Metal organic Frameworks as Robust Host of Pd Nanoparticles in Heterogeneous Catalysis: Synthesis, Application, and Prospect

Songhao Luo,[†]^a Zhuotong Zeng,[†]^b Guangming Zeng,^{*a} Zhifeng Liu,^{*a} Rong Xiao,^{*b} Ming Chen,^a Lin Tang,^a Wangwang Tang,^a Cui Lai,^a Min Cheng,^a Bipbo na ^a Qinghua Liang,^a Han Wang,^a, Danni Jiang^a

^a College of Environmental Science and Engineering, Hunan University and Key Laboratory of Environmental Biology and Pollution Control (Ilunar University), Ministry of Education, Changsha 410082, PR China.

^b Department of Dermatology, Second Ziangia Hospital, Central South University, Changsha 410011, P R China.

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ABSTRACT: Metal organic frameworks (MOFs) is one set of the most excellent supports for Pd nanoparticles (NPs). MOFs as the host, mainly have the following advantages: (i) Provide size limits for highly dispersed Pd NPs; (ii) Fixing Pd NPs is beneficial for separation and reuse, avoiding the loss of expensive metals; (iii) The MOFs skeleton is diversified and functionalized, which is beneficial to enhance the interaction with Pd NPs and prolong the service life of the catalyst. This review discusses the synthesis strategy of Pd@MOF, which provides guidance for the synthesis of similar materials. After that, the research advance of Pd@MOF in

heterogeneous catalysis is comprehensively summarized, including C–C coupling reaction, benzyl alcohol oxidation reaction, simple olefin hydrogenation reaction, nitroaromatic compound reduction, tandem reaction, and the photocatalysis, with the emphasis in providing a comparison with the performance of other alternative Pd-containing catalysts. In the final section, this review presents the current challenges and which are the next goals in this field.

1. INTRODUCTION

In recent years, heterogeneous catalytic systems have received increasing attention due to their ease of separation from liquid phase reaction matrices.¹⁻³ Metal organic frameworks (MOFs) are widely used for heterogeneous catalysis.⁴⁻⁵ In addition, MOFser often used as the host of the catalytically active component.⁶ Encapsulation of the catal In active component with a porous solid material (such as MOFs) facilitates recover of the catalytically active material.⁷⁻ ⁹ The principle of this method is to utilize the ri of the porous material, which to provides space limitations for the catalytically active components and prevents aggregation and leaching.¹⁰ So far, this method has been widely reported. Many inert porous solid materials, solids,¹² carbon polymorphs,¹³ metal oxides,¹⁴ and their such as porous polymers,¹¹ mesopord orting materials. Compared to MOFs materials, these porous variants¹⁵ are widely used a materials can provide good port and space limitations, but the pores of these materials are not uniform and are easily clogged. This affects the diffusion of reactants and products, resulting in reduced catalytic activity.¹⁶ Therefore, in this review, we will focus on the case where MOFs materials are the host.

Metal organic frameworks are a new type of porous crystal network composed of metal nodes and organic links, which were discovered in the early 1990s.¹⁷⁻¹⁸ In recent years, they have been widely concerned as an excellent supporting material.¹⁹⁻²¹ MOFs have many advantages as catalyst supports,^{6, 22-23} such as (i) high metal node density, high surface area, porosity, and uniform pore structure; (ii) the unique functional groups on the organic chain of MOF which can immobilize catalytically active metal ions, avoid the loss of expensive metals and prolong the service life of the catalysts; (iii) MOFs material acts as a shell, which facilitates selective catalysis due to its uniform pores; (iv) it is possible to assemble MOFs with diverse structures by changing the types of organic links and inorganic nodes.

