Short communication

Synthesis and post-metalation of a covalent-porphyrinic framework for highly efficient aerobic epoxidation of olefins

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ARTICLE INFO

ABSTRACT

We report a stable and porous 3D covalent-porphyrinic framework CPF-2, which is easily post-metalated with different metal ions to tune the catalytic properties. The cobalt(II) metalated material Co-CPF-2 exhibits high efficiency in heterogeneous catalysis of the aerobic epoxidation of olefins under mild conditions, in which > 99% conversion, 93% epoxide selectivity, 29,215 turnover number (TON) and 3434 h^{-1} turnover frequency (TOF) have been realized for the aerobic epoxidation of styrene.

1. Introduction

Covalent-organic frameworks (COFs) are an emerging class of crystalline porous materials, building from highly ordered organic moieties linked by covalent bonds [1–4]. The framework structures of COFs are majorly defined by the geometries and the directionalities of organic synthons based on the principle of the reticular chemistry. Compared with metal-organic frameworks (MOFs), COFs are highly robust and stable as the organic components are connected by strong covalent bonds, whereas MOFs are stabilized by coordination bonds [5–14]. To tune the pore structures and modify the functional groups of porous COFs, the emerging porous materials demonstrate great potential for practical applications in many fields [15–25].

It has been illustrated that the 3D porphyrinic MOFs with substrate accessible metalloporphyrin sites in the channel walls are highly active in heterogeneous catalysis [26]. The 3D porphyrinic COFs, being the analogs of porous porphyrinic MOFs, should be also highly efficient for heterogeneous catalysis [27]. Moreover, the instability will be overcome and the catalytic efficiency will be superior to that of homogeneous metalloporphyrins. To synthesize porous and stable 3D covalent-porphyrinic frameworks (CPFs) for highly efficient heterogeneous catalysis, we chose the four-branched tetraphenylamine porphyrin (T-APP) and the trigonal 1,3,5-triformylbenzene (TFB) as reaction reagents, based on the principle of reticular chemistry. Condensation of TAPP with TFB produced by dehydration a porous COF material (denoted as CPF-2), consisting of metal-free porphyrin moieties. CPF-2 is facilely post-metalated to yield different covalent-metalloporphyrinic frameworks (M-CPFs), in which Co-CPF-2 exhibits very high efficiency on catalyzing the aerobic epoxidation of olefins under mild conditions

with very high turnover number (TON) and turnover frequency (TOF).

