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Boosting selective oxidation of cyclohexane over a metal–organic framework by hydrophobicity engineering of pore walls†

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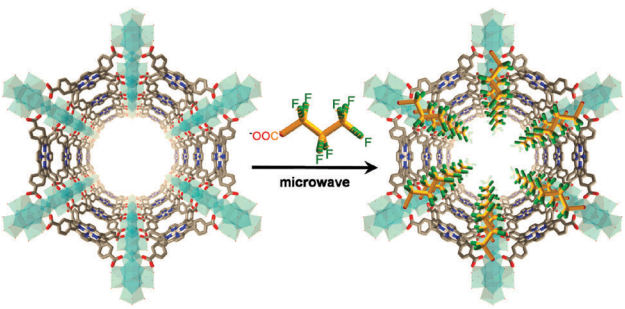
A porphyrinic metal–organic framework (MOF), PCN-222(Fe), was found to exhibit sound activity and selectivity to cyclohexanone and cyclohexanol (known as KA oil) toward cyclohexane oxidation. Remarkably, hydrophobicity engineering of the MOF pore walls led to significantly enhanced activity and selectivity to KA oil, far superior to that of the homogeneous porphyrin catalyst.

The oxidation of cyclohexane, one of the most valuable reactions in industrial and synthetic chemistry,[1] usually takes place under harsh conditions to give complex products, such as cyclohexanol, cyclohexanone, adipic acid and acid anhydride, *etc.* Amongst them, cyclohexanol and cyclohexanone, also called KA oil, the intermediates in the production of Nylon-6 and Nylon-66, are important petrochemical feedstock and more expected than others. Thus, the selective C–H bond insertion of cyclohexane to produce KA oil under mild conditions is of considerable interest and many catalysts have been developed.[1,2] Particularly, metalloporphyrin, a type of biomimetic homogeneous catalyst, presents sound activity in the oxidation of cyclohexane at mild temperatures and pressures.[2] Nonetheless, the intrinsic difficulty in the recyclability of homogeneous catalysts and the tendency to dimerization of metalloporphyrin greatly impede their further applications.[3] Therefore, the development of heterogeneous catalysts involving the active metalloporphyrin would be highly desired.

Metal–organic frameworks (MOFs), a promising platform with great potential for applications in diverse fields,[4] are built by metal ions/clusters and a variety of organic building units and could be ideal porous materials to immobilize metalloporphyrin units by using M–TCPP (M = Fe, Mn, Co, Ni, Cu, Zn, H_2; TCPP = tetrakis(4-carboxyphenyl)porphyrin) as organic ligands. The periodic structure of MOFs leads to the separation of the catalytic sites and avoids their dimerization during the reaction.[5] Moreover, given the highly tunable character of MOFs, the pore environment can be furnished to be hydrophobic by grafting particular molecules, contributing to the concentration of hydrophobic substrates and facilitating their rapid conversion.[6] Unfortunately, to our knowledge, a highly efficient metalloporphyrin-based MOF catalyst with a stable recyclability performance for cyclohexane oxidation has not been reported yet, which might be attributed to the following reasons: (1) most metalloporphyrin MOFs are easily destroyed in the presence of the strong oxidant (*e.g.* peroxide); (2) the rapid transport of substrates/products in small sizes of MOF pores is difficult, thus lowering the catalytic activity. Therefore, the fabrication of a highly stable metalloporphyrinic MOF catalyst with large hydrophobic pores would be of great importance and highly desired to achieve excellent activity of cyclohexane oxidation with satisfied selectivity to KA oil.

Bearing these in mind, we rationally fabricated PCN-222(Fe) decorating with a hydrophobic pore environment *via* post-synthetic modification (Scheme 1). The grafting PCN-222(Fe) with different chain lengths of perfluoroalkyl acids by the microwave reaction gave a series of modified PCN-222(Fe). Delightedly, the modified samples showed desired hydrophobicity and better adsorption for cyclohexane than the parent PCN-222(Fe). Particularly, thanks to the hydrophobic pore environment,



Scheme 1 Schematic illustration showing the fabrication of PCN-222(Fe)-F_n *via* postsynthetic modification.

