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Flexible and Hierarchical Metal-Organic Framework Composites for High-Performance Catalysis

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Abstract: The development of new types of porous composite materials is of great significance owing to their potentially improved performance over those of individual components and extensive applications in separation, energy storage, and heterogeneous catalysis. In this work, we integrated mesoporous metal-organic frameworks (MOFs) with macroporous melamine foam (MF) using a one-pot process, generating a series of MOF/MF composite materials with preserved crystallinity, hierarchical porosity, and increased stability over that of melamine foam. The MOF nanocrystals were threaded by the melamine foam networks, resembling a ball-and-stick model overall. As a proof-of-concept study, the resulting MOF/MF composite materials were employed as an effective heterogeneous catalyst for the epoxidation of cholesteryl esters. Combining the advantages of interpenetrative mesoporous and macroporous structures, the MOF/melamine foam composite provided higher dispersibility and more accessibility of catalytic sites, exhibiting excellent catalytic performance. This strategy constitutes an important step forward the development of other MOF composites and exploration of their high-performance catalysis.

Metal-organic frameworks (MOFs) are a class of crystalline porous materials, which are constructed with metal or metal clusters as nodes and organic ligands as linkers.^[1] MOFs are well known for their extraordinarily high porosity and internal surface areas.^[2] Owing to their crystalline and porous structures, MOFs have been widely used in many application, including gas storage,^[3] gas separation,^[4] heterogeneous catalysis,^[5] light emission,^[6] drug delivery,^[7] and proton conduction.^[8] However, most MOFs are rigid, brittle, and very easy to be crumbed.^[9] In addition, MOFs are insoluble in any solvents and have no exact melting points, which means that they cannot be processed by traditional solvent or heat-based techniques.^[10] All of these disadvantages have largely limited their practical applications in various domains. To tackle this problem, tremendous efforts have been made to hybridize MOFs with other materials, thus realizing the combination of their advantages and circumventing shortcomings. A variety of MOF composites have been successfully developed, such as MOF/graphene,^[11a] MOF/graphite,^[11b] MOF/carbon nanotubes,^[11c] MOF/polymers,^[11d]

MOF/enzymes,^[11e] and MOF/metal nanoparticles,^[11f] generating new properties unavailable from either component. Very recently, Wang and coworkers successfully developed the MOF/mesh, MOF/cloth, and MOF/sponge composites *via* the roll-to-roll mechanical production and utilized them for efficient particulate matter removal.^[12] Eddaoudi group reported the MOF/silica composite by the stepwise layer-by-layer strategy.^[13] Su and Zhu groups also developed new hierarchical Al-metal-organic aerogels based on a post-synthetic process using MOFs and other additives.^[14] However, these methods are synthetically tedious and cannot retain the original crystalline morphology of MOFs. We aim to develop stable MOF/foam composite materials by a one-pot procedure, which enables the direct preparation of high-quality composite materials. More importantly, this would provide a general strategy to prepare MOFs for practical applications, especially in heterogeneous catalysis over a scope broader than ever before.

Heterogeneous catalysts have many advantages over their homogeneous counterparts in reactor design, such as easy operation, excellent activity, good selectivity, and catalyst reusability. To improve the catalytic performance of MOFs, a great variety of approaches have been explored, but it remains a daunting challenge to create macropores in a coordination network.^[15] Considering all of these issues, we seek to grow MOF crystals within macroporous melamine foam (MF) to form MOF/MF composites, which possess many advantages of low density, good mechanical capacity, excellent thermal and chemical stability, and high void fractions. In this means, a new dimension can be created via the combination of the inherent micropores or mesopores with additional macropores. In addition, the effects of the composited hierarchical structure on catalytic activity, selectivity, and stability have been investigated. Notably, significant improvement of catalytic performance was readily achieved. Owing to the high chemical robustness of the MOF/MF composites, they can be recycled more than six times without significant loss of activity and selectivity. This strategy provided a general strategy to prepare high-quality MOF composites and made an essential step towards future practical applications of MOFs.

In this work, we developed a one-pot strategy to integrate PCN-224 and melamine foam into a hierarchical composite. As reported previously, the crystalline structure of PCN-224 was classified as cubic crystal system (Figure 2a, b). The MOF/MF composite was prepared under a straightforward solvothermal condition (Figure 1c). The macroporous melamine foam provided abundant voids for the loading of PCN-224 (Figure 1d,e). It's well known that PCN-224 is constructed with Zr₆ clusters and square planar tetrakis(4-carboxyphenyl)-porphyrin (TCPP) ligands in the space group *Im*3-m.^[16] One Zr₆ cluster is connected with six TCPP ligands forming a "she" type network, which possesses extraordinary chemical stability and high structural tunability.

