CMPs as Scaffolds for Constructing Porous Catalytic Frameworks: A Built-in Heterogeneous Catalyst with High Activity and Selectivity Based on Nanoporous Metalloporphyrin Polymers

Long Chen,[†,§] Yong Yang,[†,§] and Donglin Jiang*,[†,‡]

Department of Materials Molecular Science, Institute for Molecular Science, 5-1 Higashiyama, Myodaiji, Okazaki 444-8787, Japan and PRESTO, JST, Japan

Received April 5, 2010; E-mail: jiang@ims.ac.jp

Abstract: This article describes the synthesis and functions of a porous catalytic framework based on conjugated micro- and mesoporous polymers with metalloporphyrin building blocks (FeP-CMP). FeP-CMP was newly synthesized via a Suzuki polycondensation reaction and was developed as a heterogeneous catalyst for the activation of molecular oxygen to convert sulfide to sulfoxide under ambient temperature and pressure. FeP-CMP is intriguing because the polymer skeleton itself is built from catalytic moieties and serves as built-in catalysts, bears inherent open nanometer-scale pores that are accessible for substrates, and possesses large surface areas (1270 $m^2\ g^{-1}$) that facilitate the transformation reaction. It is highly efficient with high conversion (up to 99%) and a large turnover number (TON = 97,320), is widely applicable to various sulfides covering from aromatic to alkyl and cyclic substrates, displays high selectivity (up to 99%) to form corresponding sulfoxides, and is highly chemoselective for the oxidation of a sulfide group even in the coexistence of other oxidative functionalities. Owing to the covalent linkages between catalytic sites in the frameworks, FeP-CMP can be recycled with good retention of its porous structure and allows for large-scale transformation. These unique characteristics clearly originate from the covalent porous catalytic framework structure and demonstrate the usefulness of CMPs in the exploration of built-in heterogeneous catalysts, a new potential of these materials that have thus far been reported to exhibit noteworthy gas adsorption functions.

Introduction

Conjugated micro- and mesoporous polymers (CMPs) are a new class of porous materials with an amorphous organic framework.[1–5] CMPs are unique owing to their high flexibility in the molecular design of components and the control of pore parameters. Systematic studies on the porous structures of CMPs have successfully demonstrated their utility for gas adsorption.[1–5] Recently, CMPs have been developed to load metal nanoclusters for the synthesis of heterogeneous catalysts.[2i,3f,g,4d] Because the polymer skeleton does not incorporate any catalytic sites, post-

† Institute for Molecular Science.
‡ JST.
§ These authors contributed equally.

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Chart 1[a]
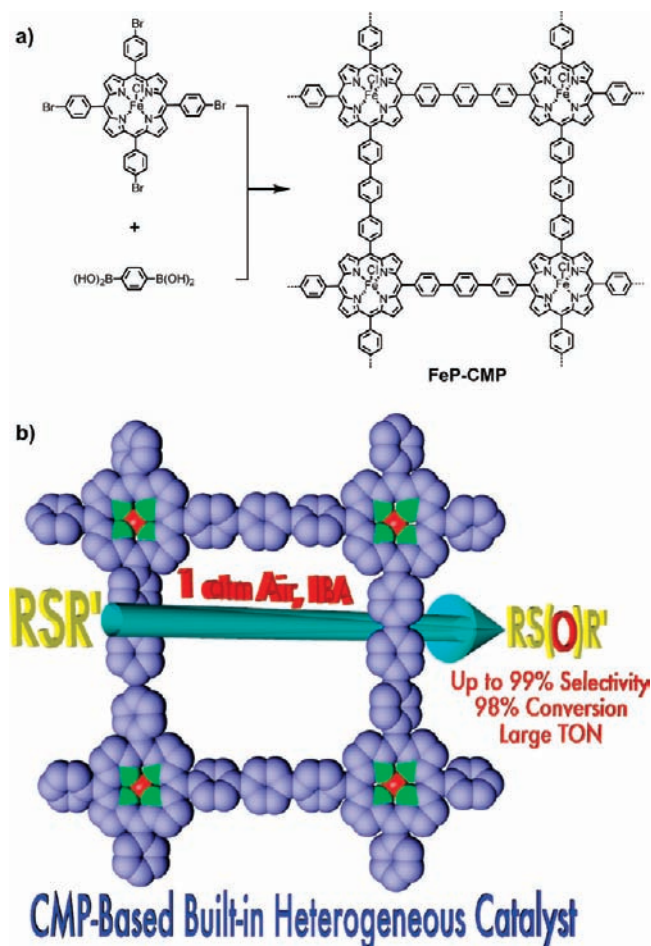
[a] (a) Schematic representation of the synthesis of nanoporous polymer with metalloporphyrin built-in skeleton (FeP-CMP). (b) Schematic representation of the transformation of sulfides to sulfoxides catalyzed by FeP-CMP.