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all modified PCN-222(Fe) exhibit superior activity and ~90% selectivity to KA oil, far surpassing the selectivity requirement (more than 80%) in industry,[1] in reference to the parent PCN-222(Fe) and homogenous iron-porphyrin catalysts, in cyclohexane oxidation.

The iron-porphyrinic MOF, PCN-222(Fe) (also called MOF-545 or MMPF-6),[7] featuring high chemical and thermal stability, is constructed by $Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(OH)_4(H_2O)_4(COO)_8$ clusters and TCPP linkers with Fe(III) centers (Fe-TCPP) to give a 3D network, in which zirconium-carboxylate layers form a Kagome-type pattern in the *ab* plane, pillared by Fe-TCPP linkers. Importantly, it exhibits very large hexagonal 1D open channels with a diameter of as large as 3.7 nm along the *c*-axis, as can be observed by a transmission electron microscope (TEM) (Fig. S1, ESI†). To introduce the hydrophobic pore environment, three perfluorocarboxylic acids with different chain lengths, trifluoroacetic acid (F_3), pentafluoropropionic acid (F_5) and heptafluorobutyric acid (F_7), were grafted onto the pore walls by replacing the –OH groups of $Zr_6(\mu_3\text{-}OH)_8(OH)_4(H_2O)_4(COO)_8$ clusters in PCN-222(Fe) with carboxylates to give PCN-222(Fe)-F_n (n = 3, 5 and 7), leaving perfluorinated alkyls toward the pore space to feature hydrophobic properties.[8] The successful introduction of perfluorinated alkyls into PCN-222(Fe) was demonstrated by the ^{19}F nuclear magnetic resonance (NMR) (Fig. S2, ESI†) and diffuse reflectance infrared Fourier transform spectra (DRIFTS) (Fig. S3, ESI†). Powder X-ray diffraction (XRD) patterns indicated that the crystallinity and structure of PCN-222(Fe) remained well after hydrophobic modification (Fig. 1a). In addition, N_2 physisorption isotherms of PCN-222(Fe)-F_n were similar to that of PCN-222(Fe) in shape and the appreciable decrease of surface area was ascribed to the pore space occupation and mass contribution of grafted perfluorinated alkyls (Fig. 1b). Delightedly, though the surface area decreased, the mesopore character in PCN-222(Fe)-F_n was still retained (Fig. S4, ESI†).

The created hydrophobicity for the MOF was demonstrated by the water contact angle measurement. The contact angle of water droplets on pristine PCN-222(Fe) is ~10°, while it quickly increases to 51°, 110° and 137° upon introducing F_3, F_5 and F_7, respectively (Fig. 2a upper), clearly suggesting that perfluorinated alkyls transform the MOF from hydrophilic to hydrophobic. The water adsorption experimental results for PCN-222(Fe) and PCN-222(Fe)-F_7 further support the hydrophobicity in the latter (Fig. S5, ESI†). In a more visualized experiment, the enhanced hydrophobicity of PCN-222(Fe)-F_n is observable in the water–cyclohexane biphasic mixture: the MOF gradually transfer from the aqueous phase to the organic phase along with increased chain length of perfluorinated alkyls (Fig. 2a, bottom). To further judge whether the created hydrophobicity beneficial to substrate diffusion/enrichment, liquid cyclohexane adsorption of PCN-222(Fe) and PCN-222(Fe)-F_n in acetonitrile was investigated at room temperature. The results indicated that the hydrophobic PCN-222(Fe)-F_n displayed an increased liquid-phase cyclohexane adsorption rate and amount compared to the parent PCN-222(Fe), clearly supporting the more favourable diffusion and enrichment of the substrate in hydrophobic channels (Fig. 2b).