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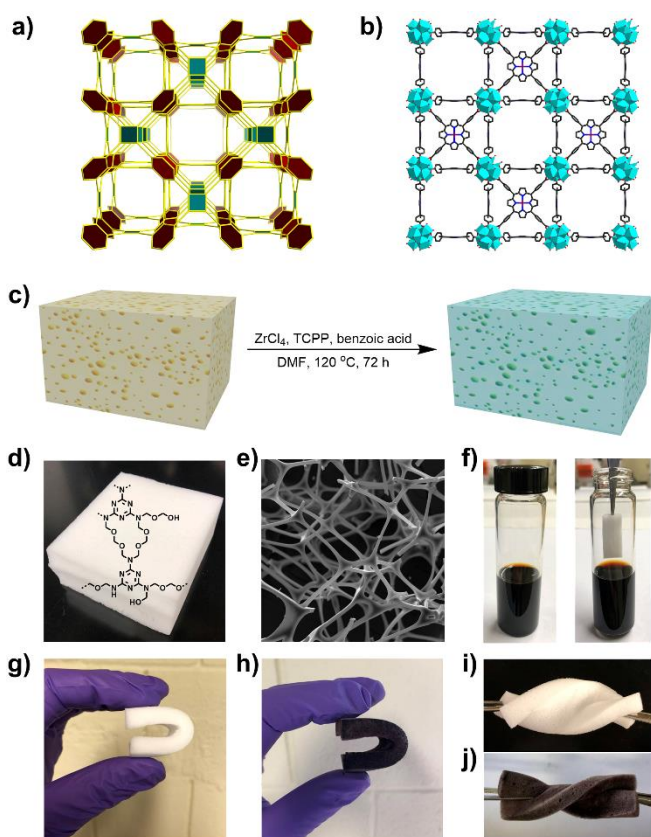


Figure 1. a) The topological structure of PCN-224. b) View down the tetragonal channels of PCN-224 (black, carbon; purple, metal; blue, nitrogen; hydrogen, omitted). c) The schematic procedure for the preparation of the PCN-224 decorated melamine foam composites. d) The photograph and chemical formula of melamine foam. e) The FE-SEM image of the melamine foam used in this work. f) The mixture of TCPP(Fe), $ZrCl_4$, and benzoic acid in DMF solution (left) and immersing the melamine foam into the solution for one-pot synthesis (right). The melamine foam (g, h) and as-synthesized PCN-224(Fe)/MF (i, j) could be compressed and distorted.

To obtain stable and high-quality MOF/MF composites, we initially selected PCN-224(Fe) as a model to screen the optimum conditions. We conducted the synthesis by assembling the TCPP(Fe) ligand and zirconium chloride in the presence of acid-pretreated melamine foam. The monolithic melamine foam was totally submerged in an *N,N*-dimethylmethanamide (DMF) solution of the mixture (Figure 1f). After the addition of benzoic acid, the mixture was sealed and stored at 120 °C for 72 h. The colourless melamine foam turned to dark brown and was homogeneously loaded with crystalline PCN-224(Fe). Owing to the flexible and elastic features of melamine foam, the resulting PCN-224/MF can withstand a certain degree of compression and exhibit elastomer characteristics (Figure 1g–j).

Field emission scanning electron microscopy (FE-SEM) visually revealed that the bare melamine foam network was homogeneously decorated with PCN-224(Fe) crystal particles (Figure 2a,b), which were penetrated through the centre by MF fibers in a ball-and-stick mode. All the crystals adopted a cubic morphology with an average size of about 20 μm . Different with other MOF composites, the morphology of PCN-224 was well