treatment of CMPs via noncovalent interactions is a prerequisite for loading catalysts in the pores. In contrast to this approach, we are interested in the exploration of covalently built-in catalysis systems based on CMPs. If catalytic functionalities could be integrated into the skeleton of CMPs, one would have a chance to create a novel porous polymer in which the skeleton itself serves as the catalysts and the pores provide spaces for the transformation. Herein we report a strategy for the synthesis of a new type CMP-based heterogeneous catalyst that consists of an inherent porous framework with built-in catalytic sites in the skeleton (Chart 1, FeP-CMP). We utilized an iron(III) porphyrin derivative, a well established catalytic species, as the building blocks and synthesized an iron(III) porphyrin-based CMP with large surface area nanometer-scale pores. FeP-CMP is significant in that it bears dense built-in catalytic sites in the covalent framework, contains inherent nanopores that are accessible to substrates, and has large surface areas to facilitate the transformation reactions. We demonstrated that FeP-CMP is highly active and highly selective for catalyzing the oxidation of sulfides to the corresponding sulfoxides with molecular oxygen under mild conditions (ambient temperature and pres-

sure). FeP-CMP is widely applicable to various sulfide substrates, is chemoselective, is readily recycled, and allows for large-scale transformations. Owing to its large turnover number (TON = 97 320), FeP-CMP represents an artificial catalyst with an activity comparable to that of natural enzymes.

Sulfoxides are versatile intermediates in the preparation of valuable compounds such as pharmaceuticals, agrochemicals, and other fine chemicals.[6] Selective oxidation of sulfides to the corresponding sulfoxides, therefore, is one of the most fundamental and challenging processes from both a synthetic and industrial point of view. This transformation is conventionally achieved using stoichiometric amounts of organic or inorganic oxidants.[7] In these cases, however, the use of toxic reagents or the production of huge amounts of heavy metal wastes is unavoidable, making these processes environmentally unfriendly. The use of molecular oxygen as a terminal oxidant under ambient conditions is very attractive because it is readily available and environmentally benign, as water is the sole byproduct. Several metal-based catalysts have been developed to achieve the oxidation of sulfides with molecular oxygen as the oxidant, but the reactions are relatively slow and require both a high pressure and an elevated temperature.[8] On the other hand, coordination polymers based on Sc, Y, and La metal sources and metal−organic framework consisting of Sc ions and terephthalate ligands have been developed for the oxidation of sulfides in the presence of H_2O_2, but these reactions require nearly stoichiometric amounts of the materials.[9a,b] In relation to this, a metal−organic framework consisting of chiral Zn-lactate clusters further interlinked by terephthalate units displayed a specific surface area of 190 m^2 g^{-1} with pores of ~5 Å and exhibited a quite low conversion of 3−64% in the presence of urea hydroperoxide as an oxidant.[9c] Therefore, it is clear that the development of green, efficient, selective and recyclable catalysts for sulfide oxidation using molecular oxygen as an oxidant is an elusive goal and remains a challenge.