In the case where the MOFs material is used as the catalytic host, metal nanoparticles (MNPs) have been widely studied. The main reason for encapsulating MNPs inside MOFs is to maintain the stability of the fine MNPs, and avoid their aggregation and growth. Pd NPs is one of the best cases to illustrate the potential of MOFs as hosts of MNPs. In the past decade, Pd nanoparticles (NPs) have been extensively studied in a variety of atalytic applications.²⁴ Pd NPs act as catalysts with high activity and high selectivity.²⁵ The loo ka a strong interaction with hydrogen molecules and are one of the most active substances in noble metals, absorbing light energy over a wide spectral range.²⁶ In addition, the we known plasma effect of Pd NPs can efficiently capture light energy to drive the read $5n.^{-28}$ Based on such excellent properties, \checkmark ¹ environmental remediation,³² and clean Pd NPs are widely used in organic con ion, aggregated during the catalytic process,³⁷ which energy.³³⁻³⁶ However, single Pd NPs are results in the deactivation of the Pd NPs catalyst. In addition, pure Pd NPs are expensive and non-recyclable, which is not conducive to their further application.³⁸⁻³⁹ Scientists have innovatively using powrful MOFs to encapsulate Pd NPs, and Pd@MOF is a heterogeneous catalyst with excellent catalytic properties.

In this review, we will focus on the case of Pd NPs encapsulated inside MOFs, and summarizes recent advances in heterogeneous catalyst Pd@MOF. Table 1 lists the examples that will be presented in this review grouped consistent with the application type, making emphasis on the particle size, Pd loading, and the stability of catalyst. We believe that the synthetic methods and their modifications applicable to Pd@MOF are equally applicable to other metal@MOF materials. It is hoped that this review will provide guidance for the synthesis of similar materials. Currently, Pd@MOF is a widely used heterogeneous catalyst. Herein, we

provide a review to discuss in detail the activity and stability of the heterogeneous catalyst Pd@MOF in the application. These applications including typical C-C coupling reaction, alcohol oxidation reaction, olefin hydrogenation reaction, and reduction reaction of nitrobenzene compounds. In addition, this review will also discuss the synergistic effects of Pd NPs and MOFs. it is well known that Pd NPs and MOFs each have good catalytic properties. In the case of synergistic catalysis between the two, the separated multi-step reactions can be connected in series. This facilitates the full utilization of the reactants and the simplification of the reaction process. Therefore, this review will also discuss the synergistic effects of Pd NPs and MOFs. Meanwhile, this review summarizes that the combination of plasma effect Pd NPs and photoreactive MOFs can play a significant role in the field of the atalysis. During the entire photocatalytic reaction, light is received by the MQFs and activates the bulk of the MOFs to produce photogenerated electron-hole pairs. The photogenerated electrons are then rapidly tili e the energy obtained from MOFs to transferred to the Pd NPs catalytic center. Pd NPs efficiently catalyze the conversion of the action matrix to the product. Finally, this review ed in this field. Readers can better understand presents points that have not yet be en Pd@MOF and its applications b v reading this review.

Table 1. Overview MOF-supported of NPs as Heterogeneous Catalysis							
Catalyst ^a	Particle size (nm)	Loading (wt.%)	Reuse times	Refs.			
Suzuki reaction							
Pd@MIL-101(Cr)-NH ₂	2.6	8.0	10	40			
PMA-MIL-101(Cr)	2.0	6.0	4	41			
Pd@MIL-101-NH ₂	-	8.0	5	42			
Pd@MIL-101(Cr)-NH ₂	-	8.0	-	43			
Pd@MOF-5	2–5	4.2	1	44			
Pd/MOF-253	-	0.23 mol% Pd	-	45			
Pd/Y-MOF	-	-	5	46			
Fe ₃ O ₄ @PDA-Pd@[Cu ₃ (BTC) ₂]	-	-	-	47			

Pd@NH ₂ -UiO-66(Zr)	9.3	0.67	3	48
Pd@UiO-66	-	2.5	5	49
Pd/DUT-67	3.5	0.5	-	50
Heck reaction				
Pd@MIL-101(Cr)-NH ₂	-	7-8	3	51
Pd@UiO-67	-	1.1	5	52
Sonogashira reactions				
Pd(II)@ZrMOF-BIPY	-	1.0	5	53
Oxidation of benzyl alcohol				
Pd@Cu(II)-MOF	-	2-5.1	6	54
Pd/Cu2(BDC)2DABCO	-		4	55
Hydrogenation of propylene				
Pd@MOF-5	0.6		-	56
Hydrogenation of styrene		\mathbf{A}		
Pd@MOF-5	-		1	57
Pd/Tm-MOF	- 🗙	1.0	3	58
Pd@UiO-66-X	1.2	2.0	5	59
Pd@UiO-67	0X	1.0	5	60
Pd@UiO-67	5	1.0 mol% Pd	5	61
4-nitrophenol reduction				
Pd@MIL-100(ke)	4.0-6.0	-	5	62
$Pd@[Cu_{3-x}Pd_x(BTC)]_n$	-	3.9-9.2	-	63
Pd@ZAD	-	1.3	3	64
Pd@Zn-BDC	-	1.7	5	65
Pd@ZIF-8	-	3.46	5	66
Hydrogenation of olefins				
Pd@ZIF-8	17 ± 3	8.7	3	67
Void@HKUST-1/Pd@ZIF-8	-	1.1	3	68
Tandem reaction				
Pd@MOF-3	-	3.2	5	69
Pd-Au@Mn(II)-MOF	2-5	Pd,13.4; Au, 14.3	5	70