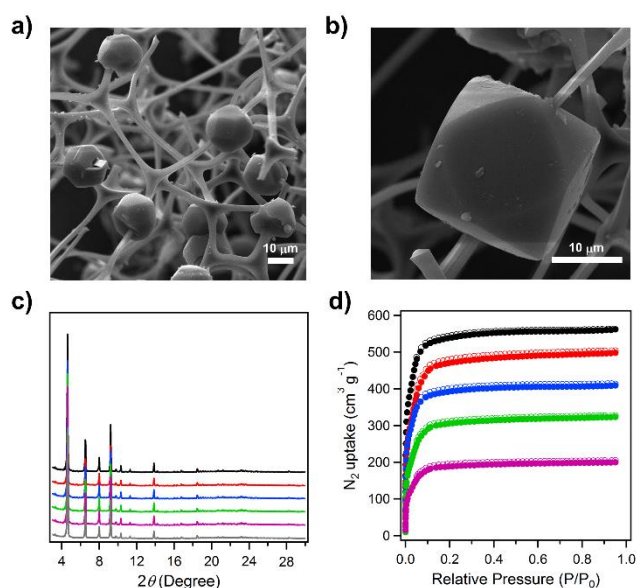


Figure 2. a, b) FE-SEM images of PCN-224(Fe)/MF composite. c) The PXRD patterns of PCN-224(Fe) (grey curve), PCN-224(Fe)_{50%}/MF (purple curve), PCN-224(Fe)_{100%}/MF (green curve), PCN-224(Fe)_{150%}/MF (blue curve), PCN-224(Fe)_{200%}/MF (red curve), and PCN-224(Fe)_{325%}/MF (black curve). d) N_2 sorption isotherms of PCN-224(Fe)_{50%}/MF (purple curve), PCN-224(Fe)_{100%}/MF (green curve), PCN-224(Fe)_{150%}/MF (blue curve), PCN-224(Fe)_{200%}/MF (red curve), and PCN-224(Fe)_{325%}/MF (black curve).

retained in PCN-224(Fe)/MF, without losing the inherent structural periodicity of crystalline materials. Thermogravimetric analysis (TGA) result revealed the PCN-224(Fe)/MF composite was thermally stable up to 300 °C in nitrogen (Figure S1 in the Supporting Information). Notably, the maximum loading content of PCN-224(Fe) is up to 325%, which is the highest value among all the MOF composites.^[12–14] As a contrast, the direct mixing of excessive PCN-224(Fe) and melamine foam lead to a maximum loading amount of 11%. In addition, we can precisely tune the loading content of PCN-224(Fe) ranging from 50% to 325% by simply adjusting feed ratios (Table S1). For example, we successfully prepared a series of PCN-224(Fe)/MF composites with loading contents of 50%, 100%, 150%, 200%, and 325%, namely PCN-224(Fe)_{50%}/MF, PCN-224(Fe)_{100%}/MF, PCN-224(Fe)_{150%}/MF, PCN-224(Fe)_{200%}/MF, and PCN-224(Fe)_{325%}/MF, respectively.

To investigate the crystallinity of these PCN-224(Fe)/MF samples, powder X-ray diffraction (PXRD) was employed for full characterization. As shown in Figure 2c, all of the PCN-224(Fe)/MF samples exhibited strong diffraction patterns, which were consistent with those of PCN-224(Fe). As the loading content of PCN-224(Fe) was different in the composites, their nitrogen uptake values deviated from that of PCN-224(Fe), with nitrogen uptake of 198, 310, 401, 497, and 564 $\text{m}^2 \text{g}^{-1}$ for PCN-224(Fe)_{50%}/MF, PCN-224(Fe)_{100%}/MF, PCN-224(Fe)_{150%}/MF, PCN-224(Fe)_{200%}/MF, and PCN-224(Fe)_{325%}/MF, respectively (Figure 2d). With the same pore size of 2.0 nm, Brunauer–Emmett–Teller (BET) surface areas for PCN-224(Fe)_{50%}/MF, PCN-224(Fe)_{100%}/MF, PCN-224(Fe)_{150%}/MF, PCN-224(Fe)_{200%}/MF, and PCN-224(Fe)_{325%}/MF were calculated

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as 645, 1084, 1320, 1645, and 2210 $\text{m}^2 \text{g}^{-1}$, respectively (Figure S2 and Table S2). This trend can be ascribed to the increasing loading amount of PCN-224(Fe) in the composites. As a control experiment, the melamine foam exhibited almost no nanoporosity in the nitrogen sorption analysis at 77 K (Figure S3). With the increasing loading amount of PCN-224(Fe), the macropores of melamine foam became increasingly crowded and were partially occupied by the crystal particles (Figure S4). The density was evaluated by the means of measuring the mass and the volume of these composites, ranging from 0.023 to 0.164 g cm^{-3} (Table S3). The homogeneity of these composites was also confirmed by tearing them into small pieces, in which uniform texture was found both outside and inside (Figure S5).