Porphyrin derivatives have been developed for the synthesis of porous materials including hydrogen-bonded supramolecular solids, polymeric materials, and metal−organic frameworks (MOFs), with the aim of creating catalytic functionalities.[10] However, only two examples of these MOFs have been found to exhibit catalytic activities.[10] Meanwhile, the architecture of MOFs is primarily based on coordination bonds, which results in instability; the porous structure has a high probability of deteriorating when the crystalline solvents are lost or exchanged. On the other hand, immobilization of metalloporphyrin deriva-

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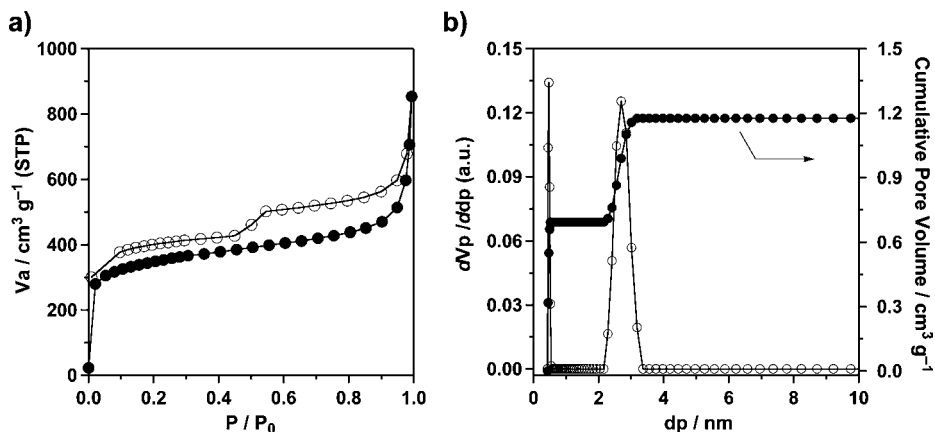
Figure 1. (a) Nitrogen adsorption (●) and desorption (○) isotherm profiles of FeP-CMP at 77 K. (b) Pore size distribution (○) and cumulative pore volume (●) of FeP-CMP by NLDFT modeling on the N_2 adsorption isotherms.

tives within the pores of zeolites or MOFs lowers the substrate accessibility of the pores and eventually results in low catalytic activity.[11] In sharp contrast to these approaches, CMPs, due to their strong covalent bonds, combine a robust catalytic framework together with an open porous structure. CMPs comprised largely of porphyrin moieties in the skeleton are materials with large surface areas that allow for exceptionally high loading of active sites in comparison with strategies involving porphyrin immobilization on other frameworks such as silica. Therefore, the advantages of CMP over other porous materials and coordination polymeric architectures are clear. CMPs constitute permanent pores within catalytic frameworks and allow for efficient and selective catalysis in the pores. Herein we report the first example of metalloporphyrin-based CMPs and wish to highlight a highly efficient, highly selective, and chemoselective heterogeneous catalyst for the transformation of various sulfides to their corresponding sulfoxides with a newly synthesized FeP-CMP (Chart 1a, b).

Experimental Section

THF was distilled over benzophenone ketyl under Ar before use. Other organic solvents for reactions were distilled over appropriate drying reagents under argon or obtained as dehydrated reagents from Kanto Chemicals. Deuterated solvents for NMR measurements were obtained from Cambridge Isotope Laboratories, Inc. Pyrrole, *p*-bromobenzaldehyde, and acetic acid were obtained from Aldrich. Iron(II) chloride tetrahydrate was obtained from Merck Co. IBA

and 1,4-phenyl diboronic acid were obtained from Tokyo Kasei Co. (TCI). Potassium carbonate and tetrakis(triphenylphosphine)palladium(0) were obtained from Kanto Chemicals.

A mixture of [*p*-Br]₄PFe[12] (204 mg, 0.2 mmol; Supporting Information) and 1,4-phenyldiboronic acid (66.4 mg, 0.40 mmol) in 1,4-dioxane (16 mL) was degassed by three freeze−pump−thaw cycles. To the mixture were added an aqueous solution (4.0 mL) of K_2CO_3 (221 mg, 1.6 mmol) and tetrakis(triphenylphosphine)palladium(0) (23.2 mg, 20 μmol). The mixture was degassed by three freeze−pump−thaw cycles, purged with Ar, and stirred at 110 °C for 24 h. Finally, the mixture was allowed to cool at room temperature and poured into water. The precipitate was collected by filtration; thoroughly washed with water, THF, methanol, and acetone; rigorously washed by Soxhlet extraction for 24 h with THF, methanol, and acetone, respectively; and then dried in vacuum to give FeP-CMP (153 mg) as a dark green solid in 92% isolated yield.

