Activation of Molecular Oxygen with Nanoporous Metalloporphyrin Frameworks in Heterogeneous Systems

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Activation of molecular oxygen is a subject of increasing interest in relation to the bioinspired function mimicry of cyctochrome P450 and the development of highly active catalysts for oxidation reactions. In this sense, metalloporphyrin is a well-established motif with a similar active center to that of cyctochrome P450 and has been developed for various oxidation reactions.[1] Studies of metalloporphyrin catalysts have mainly focused on homogeneous systems with the aim to improve activity in the activation of molecular oxygen via the molecular design along with precise synthesis of porphyrin macrocycles. In contrast, examples of metalloporphyrin-based heterogeneous catalysts have been very limited to few metalloporphyrin-based metal-organic frameworks (MOFs)[2] and porous polymers[3]. In the case of MOFs, the framework is fragile to break down once the crystalline solvents are lost during reactions, which deteriorates their further utility in catalysis. Therefore, the rational design of metalloporphyrin-based heterogeneous catalysts is a challenging subject in relation to the activation of molecular oxygen.

Conjugated micro- and mesoporous polymers (CMPs) are a class of porous frameworks with 3D polymer frameworks and high surface areas.[4–8] CMPs are intriguing platforms for the molecular design of porous skeletons because they allow elaborate control of the frameworks and tuning of the pore parameters.[4] One of the remarkable characteristics of CMPs is their crosslinked 3D molecular skeletons. These structural features offer an opportunity for creating robust heterogeneous catalysts, provided that the catalytic sites can be covalently integrated into the CMP skeleton.[8b]

Here, we report an excellent heterogeneous system using iron(III) porphyrin-based CMP (**Scheme 1**, FeP-CMP) for the activation of molecular oxygen. We highlight that FeP-CMP can activate molecular oxygen for highly efficient epoxidation of olefins[9] with large turn over number (TON) and turn over frequency (TOF) values, high selectivity, and adaptability to a broad range of substrates including alkyl, aromatic, and cyclic olefins. FeP-CMP is robust for recycling and allows the activation of molecular oxygen under ambient conditions. The porous framework outperforms the monomeric metalloporphyrin and nonporous metalloporphyrin polymer analogues. With these outstanding features, FeP-CMP offers a breakthrough for the activation of molecular oxygen.

FeP-CMP (Scheme 1a,b) was synthesized by Suzuki cross-coupling polycondensation of iron(III) 5,10,15,20-tetrakis-(4'-bromophenyl)porphine and 1,4-benzene diboronic acid in the presence of $Pd(PPh_3)_4$ as a catalyst under alkaline conditions. FeP-CMP was unambiguously characterized by various instrumental analyses.[8b] As a control for FeP-CMP, FeP-LP with a linear polymer structure was synthesized (Scheme 1). The average molecular weight (M_w) of FeP-CMP was estimated to be 490 000, which corresponds to a polymerization degree of 570. From field-emission scanning electron microscopy (FE-SEM) images, FeP-CMP adopts flake-shaped monoliths with sizes of 1–2 μm (**Figure 1**a–e). Of further interest is the fact that each monolith consists of layers of much smaller flakes with a size of approximately 100–200 nm (Figure 1f). Such a hierarchical structure from a molecular level framework to nanoscale layers and further to micrometer scale monoliths is highly interesting because it is common to biological catalytic systems. High-resolution transmission electron microscopy (HR-TEM) measurements reveal the presence of nanometer-scale pores (Figure 1g,h). The Brunauer–Emmett–Teller (BET) surface area is as high as 1270 $m^2\ g^{-1}$, while the pore widths and pore volume calculated by nonlocal density functional theory are 0.47 nm, 2.69 nm, and 1.18 $cm^3\ g^{-1}$, respectively. It is noteworthy that the surface area is much higher than that of metalloporphyrin-based crystalline MOFs (typically ≈500 $m^2\ g^{-1}$).[2] These results suggest that the amorphous FeP-CMP possesses dense catalytic sites, holds inherent nanopores, and has large surface areas. As a high surface area material, FeP-CMP, which is comprised largely of metalloporphyrin moieties in the skeleton, has an exceptionally high loading of catalytic sites, which is in sharp contrast to strategies involving porphyrin immobilization on other frameworks such as silica.