2. Results and discussion

The synthesis of CPF-2 was carried out by solvothermal reaction of TAPP and TFB in a mixed solvent of ethanol, mesitylene and aqueous acetic acid (Scheme 1). The material is very stable in water and common organic solvents such as methanol, acetone, $CHCl_3$, THF, DMSO and DMF. Thermogravimetric analysis (TGA) shows that CPF-2 is stable up to 450 °C (Fig. S13). The formation of imine linkages in CPF-2 was confirmed by FT-IR, NMR and UV–Vis spectra. The FT-IR spectrum of CPF-2 shows the strong C=N stretch at 1617 and 1182 cm^{-1}, indicating the formation of imine bonds (Fig. S1). Meanwhile, the aldehyde (1699 cm^{-1}) and amino (3351 cm^{-1}) bands in the FT-IR spectrum of CPF-2 almost disappeared in comparison with those of the starting materials, which offers further evidence for the formation of imine bonds via the condensation of aldehyde and primary phenyl amine. ^{13}C solid-state NMR (CP/MAS) and UV–Vis spectra proved that CPF-2 contains the expected moieties (Figs. S2 and S3). SEM and TEM images of the solid samples of CPF-2 showed that CPF-2 exhibited a regular shape of morphology and was obtained as the uniform microparticles (Fig. S5a). As shown in Fig. 1, the regularity and long-range order of the structure of CPF-2 were confirmed by powder X-ray diffraction (PXRD). According to reticular chemistry, CPF-2 should be a 3D 3,4-connected network with the topology of tbo or pto. Unfortunately, we could not simulate a reasonable structure to match the observed diffraction peaks in the experimental PXRD of CPF-2. The permanent porosity of CPF-2 has been examined by N_2 adsorption experiment at 77 K (Fig. S6). The activated solid sample of CPF-2 takes up
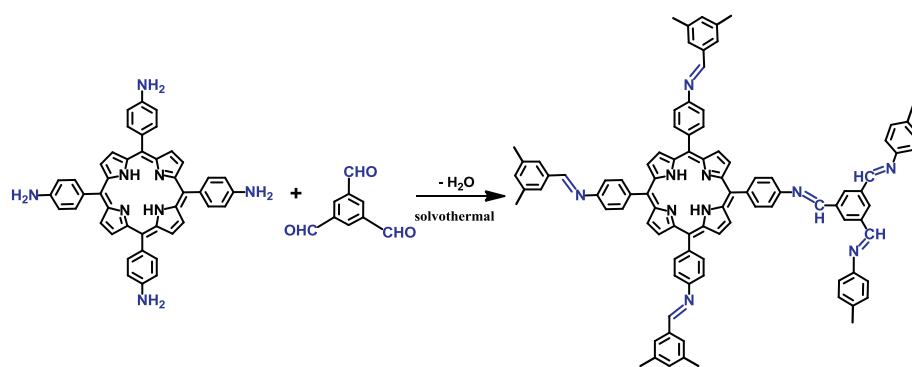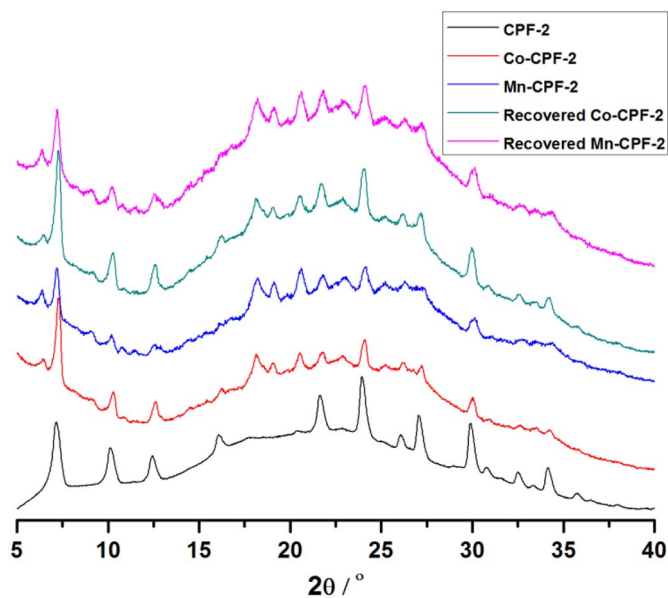
Fig. 1. PXRD patterns for CPF-2, Co-CPF-2, Mn-CPF-2, and the recovered Co-CPF-2 and Mn-CPF-2 after catalysis.

$531 \, cm^3 \, g^{-1} \, N_2$ at 77 K and 1 bar, resulting in a BET surface area of $660 \, m^2 \, g^{-1}$. The pore-size distribution of CPF-2 showed a narrow pore width with the pore diameter of 1.55 nm (Fig. S7). The above features of CPF-2 suggest that it is readily available for subsequent post-metalation to tune its catalytic property.

If metal-TAPP would react directly with TFB under otherwise identical conditions, an amorphous solid would be obtained, because the amino groups on TAPP easily combine with porphyrin metal ions. Therefore, the post-metalation provided an effective strategy for the synthesis of metalloporphyrinic COFs. CPF-2 was easily post-metalated by heating a mixture of CPF-2 and MCl_2 ($CoCl_2$ for Co-CPF-2, and $MnCl_2$ for Mn-CPF-2) in DMF. The surface adsorbed metal ions on the resulting solids M-CPF-1 were removed by sufficiently washing with DMF, dilute HCl aqueous solution and methanol. Inductively coupled plasma mass spectrometry (ICP-MS) reveals that Co-CPF-2 and Mn-CPF-2 contain 4.71% Co and 4.03% Mn ions, respectively. As shown in the broad scan XPS spectra of Co-CPF-2 and Mn-CPF-2, there exist the typical peaks corresponding to M2p (M = Co and Mn), O1s, N1s, C1s and Cl2p (Figs. S8–S10). From the high resolution XPS spectrum of Co-CPF-2, the signals of porphyrin Co2p are observed at 780.6 and 795.8 eV corresponding to the Co $2p_{3/2}$ and $2p_{1/2}$, respectively [28]. In addition, the monodentate-imine coordinated metal ions in the solid have been removed by thoroughly washing with dilute HCl aqueous solution as confirmed by comparison of the XPS spectra (Figs. S8 and S9). The characteristic binding energies for the trivalent Mn $2p_{3/2}$ and $2p_{1/2}$ are at 641.6 and 653.3 eV, respectively. The crystallinity of Co-CPF-2 and Mn-CPF-2 was confirmed by PXRD patterns (Fig. 1), while their