Results and Discussion

FeP-CMP was synthesized by the Suzuki−Miyaura cross-coupling polycondensation of an iron(III) tetrakis(4′-bromophenyl)porphyrin derivative ([*p*-Br]₄PFe)[12] and 1,4-phenyldiboronic acid (PDBA) in the presence of Pd(0) as catalyst under alkaline conditions. Such a polycondensation reaction leads to an inherent porous polymer with a built-in iron(III) porphyrin framework. We investigated the polycondensation reaction using different solvent systems including THF/H_2O, toluene/EtOH/H_2O, DMF/H_2O, and dioxane/H_2O, with the aim of achieving large surface areas for the resulting polymers (Figure S1). As an optimal condition, polycondensation in dioxane/H_2O (4/1 in vol.) in the presence of K_2CO_3 as base and Pd(PPh₃)₄ as catalyst allows for the preparation of FeP-CMP with large surface areas in 92% isolated yield (Supporting Information). After repeated rinse with water, THF, methanol, and acetone, FeP-CMP was rigorously washed by Soxhlet extraction for 24 h with THF, methanol, and acetone as solvents, respectively, to remove any entrapped molecules and impurities and then dried under vacuum overnight. Nitrogen sorption isotherm measurements of FeP-CMP at 77 K displayed a typical type-III sorption isotherm curve along with a large adsorption at low pressure ($P/P_0 < 0.1$), which is suggestive of the coexistence of micro- and mesopores in the framework (Figure 1a).[13] The Brunauer−Emmett−Teller (BET) surface area was determined to be as high as 1270 m²

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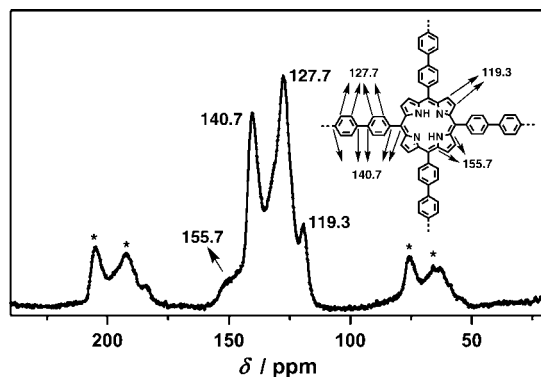(12) Wang, L.; She, Y.; Zhong, R.; Ji, H.; Zhang, Y.; Song, X. *Org. Process Res. Dev.* **2006**, *10*, 757−761.

Figure 2. Solid-state ^{1}H$-^{13}$C CP/MAS NMR spectrum of free-base porphyrin CMP, recorded at a MAS rate of 15 kHz and a CP contact time of 2 ms. Signals with * are sidebands.

g^{-1}, and the pore widths and pore volume calculated by the nonlocal density functional theory (NLDFT) method were 0.47 nm, 2.69 nm, and 1.18 cm^3 g^{-1}, respectively (Figure 1b; ○). The cumulative pore volume profile revealed that the contributions of 0.47-nm-width and 2.69-nm-width pores to the pore volume are 58 and 42%, respectively (●).