To elucidate the porous structure, we first carried out semiempirical calculations at the PM3 level and then performed further calculations using hybrid density functional theory (DFT) at the B3LYP/3–21G level using the Gaussian 03 program.[[12]] We performed the calculations on two typical frameworks of free-base porphyrin. The elementary closed tetragon gives a nearly flat structure with a pore width of 2.4 nm (**Figure 2**a).

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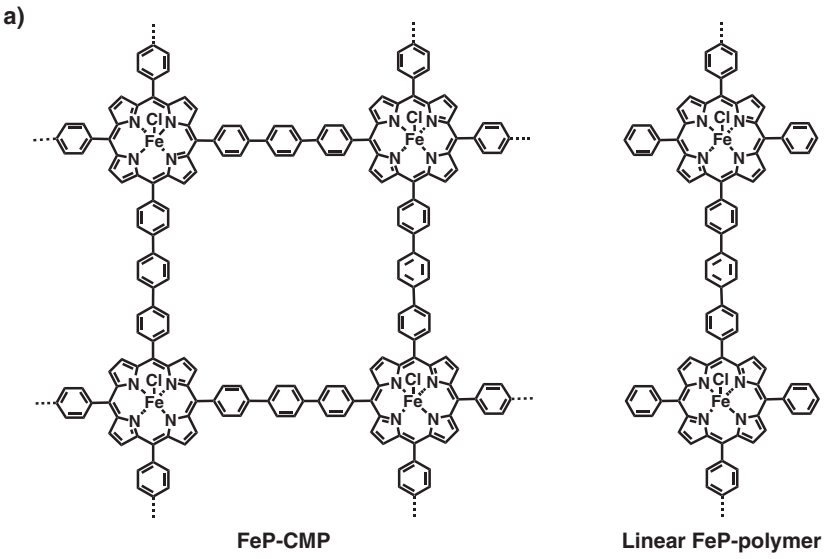


Scheme 1. a) Structure of the microporous iron(III) porphyrin framework FeP-CMP and its linear polymer analogue FeP-LP. b) Schematic representation of the aerobic epoxidation of various olefins catalyzed by FeP-CMP under ambient conditions. The tetragonal FeP-CMP structure is a simple representation and is not meant to imply an infinite 2D structure (purple: porphyrin; blue: phenyl; green: N; red: Fe).

This tetragonal structure accounts for the presence of mesopores in FeP-CMP. The eight-member porphyrin framework significantly twists between the two flat tetramer counterparts and this distortion eventually leads to the growth of the CMPs into an amorphous and 3D network (Figure 2b). Such a porous framework is permanent because the skeleton is crosslinked and both the phenylene connections and porphyrin units are conformationally rigid.

Epoxidation reactions were carried out under the same conditions as those used for typical systems such as the Mukaiyama Ni(II) catalyst, employing a combination of isobutyraldehyde (IBA) and O_2.[6b,e] IBA/O_2 has been well studied with various catalysts for aerobic oxidations including epoxidation, C–H oxidation,[10] and Baeyer–Villiger oxidation.[11]

FeP-CMP exhibited outstanding catalytic performance for the selective epoxidation of *trans*-stilbene with IBA/O_2. Under ambient pressure (1 atm) and temperature (298 K) with 1 mg FeP-CMP (sub-ppm order Fe), *trans*-stilbene oxide was produced in 98% conversion with 97% selectivity after 9 h without any sign of the formation of *cis*-stilbene oxide (**Table 1**). Benzaldehyde (3%) was the sole byproduct, and no diol or ester overoxidation compounds were observed. Similar to the typical systems,[9b–d] FeP-CMP also requires the coexistence of IBA and O_2; epoxidation was completely halted in the absence of either IBA or O_2. On the other hand, in the absence of FeP-CMP, the conversion dropped significantly to only 30% after 24 h, which is much lower than that in the presence of FeP-CMP. This result indicates the catalytic nature of FeP-CMP. We noticed that the catalytic performance could be enhanced in the presence of an excess amount of IBA. For example, the conversion increased from 46% (24 h) to 96% (17 h) when the molar ratio of IBA/*trans*-stilbene was increased from 1 to 2. Notably, when the molar ratio was 3, 97% conversion was achieved in the much shorter time of 9 h.