Photocatalysis

Pd@MIL-100(Fe)	8.0	1.0	-	71
Pd@UiO-66(NH ₂)	3-6	-	3	72

^a MIL: material of Institute Lavoisier; BTC = benzene-1,3,5-tricarboxylate; ZAD = $Zn_2(azoBDC)_2(dabco)$; Zn-BDC = {[Zn(BDC)_{1/2}(trz)]·DMAC}_n; DABCO = 1,4diazabicyclo[2.2.2]octane; ZrMOF-BIPY = $Zr_6O_4(OH)_4(bpydc)_6$, bpydc = 2,2'-bipyridine-5,5'dicarboxylate; ZIF=zeolitic imidazolate frameworks; X=H, NH₂, OMe. ^b Reported maximum conversion rate. ^c Turnover frequency (TOF) value of 51 mol_{H2} mol_{cat}⁻¹ min⁻¹.

2. SYNTHETIC STRATEGY FOR PD@MOF CATALYSTS

2.1 Precursor injection method. The traditional method of synthesizing Pd@MOF is to first fully mix the pre-synthesized MOFs crystals with the metal precursor. These precursors are generally metal inorganic salts. The metal precursor solution perenates into the pores of the MOF under capillary action and is then reduced in situ to Pd NPs diversed in the MOF pores. ⁷³ Pd NPs are highly dispersed in the pores of MOFs of somotic injection. MOFs provide support and space limitations for Pd NPs to minimize Pd NPs leaching.^{64, 74} Meanwhile, Pd NPs encapsulated in the pores of MOFs can work synergistically with MOFs and are easier to recycle.^{54, 75} Moreover, this catalyst is year staple and can be reused many times.

Traditional injection methods on well encapsulate Pd NPs in the pores of MOFs. Meanwhile, as a cage for encapsulating of NPs are structure of the synthesized MOFs is also a factor to be considered in the injection process. The superior structure is more conducive to providing support and limitations for Pd NPs. For example, Du's group⁷⁶ reported a rare and excellent structure of MOFs (Figure 1a-i). The cage-within-cage topology, there are small cages in the big cage. The two cages interpenetrate to form a unique two-layer three-dimensional cavity structure. This structure is more favorable for the penetration of the metal precursor solution. Pd²⁺ are completely reduced at 80 °C for one hour, resulting in larger Pd-NPs in **1** (denoted as Pd-NPs@**1**). we can see Pd-NPs with uniform size and uniform distribution in Figure 1j. This structure also helps prevent the growth and aggregation of Pd NPs in the cage during subsequent reductions. As shown Figure 1k, we can see that the granular particles of the catalyst are well

kept after six successive runs, the TEM image reveals that the average of particle size of the fine particles is only slightly increased to 4.29 ± 0.31 for Pd-NPs@1, and no observable aggregation of Pd NPs was detected.



Figure 1. (a) Interpenetration of two identical oD cage nets. (b–d) The cage-within-cage motif of Ln-MOF. Ln-MOF: $[Me_2NH_{124}]$ To_{124} $(TATB)_{16}$ $(HCOO)_{12}] \cdot 12DMF \cdot 48H_2O$ (1) $(H_3TATB = 4,4',4'')$ -s-triazine-2,4,6-trifenzoic acid. (e and f) The large/small cage enriched by eight small/large cages. (g) Gage within-cage motif resulting from the interpenetration of two identical 3D nets. (h and i) The approximate diameters of the small and large cages. (j) The TEM images of Pd-NPs@1. (k) The TEM images of the catalysts after six runs for Pd-NPs@1. Adapted with permission from ref⁷⁶, Copyright the Royal Society of Chemistry 2015.