FeP-CMP is stable and insoluble in common organic solvents as a result of a cross-linked network (Table S1). Magnetic susceptibility measurements displayed that FeP-CMP at room temperature is at high spin state due to the d^5 electron configuration of Fe(III) (Figure S2). Owing to the high-spin paramagnetic effect, the solid-state ^{1}H$-^{13}$C CP/MS NMR spectrum of FeP-CMP gave only a weak and broad peak (Figure S3). On the other hand, the free-base porphyrin CMP displayed two broad peaks at 127.7 and 140.7 ppm assignable to the phenylene linkages and signals at 119.3 and 155.7 ppm owing to the porphyrin macrocycles (Figure 2). Electronic absorption spectroscopy displayed absorption bands at 470 nm attributed to the Soret band and bands at 576, 622, and 690 nm representing the Q bands of iron(III) porphyrin units, respectively (Figure S4). Fluorescence spectroscopy confirmed that FeP-CMP is not photoluminescent, which excludes the existence of an emissive free-base porphyrin in the polymer skeleton. In relation to this, the IR spectrum of FeP-CMP exhibited the characteristic N$-$Fe vibration band at 1001.8 cm^{-1}, which is close to that of [p-Br]$_4$PFe (998.3 cm^{-1}). A new vibration band appeared at 3025.8 cm^{-1}, which was assignable to the aromatic C$-$H stretching of the phenylene linkages between iron(III) porphyrin units (Figure S5, Table S2). Elemental analyses revealed that the C, H, N, Br, B, Cl, and Fe contents of FeP-CMP are 67.53, 3.80, 5.13, 16.20, 1.98, 2.01, and 3.27 wt %, respectively. X-ray fluorescence spectroscopic measurements also confirmed the existence of Fe, Cl, and Br (Figure S6). These results indicate that iron(III) porphyrin units were covalently integrated into the porous framework of FeP-CMP.[14]

The morphology and crystallinity of FeP-CMP were investigated by field-emission scanning electron microscopy (FE-SEM), transmittance electron microscopy (TEM), and powder X-ray diffraction (PXRD) measurements. FE-SEM images displayed that FeP-CMP adopts plate-shaped monoliths of
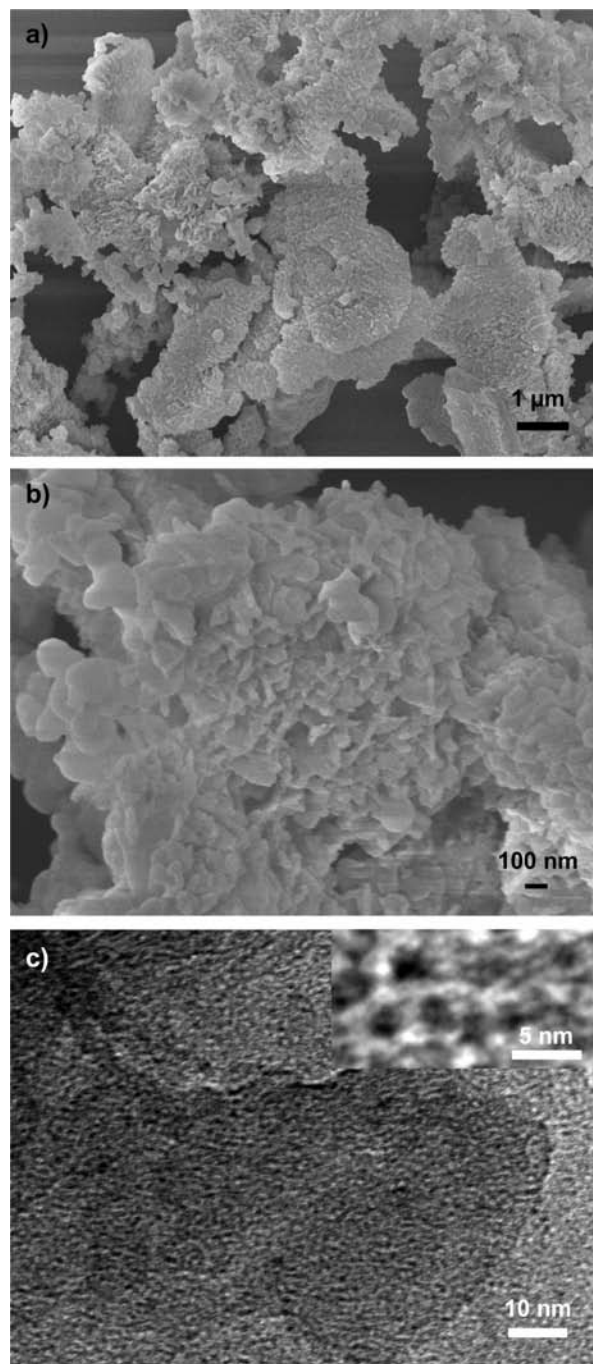
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(14) According to the EDX results (Supporting Information), we estimated roughly the average degree of polymerization to be ∼570, which corresponds to a molecular weight (M_w) of 490 000.