In control experiments, a monomeric metalloporphyrin complex used as a homogeneous catalyst showed low activity (Table 1).[9e] Therefore, the porous framework outperforms the monomeric metalloporphyrin calalyst. We postulated that the enhanced activity of FeP-CMP may be related to its porous structure. Thus, we prepared FeP-CMP samples with different surface areas and pore sizes and utilized them in the epoxidation under otherwise identical conditions. Surprisingly, all FeP-CMP samples displayed catalytic activity with high selectivity. This observation suggests that the catalytic CMP skeletons are excellent for the selective epoxidation of olefins. The catalytic activity is highly dependent on the surface area. An increase in the activity was observed as the surface area of the catalyst increased. The pore size distribution had less of an effect on the catalytic activity. This result is reasonable because the epoxidation takes place on the skeleton, which consists of highly dense active sites. Consequently, a large surface area can facilitate the epoxidation reaction. The positive surface area effect is encouraging for the development of porous heterogeneous catalysts and has implications for designing catalytic frameworks based on CMPs. Along this line, we synthesized a linear control FeP-LP without porous structure and utilized it as a

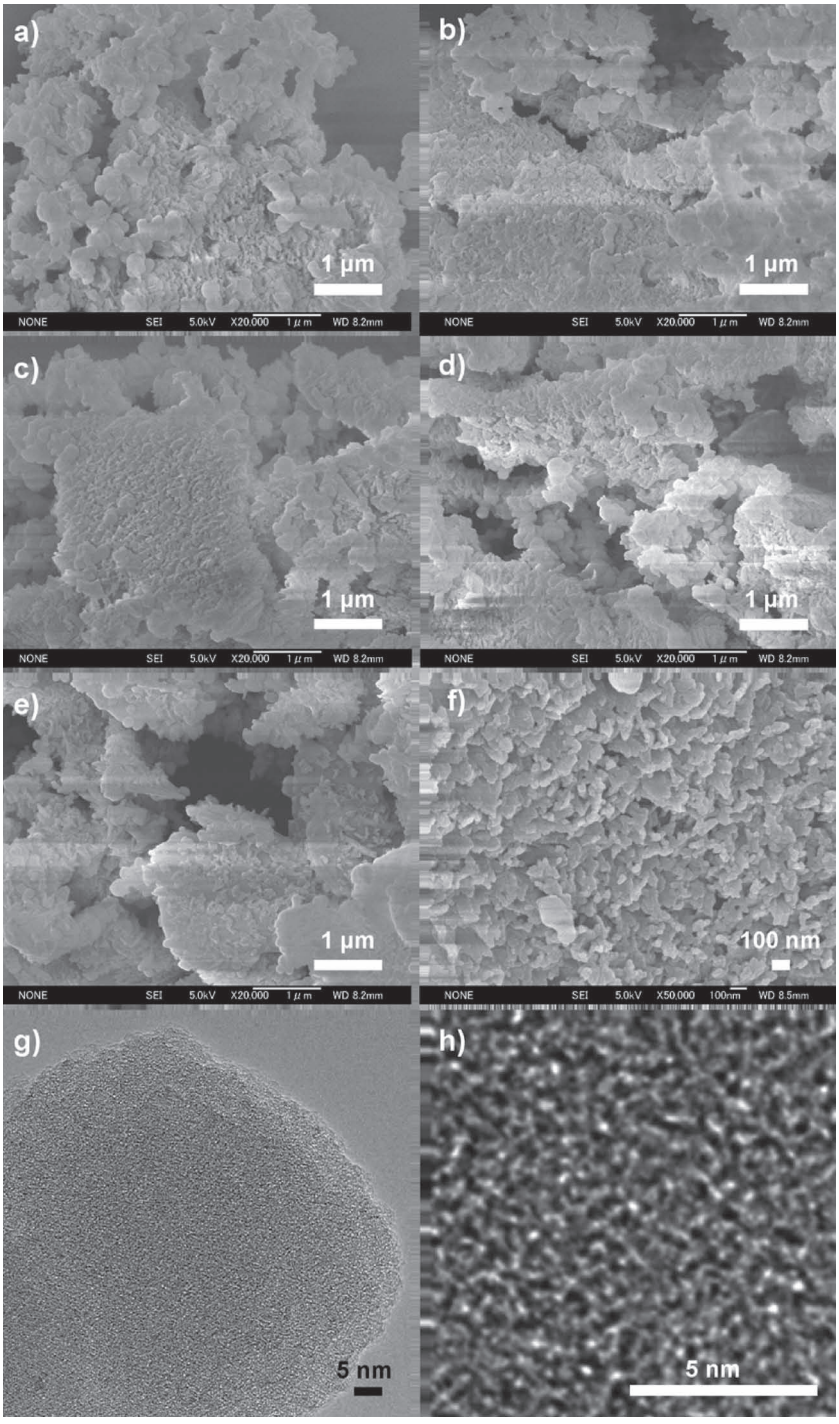


Figure 1. a–f) FE-SEM images and g,h) HR-TEM images of FeP-CMP.