Traditional injection methods are not limited to embedding a single Pd NPs into the pores of MOFs. Bimetals can also be embedded in the pores of MOFs using traditional injection methods. It is worth noting that synergistic effects can also be produced between the embedded bimetals. As a result, bimetals have higher catalytic activity than single metals.^{70, 77} For example, by

embedding a bimetallic Pd/Ni alloy into the pores of MOFs using traditional injection methods, enhanced catalytic performance can be obtained.⁷⁸ The alloy structure in the pores of the MOFs has adjustable electronic properties. The electronic environment of the catalyst surface can be adjusted to increase the charge transfer rate by adjusting the ratio of the injected bimetals, thereby improving the catalytic efficiency. In addition to implanting the alloy, the introduction of the semiconductor can also enhance the catalytic performance of the catalyst. For example, TiO₂ and rGO can also be introduced.⁷⁹⁻⁸⁰

2.2 Double solution precise infiltration method. While the traditional synthesis strategy described above has many advantages, it is difficult to accurately at the precursors into the pores of the MOFs. If this disadvantage is not solved, the mean plea ursor remaining outside the pores of the MOFs is reduced to form Pd NPs which are easily aggregated. In order to overcome this shortcoming, Xu's group⁸¹ reported olution precise infiltration method (DSPIM) for accurately injecting Pd metal procursors into the pores of MOFs (Figure 2a). The volume of the aqueous solution of the mulal precursor is smaller than the pore volume of MILis doubed onto the hydrophilic inner pore surface of 101, and the metal precursor so MIL-101 by the capillary f the infiltration process. Pd^{2+} and Co^{2+} supported in MILder the action of reducing agent (such as Ammonia borane). 101 are successively Among them, Pd²⁺ are first reduced, then Pd NPs are used as nuclei, and Co²⁺ are reduced in situ to form shells. Subsequently, Pd@Co was encapsulated in the pores of MIL-101 to obtain Pd@Co@MIL-101. As shown in Figure 2b-g, the core-shell structure has been explicitly observed by TEM images, HAADF-STEM images, and EDS mapping for Pd and Co NPs. The key to the success of this work is the need to use two solvents of different nature, a hydrophilic solvent containing a Pd metal precursor and a hydrophobic solvent containing no Pd metal precursor. Meanwhile, the volume of the hydrophilic solvent containing the Pd metal precursor should be less than or equal to the pore volume of the MOFs. The MOFs used should be some MOFs with hydrophilic pores, such as MIL-101(Cr).⁸²⁻⁸³ The hydrophobic solvent has an effect of promoting penetration during the injection process, a small amount of a hydrophilic solvent containing a Pd metal precursor can completely enter the hydrophilic pores of the MOFs under the action of capillary force.^{48, 81, 84-85}



Figure 2. (a) Synthesis of Pd@Co@MIL-101, Pd@Co/MIL-101, and PdCo@MIL-101 catalysts by different procedures and reducing agents. TEM images for (b) Pd@Co@MIL-101, HAADF-STEM images for (c) Pd@Co@MIL-101 showing the overall small sizes of Pd@Co NPs, and (d) Pd@Co@MIL-101 particularly presenting relatively larger particles, where the core–shell nanostructure with a brighter core coated

by a darker shell for each particle is faintly observable. (e–g) The elemental mapping of Co (red with green circle) and Pd (green with red circle) for a Pd@Co NP highlighted with red square in Pd@Co@MIL-101. Adapted with permission from ref ⁸¹, Copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

2.3 Others synthetic improvement. In addition to DSPIM, scientists are still looking for a synthesis method that is simple to operate and mild in operating conditions. One-step in-situ assembly is an excellent example. With a one-step in-situ assembly strategy, MOFs are not pre-synthesized. In this method, a Pd metal precursor is introduced during assembly of the MOFs.⁶⁰

The stepwise assembly strategy can form a core-shell structure of a double-shell structure. The outer MOFs in core-shell structure of Pd@MOF can serve at a screening function to achieve size selective catalysis compared to dispersed structure.^{34, 47, 67-68, 86-87} For example, Pd NPs have finer particle size and higher stability in the case of double layer protection of MOF@SiO₂ compared to simple Pd@SiO₂.⁸⁷