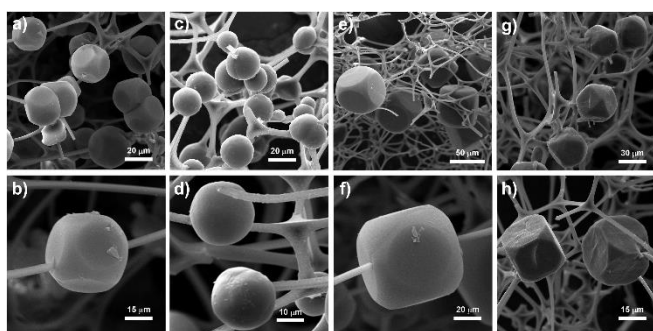


Figure 3. The SEM images of PCN-224(Ni)_{200%}/MF (a, b), PCN-224(H₂)_{200%}/MF (c, d), PCN-224(Co)_{200%}/MF (e, f), and PCN-224(Ru)_{200%}/MF (g, h).

Metalloporphyrins are widely employed as catalysts for the epoxidation reaction of unsaturated alkenes.^[17] To investigate the advantages of the MOF/melamine foam composites in heterogeneous catalysis, other PCN-224(M)_{200%}/MF (M = Ni, H₂, Co, and Ru) with different metal centres were prepared and employed to screen the optimum conditions in the epoxidation of *cis*-stilbene (Table S4). Similar with the properties of PCN-224(Fe)_{200%}/MF, PCN-224(M)_{200%}/MF (M = Ni, H₂, Co, and Ru) samples displayed good crystallinity and high porosity (Figures S6 and S7). Nitrogen sorption isotherm at 77 K revealed that their BET surface areas were 1704, 1682, 1655, and 1623 $\text{m}^2 \text{g}^{-1}$ for PCN-224(Ni)_{200%}/MF, PCN-224(H₂)_{200%}/MF, PCN-224(Co)_{200%}/MF, and PCN-224(Ru)_{200%}/MF, respectively (Figure S8). The morphology of these PCN-224(M)_{200%}/MF (M = Ni, H₂, Co, and Ru) samples was investigated by FE-SEM to visualize their hierarchical structures. As shown in Figure 3, the PCN-224(M) crystals were closely anchored on the melamine foam fibers. Scanning electron microscopy coupled with energy dispersive X-ray (SEM/EDX) indicated the content of Fe, Ni, Co, and Ru were 4.98%, 5.15%, 5.41, and 8.65%, which were consistent with their theoretical values (Figures S9–S13). The chemical stability of PCN-224(M)_{200%}/MF (M = Fe, Ni, H₂, Co, and Ru) were also examined in different solvent conditions, including water, ethanol, DMF, THF, and hexane. All of the MOF/MF composites can stay stable in these solutions for 7 days without any loss of PCN-224 powder (Figure S14). Combining the good crystallinity, high porosity, and excellent stability, PCN-224/MF exhibited a broad prospect in heterogeneous catalysis.

Table 1. The epoxidation reaction of cholesteryl esters catalyzed by PCN-224(M)/MF.^[a,b]

Entry	Catalyst	Amount (mol%) ^[c]	Oxidant	Time (h)	Yield (%) ^[d]
1	PCN-224(Ru) _{200%} /MF	2	Cl ₂ pyNO	36	92
2	PCN-224(Ru) _{200%} /MF	2	PhIO	36	73
3	PCN-224(Ru) _{200%} /MF	2	O ₂	36	15
4	PCN-224(Ru) _{200%} /MF	1	Cl ₂ pyNO	45	90
5	PCN-224(Ru) _{200%} /MF	5	Cl ₂ pyNO	36	92
6	PCN-224(Fe) _{200%} /MF	2	Cl ₂ pyNO	72	34
7	PCN-224(Co) _{200%} /MF	2	Cl ₂ pyNO	72	41
8	PCN-224(Ni) _{200%} /MF	2	Cl ₂ pyNO	72	0
9	PCN-224(H ₂) _{200%} /MF	2	Cl ₂ pyNO	72	0
10	Melamine foam	–	Cl ₂ pyNO	72	0
11	PCN-224(Ru)	2	Cl ₂ pyNO	36	56
12	TCPP(Ru)	2	Cl ₂ pyNO	36	42
13 ^[e]	PCN-224(Ru) _{200%} /MF	2	Cl ₂ pyNO	32	92
14 ^[f]	PCN-224(Ru) _{200%} /MF	2	Cl ₂ pyNO	30	92
15 ^[g]	PCN-224(Ru) _{200%} /MF	2	Cl ₂ pyNO	40	90
16 ^[h]	PCN-224(Ru) _{200%} /MF	2	Cl ₂ pyNO	40	93