catalyst in the epoxidation. FeP-LP exhibited a similar low activity to that of the monomeric metalloporphyrin complex. Therefore, the porous framework again outperforms the nonporous metalloporphyrin polymer analogues. This control experiment supports the importance of porous structure in achieving high catalytic activity. Aerobic epoxidation under an ambient air atmosphere is very versatile. Thus, we replaced O_2 with air in the epoxidation reaction. Remarkably, the reaction proceeded efficiently to afford nearly the same activity and selectivity as the reaction with O_2 (Table 1).

Epoxidation using IBA/O_2 has been reported to proceed via a free radical chain mechanism.[9f] We examined the presence of radical species using hydroquinone as a radical scavenger (Table S1, Supporting Information). Addition of hydroquinone to a reaction after 4 h resulted in the inhibition of the epoxidation reaction and simultaneous inhibition of the production of *trans*-stilbene oxide (**Figure 3**; ▪ symbols). More dramatically, when hydroquinone was present in the reaction system from the beginning, the epoxidation reaction did not occur at all (▪). The sharp difference in the results obtained in the presence (○) and absence (•) of hydroquinone suggests that the reaction involves radical species. The nature of the activation process is not yet fully clear but may be related to the high-valent metal-oxo porphyrin complex, as suggested by the characteristic green color observed for the catalyst during the reaction. These features are similar to the system catalyzed by a monomeric metalloporphyrin.[9e]

Based on the above findings, we next examined the scope of substrates for the epoxidation reaction. We chose three classes of olefins as representatives: terminal olefins 1-octene and 1-heptene; internal olefins 2-octene; and 2-norborene and cyclic olefins cycloheptene, cyclooctene, and cyclododecene (**Table 2**). Even in the case of the terminal olefins, 1-octene and 1-heptene, which require relatively high activation energies in the epoxidation when compared with internal olefins, FeP-CMP also displayed good catalytic performance with conversion of about 60% and nearly 100% selectivity after 24 h. The conversions of the internal olefins were much better. For example, 2-norborene was nearly quantitatively transformed to its epoxide after 20 h. Similar good results were also obtained for cyclic olefins with conversions up to 99%. Notably, for all of these olefins, FeP-CMP displayed excellent selectivity with the highest value greater than 99%. These results are superior to those of the recently reported excellent epoxidation catalyst of Ru-loaded SiO_2 particles (40–90% selectivity) and other catalysts using IBA/O_2.[9b–e] We then investigated the epoxidation of the aromatic terminal olefin styrene. Styrene was transformed to styrene oxide with a conversion of 55% (TON = 550) and a selectivity of 69% after 24 h. This result is again superior to that of the Ru-loaded SiO_2 particles under similar conditions (e.g., TON = 25, selectivity = 38% after 48 h).[9f] All of these results indicate that FeP-CMP is widely applicable for catalyzing the