The post-synthesis functional modification can increase the interaction between Pd NPs and MOFs due to noble metals can interact strongry with some functional groups.⁸⁸⁻⁸⁹ Schiff base can also effectively stabilizered PD⁴⁹ The grafting of Schiff base to the backbone of MOFs by post-synthesis modification can change the weak molecular interaction between Pd NPs and MOFs and improve the stability of Pd@MOF. In 2011, Stock's group⁹⁰ reported for the first time that a MIL-101 network was synthesized by nitrating terephthalate linker molecule to rapidly implement MIL-101 functionalization. The modification is an important breakthrough considering the affinity of Pd NPs for nitrogen atoms because it minimizes Pd NPs. Followed this view, Cao's group⁹¹ demonstrate that the stability of Pd NPs in amino-functionalized MIL-53(Al)-NH₂ is higher than that of unfunctionalized MIL-53(Al).

Finally, we would like to briefly introduce the assistance methods used to improve Pd@MOF synthesis. The synthesis of Pd@MOF by chemical reaction is an inevitable path, but slow

chemical reactions are not conducive to the rapid requirements of industrial applications. In order to meet this requirement, various assistance methods such as microwave irradiation, ultrasonic irradiation, and surfactant-assisted synthesis can be utilized.^{46, 92} But the problem is that these assistance methods need to consume extra energy. Finding a better synthesis strategy is for further study.

3. HETEROGENEOUS CATALYTIC APPLICATIONS OF PD@MOF

3.1 Pd@MOF catalysts for the C-C cross-coupling reaction. 3.1.1 Suzuki-Miyaura reaction. Pd@MOF as excellent catalysts, which has great catalysis performance for Suzuki reaction. ⁴⁶ Wang's group⁵⁰ chose a stable zirconium-based MOF on as a support carrier to encapsulate Pd NPs. Pd@DUT-67 has high catalytic active and can achieve 99% conversion and 89% selectivity under optimized conditions. In another excellent example, Pd@MIL-101-NH₂ with a Pd loading of 8 wt.% v fully used to catalyze the Suzuki reaction under optimized reaction conditional More than 40 biaryl compounds have been successfully synthesized using the Suzuri reaction catalyzed by Pd@MIL-101-NH₂. Some of T ble 2. It can be found that the catalytic effect of the representative results are listed that of most commercial catalysts from the Table 2. It is Pd@MIL-101-NH₂ is high important that Pd@ML H_2 can be run continuously for many days in a flowing reactor without loss of activity. In another work, Pd@MIL-125-NH₂ can also be reused 4 times without loss of activity.⁹³ This proves the potential of Pd@MIL industrial applications.

Table 2. Pd@MIL-101-NH₂ catalyzes the coupling of (hetero)aryl iodide to bromine. Date were taken from ref ⁴², Copyright 2015 Wiley-VCH Verlag GmbH& Co. KGaA, Weinheim.





In addition to Pd@MIL, Pd@UiO also exhibits excellent catalytic performance in the Suzuki reaction. For example, Pd@UiO-66 and Pd@UiO-67. The skeleton UiO-66 of Pd@UiO-66 has a stable structure composed of an octahedral and tetrahedral mesh with diameters of 1.1 nm and 0.8 nm, respectively.⁴⁹ The synthetic path of Pd@UiO-66 is shown in the Figure 3a. It can efficiently catalyze the Suzuki coupling reaction of different halogenated aromatic hydrocarbons with arylboronic acid under the optimal reaction conditions (K₂CO₃ is a base and

1:1 alcohol-water mixed solvent is the medium) (Figure 3b).⁴⁹ The results showed that the yield of the Suzuki coupling reaction catalyzed by Pd@UiO-66 depends on the type of halide, the position of substitution and the electron-withdrawing/electron-supplying ability of the halide. The transmission electron microscope image is shown in Figure 3c. The structure of Pd@UiO before and after the reaction remains stable, and the Pd nanoparticles are uniformly dispersed on the UiO-66. Circulation experiment further confirmed Pd@UiO-66 has a long service life. The initial catalytic activity was maintained after at least 5 cycles of use (Figure 3d). Another excellent example is Pd@UiO-67. It is worth noting that Pd@UiO-67 has the same high surface area and high pore volume as the parent UiO-67 of about 2,00 m²·g⁻¹ and 0.79 cm³·g⁻¹, respectively.⁵² This allows its catalytically active sites to be maximum errorsed to the reactants. Meanwhile, under the strong constraints of the UiO-67 skeleton, the leaching of Pd NPs is minimized. Pd@UiO-67 can efficiently catalyze the Strukthoupling reaction of aryl chloride with aryl boronic acid, and the activity is significately higher than that of single Pd NPs.