retained uniform morphology was proved by SEM and TEM images (Fig. S5b and c). The activated solid samples of Co-CPF-2 and Mn-CPF-2 take up 331 and $329 \, cm^3 \, g^{-1} \, N_2$ at 77 K and 1 bar, resulting in BET surface areas of 475 and $454 \, m^2 \, g^{-1}$, respectively (Figs. S11 and S12).

Epoxidation of alkenes is very important in industry because epoxides are the widely used intermediate chemicals [29]. The selective aerobic epoxidation of olefins is particularly desirable, because molecular oxygen is a green oxidant with advantages of atom economy, low cost and environmentally friendly [30]. Since cytochrome P450 enzymes can efficiently activate dioxygen under mild conditions, we expected that M-CPF-2, immobilizing the metalloporphyrin sites on the pore surfaces, should present the capability of aerobic epoxidation of olefins. The epoxidation reaction was carried out at room temperature with 1 mol% of Co-CPF-2 in the presence of isobutyraldehyde (IBA) under 1 atm O_2 atmosphere (Table 1). As shown in entry 1, it is interesting that the styrene substrate, in just 1 h, was fully oxidized by O_2 with excellent epoxide selectivity (93%). The catalytic property of Co-CPF-2 is superior to that of Mn-CPF-2, which requires relative long reaction time to complete the epoxidation reaction (entries 2 and 3). As shown in entry 4, the catalytic properties of heterogeneous Co-CPF-2 are superior to those of the homogeneous molecular catalyst Co-tetraphenylporphyrin (Co-TPP) in terms of substrate conversion and product selectivity. The high conversion and selectivity for the aerobic epoxidation of styrene at room temperature suggest that the presented catalyst system is highly efficient on activation of molecular oxygen.

To prove that the catalysis chiefly occurs inside the pores of Co-CPF-2, we have monitored the accessibility of the open channels of Co-CPF-2 to both reactant styrene and product 1,2-epoxyethylbenzene molecules by UV–Vis absorption spectroscopy. The UV–Vis spectra clearly indicate that the pores of Co-CPF-2 are accessible to styrene and 1,2-epoxyethylbenzene molecules with the uptakes of 8.7 and 7.3 wt%, respectively. Moreover, after the reaction proceeded for 0.5 h, the catalytic reaction was intentionally interrupted, and the solid catalyst was collected by centrifugation. UV–Vis absorption spectroscopy showed that the desorbed styrene from this reacted Co-CPF-2 is about 6.2 wt%, whereas only trace 1,2-epoxyethylbenzene product was detected from the desorbed species. This study clearly demonstrates that the catalytic epoxidation of styrene into 1,2-epoxyethylbenzene does occur inside the pores of Co-CPF-2. Moreover, the selective enrichment of styrene and repellence of 1,2-epoxyethylbenzene by Co-CPF-2 can keep high concentration of reactant molecules around the active sites on the pore surfaces to accelerate the reaction. Co-CPF-2 can epoxidize a series of different alkenes under the identical conditions (Table 1, entries 5–10). When the size of substrate increases, the conversion decreases gradually. These results are very similar to those obtained with homogeneous Co-TPP counterpart under the same conditions (Fig. S16). As the inside pore space of Co-CPF-2 is accessible to these different substrates (Fig. S17), the different conversions of these reactant substrates should be mainly controlled by the steric constraint and/or the electronic effect and/or the diffusion rate.

Catalyst Co-CPF-2 can be easily recovered by centrifugation to