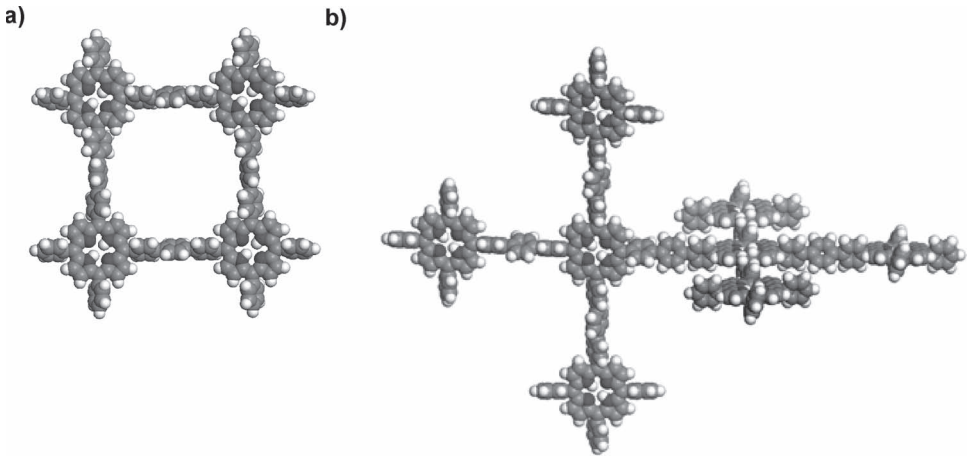


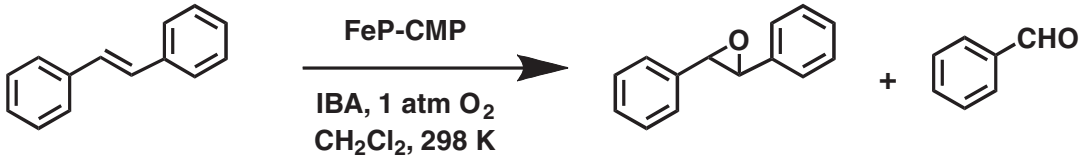
Figure 2. Simulated structures of typical molecular frameworks. a) Close tetragon and b) eight-membered porphyrin framework simulated using hybrid DFT at the B3LYP level and with the 3–21G basis set using Gaussian 03.

aerobic epoxidation of various olefins and features high efficiency and excellent selectivity.

FeP-CMP is an excellent reusable catalyst. Simple centrifugation allowed the separation of FeP-CMP from the reaction solution. We collected the FeP-CMP catalyst after the reaction and reused it in the next round of epoxidation reaction. Due to the covalently crosslinked framework, FeP-CMP maintained its catalytic skeleton structure and showed robust recycling capability with well-retained activity and selectivity after six cycles (**Table 3**). FeP-CMP after six cycles displayed a BET surface area of 1255 m^2 g^{-1}, very close to that of the pristine sample (1270 m^2 g^{-1}). Leaching experiments on the reused FeP-CMP using an inductive coupled plasma (ICP) atomic emission spectrometer showed that the Fe content (3.27 wt%) was the same as that present in the original catalyst (3.27 wt%). In addition, upon centrifugation of the reaction mixtures, the supernatants were monitored by electronic absorption spectroscopy and no traces of metalloporphyrin or related decomposition products were observed.

Based on above results, we investigated the capability of FeP-CMP for large-scale synthesis. Using 0.41 mol *trans*-stilbene in the presence of 6×10^{-9} mol [Fe], the epoxidation reaction

Table 1. Catalytic epoxidation of *trans*-stilbene by FeP-CMP under different conditions.[a)]



1 2

Entry	Catalyst	Surface area [m^2 g^{-1}]	Time [h]	Conversion [%]	Selectivity [%]		TON
					1	2	
1[a)]	FeP-CMP	1270	9	98	97	3	980
2[b)]	–	–	24	30	92	8	300
3[c)]	FeP-CMP	1270	24	n.r	–	–	–
4[d)]	FeP-CMP	1270	24	n.r	–	–	–
5[e)]	FeP-CMP	1270	24	46	91	9	460
6[f)]	FeP-CMP	1270	17	96	96	4	960
7[g)]	FeP-CMP	1270	24	90	95	5	900
8[a)]	FeP-CMP	531	15	96	97	3	970
9[a)]	FeP-CMP	233	12	91	96	4	940
10[a)]	TPPFeCl	–	20	85	82	18	850
11[a)]	FeP-LP	–	20	86	81	19	860

[a)]FeP-CMP (5.86×10^{-7} mol Fe), solvent (3 mL), 298 K, O_2 (1 atm). Fe:*trans*-stilbene:IBA = 1:1000:3000 (molar ratio); [b)]in the absence of catalyst; [c)]under N_2 (1 atm); [d)]in the absence of IBA; [e)]Fe:*trans*-stilbene:IBA = 1:1000:1000 (molar ratio), [f)]Fe:*trans*-stilbene:IBA = 1:1000:2000 (molar ratio); [g)]in air (1 atm).