[a] All reactions were carried out in CH₂Cl₂ at room temperature. [b] Catalyst:cholesteryl esters:(Cl₂pyNO) molar ratio=1:50:100. [c] The amount of catalyst. [d] Yield of isolated product based on the amount of the substrate consumed. [e] PCN-224(Ru)_{200%}/MF with 1 μm crystals as catalyst. [f] PCN-224(Ru)_{200%}/MF with 600 nm crystals as catalyst. [g] The substrate was cholesteryl palmitate. [h] The substrate was cholesteryl benzoate.

Cholesterol plays a vital role in the constitution of cell membranes and controls the state of membrane fluidity. In many cases, certain cholesterol derivatives are powerful medicines for human diseases. Therefore, the development of efficient synthetic methods for cholesterol derivatives are important for the improvement of human health. From the economic viewpoint, the catalytic epoxidation of unsaturated cholesteryl esters is of great significance to produce metabolites in the pharmaceutical industry. Although several effective catalytic transformation have been developed, most of the catalysts are homogeneous noble metal complexes, which are quite expensive and difficult to be recycled.^[18] The porous heterogeneous catalysts are promising to address this problem. The exploitation of high-efficient macroporous catalysts for epoxidation of unsaturated cholesteryl esters remains an enormous challenge. Inspired by the

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considerable efficiency of PCN-224(M)_{200%}/MF catalysts in the epoxidation of cis-stilbene, we attempted to investigate their catalytic performance in the epoxidation transformation of cholesteryl esters.

Based on the flexibility and elasticity of PCN-224(M)/MF, we compressed and filled the composites into glass columns for conventional separation and recycling use (Figure S15). Owing to the open-cell macroporous structures and uniformly distributed catalytic active sites, PCN-224(M)/MF exhibited an exceptional catalytic performance in the epoxidation of cholesteryl esters. As shown in Table 1, we treated cholesteryl acetate with 2,6-dichloropyridine *N*-oxide (Cl₂pyNO) in dichloromethane in the presence of 2 mol% of PCN-224(Ru)_{200%}/MF as catalyst (Table 1, entry 1). Under such conditions, an excellent yield (92%) of corresponding epoxide was obtained after 36 h. However, lower yield of 73% and 15% was obtained in the presence of PhIO and O₂ as oxidants, respectively (Table 1, entry 2 and 3). This result indicated that Cl₂pyNO was the prime oxidant for the epoxidation transformation. To screen the optimum catalyst amount, we adjusted the dosage of PCN-224(Ru)_{200%}/MF as 1 mol% and 5 mol%. When the amount of PCN-224(Ru)_{200%}/MF was reduced to 1 mol%, a lower yield of 90% was achieved after 45 h (Table 1, entry 4). Meanwhile, the same yield of 92% was observed in the presence of 5 mol% PCN-224(Ru)_{200%}/MF (Table 1, entry 5). As control experiments, PCN-224(Fe)_{200%}/MF, PCN-224(Co)_{200%}/MF, PCN-224(Ni)_{200%}/MF, PCN-224(H₂)_{200%}/MF, bare melamine foam, and powdered PCN-224(Ru) were employed as catalysts for the epoxidation reaction (Table 1, entry 6–11). However, after 72 h, PCN-224(Fe)/MF and PCN-224(Co)/MF produced the epoxide product in the yield of 34% and 41%, respectively (Table 1, entry 6 and 7). PCN-224(Ni)_{200%}/MF, PCN-224(H₂)_{200%}/MF, and melamine foam exhibited no catalytic effects on the epoxidation transformation (Table 1, entry 8–10), which revealed their chemical inertness in the catalysis. To make the control experiment more comparable, we prepared powdery PCN-224(Ru) samples with the same crystal size with those in PCN-224(Ru)_{200%}/MF. All the crystals of powdery PCN-224(Ru) aggregate in masses (Figure S16), which reduced the accessibility to catalytic sites and greatly limited the intergranular diffusion of substrates. Under the same conditions, the powdery PCN-224(Ru) and the TCPP(Ru) ligand generated the epoxidation product in the yield of 56% and 42%, respectively, which was much lower than that of PCN-224(Ru)_{200%}/MF composite (Table 1, entry 11 and 12). Compared with the TCPP(Ru) ligand, PCN-224(Ru) lead to a higher yield on account of the enrichment of substrates within the mesopores. In addition, all the epoxidation reactions were conducted in the glass column filled with PCN-224(Ru)_{200%}/MF composites or powdery PCN-224(Ru) without stirring. Under such conditions, the catalytic centres in PCN-224(Ru)_{200%}/MF were evenly distributed in the whole reaction system, while the powdery PCN-224(Ru) accumulated at the bottom. Therefore, PCN-224(Ru)_{200%}/MF exhibited great superiority over its PCN-224(Ru) counterpart owing to the higher dispersibility and more accessibility of catalytic sites. It seems no matter that PCN-224(Ru) or PCN-224(Ru)_{200%}/MF composite was used, the high porous structure could increase the overall reaction rate, and further leading to an enhanced catalytic efficiency. Therefore, all of these results