Figure 3. (a, b) FE SEM and (c) HR TEM images of FeP-CMP.

several micrometers in size (Figure 3a, Figure S7). A closer look at high magnification FE-SEM images showed that the monoliths consist of ∼100−300 nm sized elementary platelets, while their surfaces are quite rough (Figure 3b). High resolution TEM images revealed the presence of nanometer-scale cavities (Figure 3c and inset). The PXRD profile confirmed the amorphous character of FeP-CMP (Figure S8). Therefore, FeP-CMP is an amorphous, insoluble, and nanoporous polymer bearing covalently linked iron(III) porphyrin functionalities in the skeleton.

With these structure features in mind, we utilized FeP-CMP as a solid catalyst for the activation of molecular oxygen. We explored this possibility using thioanisole as the substrate in a heterogeneous system. The oxidation of thioanisole (**1a**) using

Table 1. Catalytic Oxidation of Thioanisole by FeP-CMP[a]
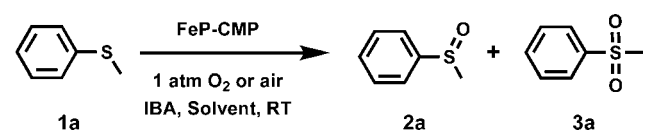
Entry	Solvent	Time [h]	Conversion [%]	Selectivity [%] 2	Selectivity [%] 3	TON
1[b]	EtOAc	4.5	98	99	1	980
2[b]	THF	19	91	89	11	910
3[b]	CH₂Cl₂	22	98	99	1	980
4[b]	CH₃CN	24	97	98	2	970
5[b]	Toluene	1.5	97	98	2	970
6[c]	Toluene	48	0	–	–	–
7[d]	Toluene	48	0	–	–	–
8[e]	Toluene	60	38	>99	<1	380
9[f]	Toluene	48	33	>99	<1	330
10[g]	Toluene	48	70	>99	<1	700
11[h]	Toluene	4	94	99	1	940

[a] Reaction conditions: FeP-CMP (5.86×10^{-7} mol Fe), solvent (3 mL), room temperature, O_2 (1 atm). [b] Fe/thioanisole/IBA = 1/1000/3000 (molar ratio). [c] In the absence of IBA. [d] Under N_2 (1 atm). [e] In the absence of catalyst. [f] Fe/substrate/IBA = 1/1000/1000 (molar ratio). [g] Fe/substrate/IBA = 1/1000/2000 (molar ratio). [h] Under air (1 atm).

FeP-CMP as catalyst (1 mg, 0.586 μmol Fe) was examined with molecular oxygen and isobutyraldehyde[15] (IBA; Fe/**1a**/IBA = 1/1000/3000, molar ratio) in toluene at room temperature. As a result, the corresponding methyl phenyl sulfoxide (**2a**) was obtained in 97% conversion and up to 98% selectivity after 1.5 h (Table 1, entry 5). We then investigated the solvent effects on the oxidation reaction. Among the solvents tested, toluene exhibited the highest activity. EtOAc, THF, CH₂Cl₂, and CH₃CN (entries 1−4) also gave high activities and selectivities but required a longer reaction time than that in toluene. To determine the necessity for each of the components in the oxidation, we studied the reactions in the absence of oxygen, IBA, and FeP-CMP, respectively. The reactions did not proceed at all when the systems consist of oxygen or IBA alone (entries 6 and 7). Furthermore, only 38% of **1a** was converted to **2a** even after a long time such as 60 h (entry 8), due to the sluggish autoxidation of sulfides by oxygen and IBA as reported previously.[16] In contrast, in the presence of FeP-CMP, the reaction proceeded much more quickly with high conversion and high selectivity (entry 5). This result demonstrates the catalytic nature of FeP-CMP. We found that the catalytic performance can be enhanced using an excess of IBA.[15] Only 33% (entry 9) and 70% (entry 10) of **1a** were converted after 48 h when the molar ratios of IBA/**1a** were 1.0 and 2.0, respectively. Significantly, when the molar ratio of IBA/**1a** was increased to 3.0, 97% conversion was achieved within 1.5 h (entry 5). Additional control experiments using monomeric [*p*-Br]₄PFe as the homogeneous catalyst under otherwise identical conditions demonstrated that FeP-CMP is much more active than [*p*-Br]₄PFe (Table S3).[17] Moreover, transformations using FeP-CMP samples with dif-

