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Title: Highly Effective and Selective Catalysts for Cinnamaldehyde Hydrogenation by Hydrophobic Hybrids of Metal-organic Frameworks, Metal Nanoparticles and Micro- & Mesoporous Polymers

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Highly Effective and Selective Catalysts for Cinnamaldehyde Hydrogenation by Hydrophobic Hybrids of Metal-organic Frameworks, Metal Nanoparticles and Micro- & Mesoporous Polymers

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Abstract: As for heterogeneous catalysis, the activity and selectivity are two key factors for evaluating catalysts. Metal-organic frameworks (MOFs) as selectivity regulators for catalytic reaction have attracted much attention, especially MOFs and metal nanoparticles (NPs) shelled structures, e.g., MOFs@NPs@MOFs. Nevertheless, the hydrophilic MOFs shell is challenging to gather hydrophobic reactants. Here, we innovate a new and viable approach to solve this problem. By employing conjugated micro- and mesoporous polymers with iron(III) porphyrin (FeP-CMPs) as the new shell, MIL-101@Pt@FeP-CMP was fabricated firstly, which not only is hydrophobic and porous to enrich reactants, but also possesses iron sites to activate C=O bond and thereby regulate the selectivity for cinnamyl alcohol in hydrogenation of cinnamaldehyde. Interestingly, MIL-101@Pt@FeP-CMP^{sponge} can reach ultrahigh turnover frequency (TOF) as high as 1516.1 h⁻¹ with 97.3 % selectivity towards cinnamyl alcohol and 97.6 % conversion. The results open up a new avenue for decorating and protecting MOFs, which will play an important role in both academia and industry.

On account of limited natural source and enormous demand, selective hydrogenation of cinnamaldehyde (**A**) to cinnamyl alcohol (**B**) is very important in flavouring, perfume and pharmaceutical industries.^[1] So far, much work mainly focuses on improving the selectivity of **B**, but little attention was paid on catalytic efficiency which was simply improved by rigorous conditions (high temperature or H₂ pressure).^[2] Take catalytic efficiency of the industrial process into consideration, milder working conditions and shorter working period will bring more economical benefit. Therefore, many research groups focus on NPs catalysts, such as Pd, Au, Pt, Ru, Ir NPs, etc.^[3] Due to high specific surface, metal NPs not only exhibit excellent activity, but also can be regulated easily by supports or special surfactants.^[3]

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one side directly contacts with the support and most of the surface do not, which is usually incompetent to significantly improve the selectivity for the production of thermodynamically unfavoured products.^[3] The surfactants wrap NPs tightly but bring steric hindrance decreasing the catalytic activity.^[3] Recently, emerging as intriguing porous crystalline materials, metal-organic frameworks (MOFs) have drawn much attention by virtue of ordered and tunable pores, large surface area, diversified structure and particularly unsaturated metal sites, which offer great potential to versatile applications.^[4] Up to now, MOFs containing metal NPs have been intensively investigated, on account of unique and synergistic functionalities. In particular, MOFs@NPs@MOFs structure can change the chemical environment surrounding NPs thoroughly and simultaneously keep reactants access to active sites.^[4]

As we all know, many substrates of hydrogenation, such as cinnamaldehyde, are hydrophobic, so the environmental wettability of catalytic site plays a crucial role in modifying the catalytic performance.^[5] However, the surface and channels of many kinds of MOFs are hydrophilic, resulting in inconvenience of gathering hydrophobic molecules.^[6] Hence, the new shell should better be composed of porous and hydrophobic materials and possess iron sites to activate the C=O bond.^[3] Considering these factors, FeP-CMPs are chosen to construct the shell.^[7] Since the integration of the hydrophobic CMPs and wettable NPs is highly challenging,^[8] here we innovate a new and viable approach, using well-designed hybrids consisting of MOFs, NPs and FeP-CMPs, to solve this problem. To the best of our knowledge, it has never been reported.