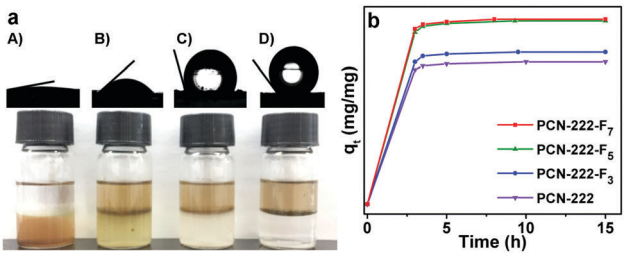


Fig. 2 (a) (upper) Static water contact angles of (A) PCN-222(Fe), (B) PCN-222(Fe)-F_3, (C) PCN-222(Fe)-F_5 and (D) PCN-222(Fe)-F_7; (bottom) photograph of corresponding samples dispersed in a water–cyclohexane (1 : 1 v/v) biphasic mixture. (b) Adsorbed cyclohexane amounts by PCN-222(Fe) and PCN-222(Fe)-F_n (n = 3, 5 and 7) in acetonitrile along with time.

It is expected that the enhanced hydrophobicity and more favourable adsorption of hydrophobic cyclohexane by PCN-222(Fe)-F_n would lead to an improved catalytic performance toward the oxidation of cyclohexane. Therefore, the reaction over PCN-222(Fe)-F_n in the presence of *tert*-butyl hydroperoxide (TBHP) as the oxidant was carried out. To examine the optimized amount of TBHP, a series of control experiments were conducted and the results showed that the yield of KA oil was improved along with more TBHP (Table 1). Given that excessive TBHP was harmful to the crystallinity of MOF due to oxidative destruction, as a result, an optimal TBHP amount (8 μL, 5.5 mM) was adopted to give balanced activity and selectivity toward cyclohexane oxidation.

It is accepted that metal ions located in the porphyrin center are critical to the catalytic activity for cyclohexane oxidation.[2a,5c,d] The Cl atom bound to the Fe(III) center in the porphyrin ligand

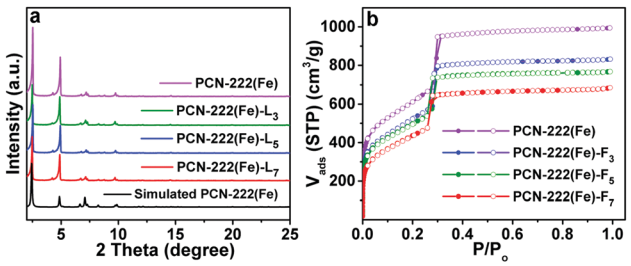
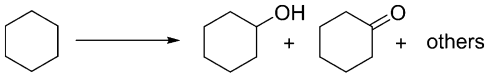


Fig. 1 (a) Powder XRD patterns for simulated PCN-222(Fe), as-synthesized PCN-222(Fe) and PCN-222(Fe)-F_n (n = 3, 5 and 7); (b) N_2 sorption isotherms for PCN-222(Fe) and PCN-222(Fe)-F_n (n = 3, 5 and 7) at 77 K.

Table 1 The cyclohexane oxidation under different conditions[a]



Entry	V(TBHP) (μL)	Conv. (%)	Sel. of KA oil (%)	Yield of KA oil[b] (%)
1	0	—	—	—
2	4	29.8	89	26.1
3	8	50.2	90	46.2
4	20	75	68	51

[a] Reaction conditions: Cyclohexane (0.1 mmol), PCN-222(Fe)-F_7 (20 mg), CH_3CN (2.5 mL), $AgBF_4$ (25.6 mg), 1 bar O_2, 80 °C, and refluxing for 24 h; A indicates cyclohexanol and K indicates cyclohexanone. [b] Catalytic reaction products were analyzed and identified by gas chromatography.

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(Fe-TCPP) is assumed to be unfavorable to catalytic activity. It was reported that the activation of the hydroperoxide O–O bond over iron-porphyrin catalysts was hampered by the electron-withdrawing ligands attached onto Fe(III), such as Cl, which was detrimental to the generation of reactive intermediates.[9] Therefore, it is desired to remove the coordinated Cl atom from Fe(III). To this end, $AgBF_4$ with a weaker coordination strength was employed to replace the Cl atom.[10] Interestingly, the presence of $AgBF_4$ was though not able to improve the catalytic selectivity to KA oil, the ratio of K/A was significantly increased to 12.4/1, which has never been observed yet in previous reports (Table S1, ESI†). Such high percentage of cyclohexanone achieved in the catalytic reaction products would be very important in the simplification of the cumbersome cyclohexanone purification for subsequent caprolactam production in industry.