Figure 3. (a) Schematic illustration of the synthetic process of Pd@UiO-66; (b) Pd@UiO-66 catalyzed Suzuki coupling reactions; (c) i) and ii) TEM images of fresh Pd@UiO-66, iii) and

iv) reused catalyst; (d) Recyclability of Pd@UiO-66 for Suzuki reaction. Adapted with permission from ref ⁴⁹, Copyright Springer Science+Business Media New York 2015.

Not all MOFs are stable, Liang's group⁴⁴ synthesized the Pd@MOF-5 composite catalyst was unstable, its catalytic performance was significantly reduced in the second round of catalytic reaction, and continued to decline in subsequent tests. The sudden decrease in the catalytic activity of Pd@MOF-5 may be caused by the collapse of the pore structure of MOF-5. In addition to the influence of the pore structure, Subsequent studies have found that the loading of Pd and the type of base also affect the activity of Pd@MOF to catalyze the Suzuki reaction. Although the catalytically active component increases and a loading increases, the surface area and pore volume decrease, which reduces the chance of the catalytically active component Pd NPs with the reaction substrate. herefore, it is necessary to find the optimum Pd loading, which helps to increase the c tivity of Pd@MOF. Zou's group⁴⁰ 1dh were studied the catalytic activities of Pd@NOF catalytic Suzuki reaction with different Pd loadings. They were found that Pd@MOC has he most efficient catalytic activity when the Pd loading is 8 wt.%. Meanwhile Pd MOF can be cycled at least ten times without ivity. In another work, It was found that the crystallinity, significantly reducing the c NPs of Pd@MOF was affected different anions (such as porosity and distribution carbonate and fluoride) and cations (such as potassium and cesium), which also affects the activity of the Pd@MOF catalyst.43

3.1.2 Heck reaction. In the Heck reaction, aryl bromide and chlorobenzene compounds are difficult to activate due to the high bond energy of C–Cl and C–Br. Thus, the reaction of brominated aryl esters or brominated chlorobenzenes with different olefins requires harsh reaction conditions and extended reaction times. Pd@MOF as a catalyst can solve this problem is used as a catalyst.⁸⁹ For example, Li's group⁵² reported that the synthesized Pd@UiO-67 composite catalyst can efficiently activate C–Cl bonds in the Heck reaction. Under the same

conditions, Pd@UiO-67 can more efficiently catalyze the coupling of chlorobenzene and styrene to produce trans-1,2-diphenylethylene to compared with other types of Pd-containing catalysts reported previously, the yield was as high as 81%,⁹⁴ which may be due to high porosity. Meanwhile, the catalytic activity of Pd@UiO-67 remained essentially unchanged after at least 5 cycles due to the structure and crystallinity of Pd@UiO-67 remained intact.

Pd@Ho-MOF can efficiently catalyze the Heck reaction of aryl iodide and methyl acrylate due to its.⁹⁵ The free polypyridyl functional group on the backbone of Pd@Ho-MOF can establish a strong interaction with Pd NPs, which is beneficial to improve the stability of the catalyst. The highly stable Pd@Ho-MOF can efficiently catalyze the Heck reaction of aryl iodide with methyl acrylate under the optimal reaction conditions (NWC+DMF; base: K₂CO₃; T=100 °C). The yield reached 99% in one hour. In general, the seation yield of the Heck reaction is related to the amount of catalyst used. Herever, it is worth noting that a small amount of Pd@MOF-3 can achieve high catalytic yield but it takes a long time.⁸⁹ The yield of the Pd@MOF-3 catalyzed the Heck reaction is between 90 and 99% under optimized reaction conditions.