MIL-101 ($Cr_3F(H_2O)_2O[(O_2C)-C_6H_4-(CO_2)]_3 \cdot H_2O)$, one of the most popular MOFs in recent researches about composite catalysts, was employed to load Pt NPs on the surface, due to very large pore sizes (~30 to 34 Å), surface area (SLangmuir = 3100 m²/g) and excellent stability.^[9] The fantastic crystal structure and ultrastable framework endowed MIL-101 with possibility of postsynthetic modification (PSM), such as decorating skeleton, exchanging metals, loading NPs and coating the surface with polymers, etc.^[10] By a simple method, as-synthesized Pt NPs were adsorbed on the surface of MIL-101.^[11] However, on the basis of literatures and experimental results (Figure S1), MIL-101 was not stable in alkaline aqueous solution at high temperature, so the synthetic conditions of shell were slightly modified (Supplementary information for details).^[12] Finally, by liquid epitaxial growth, we succeeded in coating MIL-101@Pt with FeP-CMPs (Figure 1a). In order to study the function of iron sites, a series of MIL-101@Pt@CMP without iron was prepared.

By scanning electron microscopy (SEM) and transmission electron microscopy (TEM), we approximatively determined the distribution of MIL-101, Pt NPs and FeP- CMP in the composite. As the growth of organic shell, the surface of sandwich hybrids became gradually rougher (Figure S2). Figure 1c exhibited that

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Pt NPs were distributed uniformly on the surface of the MIL-101. Due to the heavier contrast of Pt, sandwiching Pt NPs between the two kinds of porous materials were easily distinguished (Figure 1d-h). The resulting shell of MIL-101@Pt@FeP-CMP^{sponge} became thick but non-flat morphology looking like sponge and the other one was only about 5.5 nm thickness by decreasing amount of precursors (Figure S3). Similarly, the thickness of shell in MIL-101@Pt@CMP system could be adjusted from 9.3 nm to 7.9 nm to 3.1 nm (Figure S4). In order to get more direct evidence, we applied energy dispersive spectra (EDS) to map the distribution of different metals (Cr and Fe) using TEM. Fe was dispersed more widespread and outer than Cr in images of MIL-101@Pt@FeP-CMP system, proving that FeP-CMP wrapped MIL-101@Pt (Figure 1i and j). Aforementioned results of TEM and SEM all exactly matched our design.



Figure 1. a, Design strategy to synthesize MIL-101@Pt@FeP-CMP. TEM images of MIL-101 (b), MIL-101@Pt (c), MIL-101@Pt@FeP-CMP^{sponge} (d), MIL-101@Pt@FeP-CMP^{5.5} (e), MIL-101@Pt@CMP^{9.3} (f), MIL-101@Pt@CMP^{7.9} (g) and MIL-101@Pt@CMP^{3.1} (h). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and corresponding EDS elemental (Cr and Fe) mapping of MIL-101@Pt@FeP-CMP^{sponge} (i) and MIL-101@Pt@FeP-CMP^{5.5} (j).

The Fourier Transform Infrared Spectrometer (FT-IR) analysis was carried out to verify the existence of FeP-CMP. As shown in Figure 2a, by contrasting spectra of the sandwich heteroarchitectures and MIL-101@Pt, the new characteristic peaks at 653cm⁻¹, 697 cm⁻¹, 801 cm⁻¹, 1001 cm⁻¹ (Fe-N), 1072 cm⁻¹, 1203 cm⁻¹, 1336 cm⁻¹, 1485 cm⁻¹, originating from the new shell, confirmed the formation of FeP-CMP, and some others were covered. Note that the presence of peak at 1001 cm⁻¹ caused by N-Fe bond vibrating and the absence at 960 cm⁻¹ resulting from N-H bond stretching both proved iron containing in porphyrin. Moreover, the UV-vis absorption spectra of MIL-101@Pt@FeP-CMP displayed new bands at 432 nm attributing to the Soret band and 580, 624 and 672 nm representing the Q bands of iron(III) porphyrin units, which were all indexed to FeP-CMP and the relative intensity increased with the thickness of FeP-CMP growing (Figure 2b and S5). Analogously, the forming of CMP shell was also certified by FT-IR and VU-vis absorption spectra (Figure S6 and S7).