clearly demonstrated that both the mesopores and the macropores contributed to the extinguished catalytic performance of PCN-224(Ru)_{200%}/MF.

To investigate the effects of crystal sizes on catalytic performance, we prepared two additional PCN-224(Ru)_{200%}/MF samples with smaller crystal sizes (1 μm and 600 nm, Figures S17 and S18). In the presence of PCN-224(Ru)_{200%}/MF with 1 μm and 600 nm crystals, the same yield of 92% can be obtained after 32 h and 30 h, respectively (Table 1, entry 13 and 14). The shorter reaction time reveals that PCN-224(Ru)_{200%}/MF with smaller crystal sizes exhibited better catalytic performance than the one with large crystals (Table 1, entry 1). However, when the crystal size decreased to the nanoscale, PCN-224(Ru) was just coated on the surface of MF matrix. The MOFs were very easy to strip off from MF matrix due to the weak fixation ability (Figure S19). Even one-time catalytic use can lead to significant loss of MOF powder, which greatly limits its recyclability in practical applications.

Remarkably, the PCN-224(Ru)_{200%}/MF composite also displayed considerable catalytic efficiency for the epoxidation of cholesteryl palmitate and cholesteryl benzoate with high yield of 90% and 93% (Table 1, entry 15 and 16), respectively. On account of the exceptional chemical and mechanical stability of PCN-224/MF composites, the catalyst PCN-224(Ru)_{200%}/MF can be recycled more than six times. After each cycle of catalytic epoxidation, PCN-224(Ru)_{200%}/MF composite could be easily separated and recovered by washing with eluents. The recycling of the PCN-224(Ru)_{200%}/MF catalyst in totally six runs did not bring out significant loss of its original catalytic activity (Figure S20). In addition, it can be proven that the crystallinity and porosity of PCN-224(Ru)_{200%}/MF were well maintained from the PXRD patterns and N₂ sorption isotherms (Figures S21 and S22).

In summary, we have developed a one-pot strategy for the preparation of hierarchical MOF/melamine foam composites, wherein MOF crystal nanoparticles were decorated on the fibers of the melamine foam in a ball-and-stick model. The bottom-up strategy is possible to be broadly applied to many other MOFs and substrates. In addition, the combination of mesopores and macropores in the MOF/melamine foam composite was achieved. The specific MOF/melamine foam composites have high stability, hierarchical porosity, flexible and elastic texture, which are significantly favourable for heterogeneous catalysis. Finally, this work highlighted the distinguished catalytic performance of MOF/melamine foam for the epoxidation of cholesteryl esters. The additional macroporous melamine foam contributed greatly to the diffusion process and positively improved the catalytic activity of MOFs. This strategy would be extensively employed in the development of functional MOF composite materials and high-performance heterogeneous catalysts.

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COMMUNICATION

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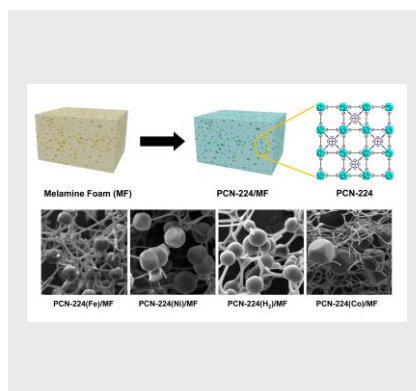
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A series of flexible and hierarchical MOF composite have been developed by integrating mesoporous MOFs with macroporous melamine foam using a one-pot process. These composite materials can be employed as an effective heterogeneous catalyst for epoxidation reactions.



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Page No. – Page No.

Flexible and Hierarchical Metal-Organic Framework Composites for High-Performance Catalysis