Pd@MOF has improved cata vtic properties and can be recycled many times to compared with the traditional node metal d catalysts.⁹⁶ But in fact, at the mechanistic level, we know very little about the Heck reaction catalyzed by Pd@MOF.⁹⁷ In order to further promote the application of Pd@MOF in the Heck reaction. We need to study the reaction mechanism of Pd@MOF in the whole Heck reaction, including the catalytic mechanism and the deactivation mechanism. This information helps to further extend the life of Pd@MOF. Recently, Persson's group⁵¹ had made research in this regard (Figure 4). They used a newly developed custom reactor to study in detail the mechanism by which Pd@MOF catalyzes the Heck reaction (Figure 4a). Figure 4c shows the sequence of operations. The activation and deactivation pathways of the active substances are different under different reaction conditions and reaction

stages (Figure 4b). They pointed out that the irreversible deactivation of the catalyst is neither caused by the leaching of the active material nor by the decomposition of the crystal structure. Instead, they discovered a new chemical deactivation mechanism in which chloride ions cover the surface of Pd NPs (Figure 4d). This information is important to study how to extend the life of the catalyst. Meanwhile, this information will help improve future catalytic systems. Monitoring the entire experimental process by TEM and STEM/EDS, and the results are shown in the Figure 4e and 4f. Although Pd nanoparticles were observed in all samples except the initial sample, it was found that smaller Pd species (monomers, nanoclusters) were uniformly

distributed throughout the reaction in the MIL-101-NH₂ crystal. , LO , ccet



Figure 4. (a) Custom-made reactor for combined operando XAS and PXRD measurements; (b) Proposed Pd species at different stages during the Heck coupling reaction using Pd(II)@MIL-101-NH₂ as a catalyst. The red trace shows the temperature and the blue trace shows conversion to the desired product. The value of CN in the figure refers to the coordination number of Pd–Pd in the first shell; (c) Timeline of the operando XAS and PXRD experiments; (d) Proposed mechanism for the Heck coupling reaction catalyzed by Pd(II)@MIL-101-NH₂; TEM images (e) and STEM image and EDS mapping (f) of Pd(II)@MIL-101-NH₂ at various stages during the Heck reaction at 0% (e_1 - f_1), 25% (e_2 - f_2), 54% (e_3 - f_3) and >99% (e_4 - f_4) conversion. The

arrows in f₃ indicate a Pd nanoparticle on the surface of the MOF. Adapted with permission from ref ⁵¹, Copyright 2018 American Chemical Society.

3.1.3 Sonogashira reaction. Pd@MOF-5 can efficiently catalyze the Sonogashira reaction of aryl iodide and terminal acetyl in the absence of assistance from copper and ligands.⁹⁸ Electron-deficient aryl iodine exhibits higher activity than electron-rich aryl iodine in the Pd@MOF-5 catalyzed Sonogashira coupling reaction. The substitution position of aryl iodide also affects the reaction yield due to the spatial effect. The stability of Pd@MOF-5 is poor, and the catalytic activity drops significantly during the third cycle. With the further development of the research, the high stability Pd @ MOF used to catalyze the Sorogashira coupling reaction appeared. Li's group⁵³ reported a stable catalyst system Pd@ efficiently catalyze Sonogashira reaction at atmospheric pressure. The characterization results of Pd@ZrMOF before and after the catalytic reaction indicate that the catalytic structure remains stable. Simultaneous reproducibility tests indicate that Pd Zr MOF can be recycled multiple times, reduced after at least 5 cycles. In addition, and its catalytic activity is not signific Pd@MIL-101 catalyzed Sonogashin n of 4-bromonitrobenzene with phenylacetylene a reacti reach 90%.⁹⁹ It is worth noting that the reaction yield of under optimized conditions ca electron-deficient browning of a yl groups is high in the Sonogashira reaction catalyzed by Pd@MIL-101. The reaction yields of the sterically hindered 1-bromonaphthalene and 9bromophenanthrene were also 70% and 73%, respectively.

3.2 Pd@MOF catalysts for redox reactions. **3.2.1** Aerobic oxidation of benzyl alcohol. The aerobic oxidation of benzyl alcohol is one of the most studied among various alcohol oxidation reactions.¹⁰⁰ Pd NPs encapsulated by MOFs is one of the most promising methods for catalyzing aerobic oxidation of benzyl alcohol. ^{54, 61, 87} For example, Pd@Cu-MOF catalyze the aerobic oxidation of benzyl alcohol can be obtained 100% conversion and 98% separation yield in 24 hours, and the catalyst is stable during the catalytic process.⁵⁵ The face-centered cubic Pd NPs of Pd@Cu-MOF is the main catalytic active site for the oxidation of benzyl alcohol.