In order to certify the intact crystallinity of MIL-101 and Pt NPs, the powder X-ray diffraction (PXRD) studies were conducted. As shown in Figure 3a, the PXRD profile confirmed the amorphous character of FeP-CMP and suggested that the crystalline characters of the parental MIL-101 in the hybrids were maintained. However, MIL-101@Pt@CMP^{3.1} became amorphous, which might attribute to the thin shell (Figure S8). So the thick shell could protect the core from alkali solution. The PXRD pattern of MIL-101@Pt had a very weak peak at 40°, corresponding to (111) plane of fcc Pt, ascribing to the low content and uniformly dispersion (Figure S9). Due to the limit of PXRD, the high resolution transmission electron microscopy (HRTEM) was applied to reveal the high crystallinity of embedded Pt NPs. HRTEM image further indicated that each Pt NP (3.3 nm average diameter) was highly crystalline with the interplanar spacing of 0.23 nm, corresponding to the (111) plane of face centered cubic (fcc) Pt (Figure S10). After coating the new shell, Figure S11 exhibited the same interplanar spacing of sandwiched Pt NPs, proving intact crystallinity.

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The N₂ adsorption-desorption isotherms were analyzed by Brunauer-Emmet-Teller method and the surface areas of FeP-CMP, MIL-101, MIL-101@Pt@FeP-CMP^{5.5} and MIL-101@Pt@FeP-CMP^{sponge} were measured as 255, 2949, 1480 and 1176 m²/g, respectively (Figure 3b). As the FeP-CMP thickness increased, the surface area of composite decreased. Compared with MIL-101, the reduced surface areas of MIL-101@Pt@FeP-CMP could be attributed to the inclusion of FeP- CMP in the pores of MIL-101 and the low surface area of FeP-CMP.^[8] Based on density functional theory (DFT) study, pore sizes of FeP-CMP (~0.7 and ~1.3 nm) allowed reactant molecules to diffuse through the shell and access to the encapsulated Pt NPs (Figure S12). However, the surface area of CMP (59 m²/g) was much smaller than FeP-CMP, resulting in difficulty of penetration of substrates through shell (Figure S13).



Figure 2. a, FT-IR spectra of MIL-101@Pt (black line), MIL-101@Pt@FeP-CMP^{5.5} (red line), MIL-101@Pt@FeP-CMP^{sponge} (blue line) and FeP-CMP (green line). b, UV-vis absorption spectra of MIL-101@Pt (black line), MIL-101@Pt@FeP-CMP^{5.5} (red line), MIL-101@Pt@FeP-CMP^{sponge} (blue line).



Figure 3. a, XRD patterns and (b) N₂ adsorption-desorption isotherms of MIL-101 (black line), MIL-101@Pt@FeP-CMP^{5.5} (blue line), MIL-101@Pt@FeP-CMP^{5.5} (b

In general, due to the hydrophily of surface and channels, MOFs are very good at absorbing water.^[8] Therefore, in spite of lower densities than water, MIL-101 powder was thrown into water and directly dropped to the bottom. Nevertheless, with the help of hydrophobic shell, MIL-101@Pt@FeP-CMP and MIL-101@Pt@CMP could float on the water (Figure S14). After drastic shaking, only MIL-101@Pt@FeP-CMP^{5.5} drowned, ascribing to thin shell (Figure S15). In order to precisely study chemical changes of the surface properties, water contact angle

was measured on the pellet of each material. MIL-101 showed complete water wetting, which adsorbed a drop of water immediately (Figure 4a). As shown in Figure 4b and c, the water contact angles gradually increase from 88.6° (MIL-101@Pt@FeP-CMP^{5.5}) to 122.9° (MIL-101@Pt@FeP-CMP^{sponge}), which were positively related to the FeP-CMP thickness. In the MIL-101@Pt@ CMP system, the contact angles changed from 115.4° to 138.7° to 142.7°, with the CMP shell growing (Figure 16d-f).



Figure 4. Water contact angle measurements of MIL-101 (a), MIL-101@Pt@FeP-CMP^{sponge} (b), MIL-101@Pt@FeP-CMP^{5.5} (c). Cinnamaldehyde adsorption (Details in SI) with 4 mg materials (d).