With the optimized reaction parameters, cyclohexane oxidation over different catalysts has been investigated (Table 2). The results clearly show that the Fe(III) located in the porphyrin center is indeed the active site for the reaction (entries 1 and 3). Surprisingly, the homogeneous iron porphyrin is almost inactive under similar conditions (entry 2). It is possibly due to the formation of bridged μ-oxide dimers that might hinder the access to the catalytic sites.[2b] In addition, all PCN-222(Fe)-F_n present a superior catalytic activity to the pristine PCN-222(Fe) (entries 3–6), reflecting that the hydrophobicity of pore walls is beneficial to the conversion and selectivity to KA oil. Moreover, the longer $-CF_3$ chain is grafted onto the pore walls, the better catalytic performance can be achieved. It is proposed that the hydrophobicity of the inner pore surface affords a driving force for substrate enrichment due to the interaction between cyclohexane and the terminal perfluorinated alkyls, thus promoting the catalytic process. The activity and selectivity to KA oil for PCN-222-F_7 and other MOF-based catalysts have been compared and considerable advantages are shown (Table S2, ESI†).

The oxidation reaction progress over different catalysts at 80 °C indicates that PCN-222(Fe) and PCN-222(Fe)-F_n possess the similar kinetics (Fig. 3a). The results reveal that the generated hydrophobicity in PCN-222(Fe)-F_n accelerates the conversion of cyclohexane due to the substrate confinement, while does not change the reaction order.

Upon the introduction of $AgBF_4$ into the reaction system, it is assumed that the weak ligand (BF_4^-) in reference to the chlorine atom coordinated to the Fe center is beneficial to the interaction between Fe(III) and TBHP, facilitating the generation of TCPP-Fe(IV)-oxo-active species, which is responsible for the high percentage of cyclohexanone in the KA oil product (Fig. S6a, ESI†). To gain additional experimental evidence, excess TBHP has been added to the reaction system. The results clearly show that a gradually increased K/A ratio from 7.5/1 to 10/1 can be achieved along with more TBHP introduced (Fig. S6b, ESI†). It is proposed that the TBHP complexing with TCPP-Fe(III) leads to the formation of additional TCPP-Fe(IV)-oxo. Therefore, the introduction of $AgBF_4$ and/or TBHP is beneficial to the generation of TCPP-Fe(IV)-oxo, which, assumed to be active species based on a previous report,[11] firstly oxidizes cyclohexane to cyclohexanol and then further reacts with cyclohexanol to produce cyclohexanone (Fig. 3b).

Table 2 The catalytic performance of different catalysts[a]

Entry	Catalyst	Conv. (%)	Sel. of KA oil (%)	Yield of KA oil (%)
1	PCN-222	—	—	—
2[b]	TCPP(Fe)	<2	—	<2
3	PCN-222(Fe)	20.5	81	16.6
4	PCN-222(Fe)-F_3	45	86.9	36.9
5	PCN-222(Fe)-F_5	46	89	41.0
6	PCN-222(Fe)-F_7	50.2	90.1	46.2
7[c]	PCN-222(Fe)-F_7	46.7	86.5	40.4

[a] Reaction conditions: cyclohexane (0.1 mmol), catalyst (20 mg), CH_3CN (2.5 mL), TBHP (8 μL), $AgBF_4$ (25.6 mg), 1 bar O_2, 80 °C, and refluxing for 24 h; A indicates cyclohexanol and K indicates cyclohexanone. [b] Catalyst (10 mg), DMF (1 mL) and CH_3CN (1.5 mL). A mixture of CH_3CN and DMF was used due to the low solubility of TCPP in CH_3CN. [c] 1 bar O_2 was replaced by 1 bar N_2.