ferent surface areas revealed that all the FeP-CMP samples showed high selectivity, together with an increasing tendency of the activity with surface area, i.e., the larger the surface areas, the higher the catalytic activity, while the pore size distribution had less of an effect on both activity and selectivity (Table S4). Under the optimized conditions, we further investigated the oxidation reactions by replacing molecular oxygen with an atmosphere of air. We found that the oxidation reaction in an atmosphere of air proceeds efficiently and displays almost equal catalytic activity and selectivity in comparison with those of molecular oxygen under otherwise identical conditions (entry 11). This result is important, because the ability to catalyze aerobic oxidation makes the catalyst much more appealing in potential application.

Along this line, we examined the scope of substrates for the oxidation reaction catalyzed by FeP-CMP. To our surprise, various sulfides could be efficiently oxidized under ambient conditions, and the corresponding sulfoxides were produced in high yields with high selectivity (Table 2, entries 12−23). We chose methyl phenyl sulfides **1b**−**f** bearing electron-withdrawing (entries 12−14) or electron-donating substituents (entries 15 and 16) on the phenyl ring as substrates for the oxidation reaction. Interestingly, all of the reactions proceeded selectively to afford the corresponding sulfoxides in high yields, while the reaction rates were slightly affected by the electronic properties of the substituents on the phenyl group. Compared with electron-withdrawing groups, the electron-donating substituents exhibited a positive effect on the reaction and resulted in a facilitated oxidation process, reaching a high TON value in a relatively short reaction time. We changed the phenyl groups to aliphatic chains and used the aliphatic sulfides for the oxidation. As shown in Table 2, aliphatic sulfides **1i**−**k** (entries 19−21) were also oxidized to the corresponding sulfoxides **2i**−**k**, with good catalytic performance of FeP-CMP with respect to both selectivity and activity. Furthermore, FeP-CMP showed high chemoselectivity in the transformation reaction. To demonstrate this, we employed phenyl allyl sulfide **1l** (entry 22) and (phenylthio)acetonitrile **1m** (entry 23) as substrates, because both of them have two representative oxidation sites in the skeletons. The oxidations of **1l** and **1m** proceeded chemoselectively to the corresponding sulfoxides, without epoxidation of the C=C double bond or overoxidation of the C≡N group.

A feature of the reaction that caught our attention was the precipitation of FeP-CMP from the reaction mixture. We found that, upon standing at room temperature for several hours, FeP-CMP precipitated out from the solution. We thus investigated the possibility of recycling FeP-CMP. The reaction mixture was centrifuged to collect the catalyst, which was then reused in the next round of oxidation reactions. Owing to the built-in nature of the covalently linked catalytic sites, FeP-CMP maintains its structure well and allows for a robust recycling capability with well-retained activity after three cycles (Table 3). In fact, the nitrogen sorption isotherm measurements of FeP-CMP after cycling reactions exhibited a BET surface area of 1265 m² g⁻¹, which is almost identical to that (1270 m² g⁻¹) of the pristine FeP-CMP. In relation to this, we are curious if the catalyst is applicable to the large-scale synthesis. As shown in Scheme 1, we examined this possibility using **1a** (7.3 g, 59 mmol) as substrate in 300 mL of toluene under 1 atm of O_2 at 25 °C. The reaction of **1a** in the presence of 1 mg of FeP-CMP catalyst provided 8.1 g of sulfoxide. Worthy of notice, in this case the TON was as high as 97 320 after 40 h, which is

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(16) (a) McNesby, J. R.; Heller, C. A., Jr. *Chem. Rev.* **1954**, *54*, 325–346. (b) Venkateshwar Rao, T.; Sain, B.; Kumar, K.; Murthy, P. S.; Prasada Rao, T. S. R.; Joshi, G. C. *Synth. Commun.* **1998**, *28*, 319–326.
(17) We speculate that the high activity is most likely related to the three-dimensional porous structure of FeP-CMP. The high density of active sites together with a large surface area to mediate the transformation in the porous environment of the heterogeneous catalyst may play roles in the enhancement of catalytic activity.