It was expected that the hydrophobic shell would improve catalytic efficiency significantly and iron sites could help to regulate selectivity. Hydrogenation of A, a classical and important reaction performed on Pt NPs, was chosen to evaluate catalytic performance and conducted under the similar reaction condition with previous work.^[2b] We compared the performances of catalysts, especially efficiency, at the same reaction time (15 min). The pure MIL-101, FeP-CMP and MIL-101@FeP-CMP^{sponge} did not possess catalytic ability of hydrogenation (Table 1, entries 1-3), demonstrating that Pt NPs are the only catalytic sites. MIL-101@Pt achieved 15.0% conversion of A and 23.3% selectivity to **B** and the TOF was only 203.4 h⁻¹ (Table 1, entry 4). Nevertheless, on account of coating FeP-CMP, the MIL-101@Pt@FeP-CMP^{sponge} and MIL-101@Pt@FeP-CMP^{5.5} realized 97.6% and 97.9% conversion after 15 min, respectively. Owing to the thicker shell, MIL-101@Pt@FeP-CMP^{sponge} exhibited better selectivity to **B** (97.3%) than MIL-101@Pt@FeP-CMP^{5.5} (82.6%) but still kept the ultrahigh TOF (1516.1 h⁻¹) (Table 1, entries 5 and 6). TEM images exhibited that the used MIL-101@Pt@FeP-CMP^{sponge} still kept sandwich structure, suggesting that FeP-CMP shell was not peeled off during reaction (Figure S17).

As for the ultrahigh catalytic activity, FeP-CMP shell played an important role in the catalytic reaction. Firstly, owing to the hydrophobic and porous shell, MIL-101@Pt@FeP-CMP system showed much better adsorption of **A**, proving enrichment of reactant around Pt NPs (Figure 4d). MIL-101@Pt@CMP showed the similar properties (Figure S18). However, CMP shell hindered **A** to access to active sites due to the small surface areas (Figure 3b and S13). By contrast to MIL-101@Pt, MIL-101@Pt@CMP^{3.1} (25.4% conversion, 31.7% selectivity and 398.4 h⁻¹), MIL-101@Pt@CMP^{7.9} (27.4% conversion, 18.0% selectivity and 417.5 h⁻¹) and MIL-101@Pt@CMP^{9.2} (31.6% conversion, 29.4% selectivity and 468.1 h⁻¹) showed very slight improvement in catalytic activity (Table 1, entries 7-9). In spite of excellent collection of **A**, MIL-101@Pt@CMP system couldn't improved catalytic efficiency a lot.

Furthermore, in order to verify the superiority of sandwich structure, simply physical mixtures of MIL-101@Pt and FeP-CMP (MIL-101@Pt/ x mg FeP-CMP) were tested in catalytic reaction. According to yield of as-synthesized FeP-CMP (20 mg

FeP-CMP, based on 25 mg FeP), in the catalytic system (2 ml solution of catalysts), MIL-101@Pt@FeP-CMP^{sponge} and MIL-101@Pt@FeP-CMP^{5.5} could be regarded as MIL-101@Pt@1.6 mg FeP-CMP and MIL-101@Pt@0.5 mg FeP-CMP. As expected, MIL-101@Pt/1 mg FeP-CMP only exhibited 26.3% conversion, 39.6% selectivity of **B** and TOF as 356.6 h⁻¹ (Table 1, entry 10), which was a bit better than MIL-101@Pt but much worse than sandwich composites. With increasing amount of physically mixing FeP-CMP (2 mg, Table 1, entry 11), the selectivity towards **B** (43.3%) and activity (TOF, 347.1 h⁻¹) improved slightly. These results indicated that the FeP-CMP shell of well designed structure could enrich reactants around the interface of MIL-101 and FeP-CMP, where the Pt NPs were embedded, to accelerate catalytic efficiency.

XPS measurements of MIL-101@Pt and MIL-101@Pt@FeP-CMP^{5.5} revealed that almost no electron of Pt NPs transferred to FeP-CMP (Figure S19).^[3] On the one hand, it was because of low content of Fe within FeP-CMP (3.27 wt%).^[7] On the other hand, the interaction of Pt NPs with FeP-CMP was much weaker than MIL-101, which could be confirmed by the low Pt loading amount of FeP-CMP@Pt (Figure S20). Previous works had demonstrated that the reduced electron density of Pt NPs was a possible reason for the decreased hydrogenation activity.^[13] In this work, the FeP-CMP shell succeeded in maintaining the activity of Pt NPs.

As for the selectivity towards **B**, FT-IR survey of **A** molecule adsorbed on MIL-101@Pt@FeP-CMP^{sponge} showed an obvious red shift of the v_{C=0} bond from 1678 cm⁻¹ to 1670 cm⁻¹, indicating the specific interaction between coordinatively unsaturated iron site and C=O bonds (Figure S21).^[3] As expected, MIL-101@Pt@FeP-CMP^{sponge} could also perform excellent catalytic properties in other α , β -unsaturated aldehydes (Table S3).