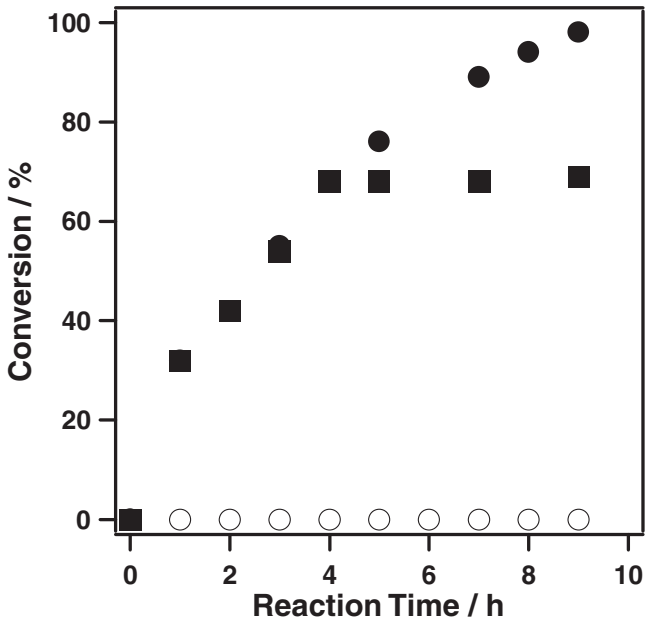


Figure 3. Effect of hydroquinone on epoxidation of *trans*-stilbene catalyzed by FeP-CMP. •: no hydroquinone; ▪: hydroquinone added after 4- h reaction; ○: hydroquinone present from the beginning)

yielded 78 g (0.4 mol) of *trans*-stilbene oxide after 120 h. Therefore, the TON and TOF of FeP-CMP were extremely high at 6.7×10^7 and 9.3×10^3 min^{-1}, respectively. These values are close to these of the enzyme cytochrome P450. All of the above excellent catalytic features mark FeP-CMP as a top-class catalyst.

In conclusion, we have developed a nanoporous metalloporphyrin framework for the activation of molecular oxygen and demonstrated its utility in highly efficient aerobic epoxidation of olefins under ambient conditions. FeP-CMP achieves high activity, excellent selectivity, broad substrate applicability, good reusability, and enzyme-like large TON and TOF values. The porous framework outperforms the monomeric metalloporphyrin and nonporous metalloporphyrin polymer analogues. Our strategy also highlights a new approach for the design of heterogeneous catalysts with built-in catalytic skeletons and inherent nanopores; these structural features together with the excellent catalytic performance were not accomplished by other heterogeneous and homogeneous catalysts reported so far.

Table 2. Catalytic epoxidation of various olefins by FeP-CMP. Conditions: 1 mg catalyst (5.86×10^{-7} mol Fe), Fe:olefin:IBA = 1:1000:3000 (molar ratio), CH_2Cl_2 (3 mL), 298 K, 1 atm O_2.

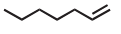
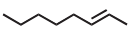
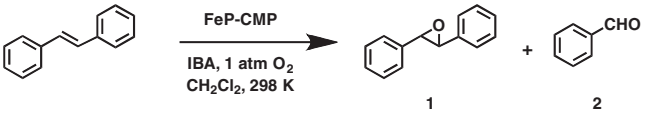
Entry	Substrate	Time [h]	Conversion [%]	Selectivity[%]		TON
				epoxide	others	
12		24	62	>99	<1	620
13		24	58	>99	<1	580
14		24	76	>99	<1	760
15		20	99	>99	<1	>990
16		24	95	>99	<1	950
17		20	95	97	3	580
18		20	99	>99	<1	>990
19		24	55	69	31	550

Table 3. Recycle of FeP-CMP for catalytic epoxidation of *trans*-stilbene.



Run	Time [h]	Conversion [%]	Selectivity [%]	
			1	2
1	6	99	96	4
2	6	97	96	4
3	6	98	97	3
4	6	99	96	4
5	6	98	97	3
6	6	98	97	3

Experimental Section

The epoxidation of olefins was carried out in 25-mL pyrex glass reactor equipped with a mechanical stirrer. In a typical protocol, FeP-CMP (1 mg, 0.586 μmol; the same sample as reported previously[5b]), dichloromethane (3 mL), olefins (58.6 μmol), and IBA (175.8 μmol) were added to the reactor and the resulting mixture was stirred under an atmosphere of oxygen at 298 K. The solution was periodically analyzed by gas chromotography mass spectrometry (GC-MS; Shimadzu GC-QP2010plus) at appropriate intervals. All products were identified by the comparison of GC retention times and mass spectra with those of the authentic samples. Selectivity, conversion, TON, and TOF were calculated using the following equations: selectivity = (produced epoxide)/(consumed olefin) × 100; conversion = (consumed olefin)/(initial olefin) × 100; TON = (consumed olefin)/(amount of Fe); and TOF = TON/(reaction time).

For recycling experiments, the reaction mixture was centrifuged for 30 min after the reaction and the liquid layer was siphoned out. The residual solid was washed with anhydrous dichloromethane and centrifuged twice. Dichloromethane, *trans*-stilbene, and IBA were then added to the reactor for the next reaction, which was run under otherwise identical conditions.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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