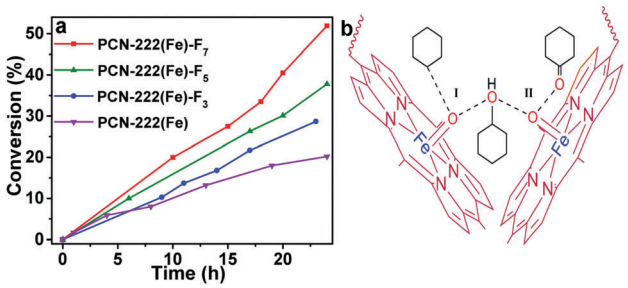

Fig. 3 (a) The conversion-time plots of cyclohexane oxidation over PCN-222(Fe) and PCN-222(Fe)-F_n (n = 3, 5, and 7). (b) Proposed mechanism for cyclohexane oxidation.

On the basis of the above experimental results and assumptions, a catalytic cycle for the formation of cyclohexanol and cyclohexanone has been proposed (Fig. S7, ESI†). It is hypothesized that TCPP-Fe(IV)-oxo is generated by transferring one electron from the Fe(III) center to the coordinated TBHP.[12] Subsequently, this reaction is initiated by TCPP-Fe(IV)-oxo complexing with cyclohexane, generating TCPP-Fe(IV)–OH($C_6H_{11}^{\bullet}$). Cyclohexanol can be produced *via* ($C_6H_{11}^{\bullet}$) oxidized by TCPP-Fe(IV)–OH^-, accordingly TCPP-Fe(III) is generated after this oxidation process. Subsequently, cyclohexanol can also coordinate with TCPP-Fe(IV)-oxo to give ($C_6H_{11}O^{\bullet}$), which is able to be oxidized by TCPP-Fe(IV)–OH^- to afford cyclohexanone.

The stability and reusability of catalysts are significant parameters for practical applications. Recycling experiments for PCN-222(Fe)-F_7 as a representative clearly demonstrate that no noticeable change occurs to its activity and selectivity during the three consecutive runs (Fig. 4a). In addition, powder XRD patterns show that the structural integrity and crystallinity of PCN-222(Fe)-F_7 well remain even after 3 runs (Fig. 4b), suggesting its high stability and great recyclability under catalytic conditions.

In conclusion, hydrophobicity engineering of pore walls for an iron-porphyrinic MOF, PCN-222(Fe), has been successfully developed to boost the catalytic performance toward cyclohexane oxidation. Grafting perfluorinated alkyls onto the pore walls significantly increases the hydrophobicity and improves the interaction with cyclohexane, resulting in enhanced conversion and selectivity to KA oil. By contrast, the homogeneous iron

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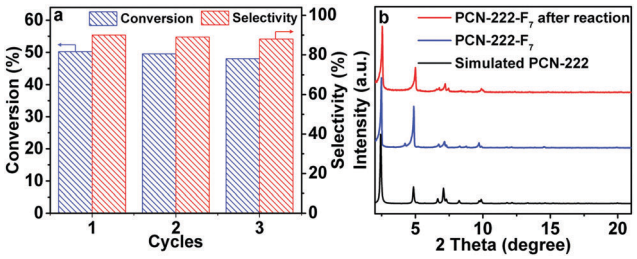

Fig. 4 (a) Catalytic conversion and selectivity of PCN-222(Fe)-F_7 during the 3 runs of cyclohexane oxidation. Reaction conditions: cyclohexane (0.1 mmol), catalyst (20 mg), CH_3CN (2.5 mL), TBHP (8 μL), $AgBF_4$ (25.6 mg), 1 bar O_2, 80 °C, and refluxing for 24 h. (b) Powder XRD patterns of simulated PCN-222(Fe), as-synthesized PCN-222(Fe)-F_7 and PCN-222(Fe)-F_7 after 3 catalytic runs.

porphyrin is almost inactive for this reaction. Remarkably, the introduction of $AgBF_4$ creates the weak coordination between the BF_4^- and Fe(III) sites and thus facilitates the formation of the Fe(IV)-oxo active species, leading to a very high percentage (>90%) of cyclohexanone in KA oil, which is an unprecedented finding and will be important for caprolactam production in industry. In addition, the optimized catalyst, PCN-222(Fe)-F_7, is readily recyclable due to its high stability and heterogeneous nature. We envision that the hydrophobicity engineering strategy for MOF pore walls opens an avenue for the improvement of catalytic performance of a variety of related catalysts toward for many important reactions.

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Conflicts of interest

There are no conflicts to declare.

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