In previous work, MIL-101@Pt@MIL-101(Fe)^{2.9} could exhibited 95.6% selectivity at almost full conversion (99.8%), which only showed a TOF of 16.9 h^{-1.[3c]} Inspiringly, within MIL-101@Pt@FeP-CMP system, the similar conversion and selectivity were maintained but a remarkable 89-fold enhancement of TOF (1516.1 h⁻¹) was realized by simply altering shell from MOF to FeP-CMP (Table 1 entry 5). Our MIL-101@Pt@FeP-CMP^{sponge} outperformed state-of-the-art catalysts, especially in terms of catalytic efficiency (Table S4).

Reaction								
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	А	В	с	D				
Entry	Catalysts	Conversion [%] ^[b]	Selectivity [%] ^[b]					
			В	C 📐	D			
1	MIL-101	0	-		-	-		
2	FeP-CMP	0	-	-	-	-		
3	MIL-101@FeP-CMP ^{sponge}	0	-	-	-	-		
4	MIL-101@Pt	15.0	23.3	76.7	0	203.4		
5	MIL-101@Pt@FeP-CMP ^{sponge}	97.6	97.3	2.6	0	1516.1		
6	MIL-101@Pt@FeP-CMP ^{5.5}	97.9	82.6	13.9	3.5	1463.9		
7	MIL-101@Pt@CMP ^{9.2}	31.6	29.4	70.6	0	468.1		
8	MIL-101@Pt@CMP ^{7.9}	27.4	18.0	82.0	0	417.5		
9	MIL-101@Pt@CMP ^{3.1}	25.4	31.7	68.3	0	398.4		
10	MIL-101@Pt/1 mg FeP-CMP	26.3	39.6	60.4	0	356.6		
11	MIL-101@Pt/2 mg FeP-CMP	25.6	43.3	56.7	0	347.1		

Table 1 Selective hydrogenation of cinnamaldehyde by different catalysts.^[a]

A, cinnamaldehyde; **B**, cinnamyl alcohol; **C**, benzenepropanal; **D**, phenylpropanol. [a] Reaction condition: 2 ml solution of catalysts; the reaction requires 125 ul triethylamine, 2.5 ul mesitylene and 0.4 mmol **A**, room temperature, 3 MPa H₂ for 15 min. [b] Determined by GC. [c] TOF was calculated by the mole number of converted **A** (mole number of total Pt)⁻¹ h⁻¹. The amount of Pt NPs of each catalyst was determined by ICP (Table S2).

In summary, our work is the first report on integration of MOFs. NPs and CMPs, which opens up a new avenue for the construction of sandwich hybrids. By replacing MOFs shell with FeP-CMP, we succeeded in modifying environmental of Pt NPs. which not only changed the wettability to enrich A, but activated C=O bond to improve selectivity to **B**. TOF of hydrogenation over MIL-101@Pt@FeP-CMP^{sponge} reached as high as 1516.1 h⁻ ¹ and kept 97.3% selectivity towards **B** at 97.6% conversion of **A**. MOFs@NPs@FeP-CMPs Hence. fabrication of heteroarchitectures may prove to be effective when targeting important but challenging reactions. We anticipate that this simple but ingenious design will provide versatile material platforms for other kinds of catalysts, aiming at resolving the phase separation problem and also achieve multiple functions in some other practical applications, such as energy, environment and so on.^[14]

Experimental Section

The experimental details included in Supporting Information.

Acknowledgements

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Keywords: metal-organic frameworks • conjugated mesoporous polymers • nanoparticles • hydrophobicity • hydrogenation

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COMMUNICATION

We synthesized a series of MIL-101@Pt@FeP-CMP coating with hydrophobic and porous shell. In hydrogenation the of cinnamaldehyde, FeP-CMP shell not only maintains selectivity with the help of iron(III) porphyrin but also promotes catalytic efficiency due to the environmental hydrophobicity. Especially, MIL-101@Pt@FeP-CMP^{sponge} catalyst reached the highest TOF (1516.1 h⁻¹) and outperformed state-ofthe-art catalysts.



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