Table 2. Catalytic Oxidations of Various Sulfides by FeP-CMP[a]

Entry	Substrate 1		Time [h]	Conversion [%]	Selectivity [%]		TON
					2	**3**	
12[b]	F–⟨⟩–S–	1b	3.5	98	>99	<1	980
13[b]	Cl–⟨⟩–S–	1c	4	90	99	1	900
14[b]	O₂N–⟨⟩–S–	1d	4	94	97	3	940
15[b]	–⟨⟩–S–	1e	2.5	98	95	5	980
16[b]	MeO–⟨⟩–S–	1f	1.5	97	95	5	970
17[b]	diphenyl sulfide	1g	2.5	95	98	2	950
18[b]	⟨⟩–S–	1h	3.5	96	94	6	960
19[b]	⟨⟩–S–	1i	18	97	98	2	970
20[b]	–S–	1j	24	92	99	1	920
21[b]	thiomorpholine-type	1k	20	89	>99	<1	890
22[b]	⟨⟩–S–allyl	1l	4	96	88	12	960
23[b]	⟨⟩–S–CN	1m	24	81	98	2	810

[a] Reaction conditions: FeP-CMP (5.86×10^{-7} mol Fe), toluene (3 mL), room temperature, O_2 (1 atm). *[b]* Fe/substrate/IBA = 1/1000/3000 (molar ratio).

Table 3. Recycle of FeP-CMP for Catalytic Transformation of Thioanisole **1a**

Run	Time [h]	Conversion [%]	Selectivity [%]	
			2a	**3a**
1st	2	96	97	3
2nd	2.2	97	97	3
3rd	3	94	99	1

Scheme 1. Large-Scale Transformation Reaction of Thioanisole to Sulfoxide Using FeP-CMP as a Catalyst
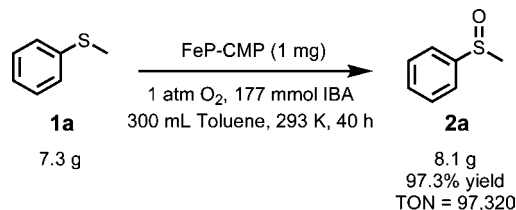
comparable to natural enzymes and is among the highest TONs so far reported for the artificial oxidation systems.

Conclusions

Exploration of conjugated microporous polymers has a high probability of leading to the development of new functional materials. In summary, we reported an unprecedented strategy for the construction of built-in catalysts based on CMP architecture and demonstrated the utility of a newly synthesized FeP-CMP as a heterogeneous catalyst for the activation of molecular oxygen under ambient conditions. FeP-CMP is unique in that it bears dense catalytic sites covalently linked in the skeleton, contains inherent nanopores that are substrate accessible, and has large surface areas that facilitate the transformation reaction. FeP-CMP is highly active and highly selective, is widely applicable to various sulfide substrates, is capable of facile recycling, and allows for large-scale transformation. These features are distinctive and highly correlated with structure characteristics. A clear future potential for CMPs is to develop a photocatalyst in which multiple functions including light-harvesting, energy transfer, and catalytic processes can be seamlessly merged in one polymer skeleton. Therefore, the CMP-based built-in catalyst constitutes a new step for the molecular design of heterogeneous catalyst systems.

Supporting Information Available: Details regarding the synthetic procedure, full methods, FT−IR, ^{1}H−^{13}C CP/MAS NMR, and fluorescence spectra, and PXRD profile are included. This material is available free of charge via the Internet at http://pubs.acs.org.

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