Highly dispersed Pd NPs were supported on MIL-101, and their activity and stability was evaluated for aerobic oxidation of benzyl alcohol.^{41, 101} Pd@MIL-101 can be used again after simple filtering, and can be reused multiple times. Pd@MIL-101 catalyzes the turnover frequency (TOF) of benzyl alcohol aerobic oxidation up to 16900 h⁻¹ in the absence of alkali and solvent-free conditions.¹⁰¹ The grafting of ethylenediamine to the MIL-101 not only does not enhance the activity of catalyzing the oxidation of benzyl alcohol, but on the contrary inhibition occurs. This phenomenon indicates that the open Cr size CateMIL-101 may play an important role in catalyzing the oxidation of benzyl alcohol.

3.2.2 Hydrogenation of olefin. Catalytic hydrogenation is one of the most important in organic conversion reactions. Until 2013, 25% of hydrogenation process.¹⁰² Catalytic selective undergoing clinical trials involved at least one hydrogenation process.¹⁰² Catalytic selective hydrogenation of olefins in the presence or the reducing functional groups such as aldehydes and ketones is one of the most mallenging hydrogenation reactions.¹⁰³⁻¹⁰⁵ Pd@C catalysts are most commonly used in the presence of the Pd@C catalyst, the Pd@MOF catalyst has a more regular structure and highly ordered pores.⁵⁹ Comparing the catalytic performance of the two, many studies have shown that Pd@MOF is better than Pd@C.⁵⁶

The Tm-MOF material is a new three-dimensional structure with one-dimensional pores (Figure 5a). Each organic link of the material contains two uncoordinated carbonyl functional groups pointing to the channels. It is a wise choice to encapsulate Pd NPs using pre-synthesized Tm-MOF as a carrier. Pd@Tm-MOF can maintain catalytic activity by repeating it for at least 3 times. ZIF-8 has a similar surface area and pore volume as Tm-MOF (Figure 5b, d).⁵⁸ But,

the catalytic activity of Pd@ZIF is lower than that of Pd@Tm-MOF, which may be because the former does not have an uncoordinated carbonyl functional group (Figure 5c, e).



Figure 5. (a) A structural diagram of the Tm-MOF; Tziwijmage (b) and EDS pattern (c) of Pd/Tm-MOF; TEM image (d) and EDS pattern (e) of 7d/21F-8. Adapted with permission from ref ⁵⁸, Copyright the Royal Society of Chemistry 2012.

Jiang's group reported that Pd@21F-8 with core-shell structure has great catalytic performance for olefin hydrogenatio).⁶⁷ This is the first attempt of Pd@2IF-8 photocatalytic olefin hydrogenation as some Figure 6a, Pd@2IF-8 can drive selective catalytic olefin hydrogenation under visible light. The selective catalytic properties may be due to the presence of ZIF-8 as a shell, and large olefin molecule are unable to reach the catalytically active sites. Figure 6b shows the core-shell structure of Pd@ZIF-8, a single Pd@ZIF-8 particle size of 250-350 nm, and an encapsulated Pd NPs of 17 \pm 3 nm. The catalytic effect of 60 mW·cm⁻² full spectrum or 100 mW·cm⁻² visible light drive at room temperature, which can be equivalent to the catalytic effect at 50 °C (Figure 6c). The excellent catalytic performance may be due to the broad absorption band and multiple active sites of Pd NPs. The recovery experiments clearly show that the yield of Pd@ZIF-8 is close to 100% in three consecutive runs, while for Pd NPs

without ZIF-8 protection, the yield gradually decreases to only 21% in the third run. (Figure 6d).



Figure 6. (a) In-situ one-step asserbly of Pd@ZIF-8 catalyst for multifunctional catalytic olefin hydrogenation: (b) of TEM and ii) HRTEM images of PdNCs, iii) SEM and iv) TEM images of PdHCC@ZIF-8, Inset in iv: Pd nanocubes inside ZIF-8; (c) The yields of the hydrogenation of 1-hexene with 1atm H₂ over Pd NCs@ZIF-8 under full-spectrum irradiation with different light intensities at room temperature or upon heating at different temperatures; (d) Conversions of the hydrogenation of various alkenes over Pd NCs@ZIF-8 and Pd NCs. Adapted with permission from ref ⁶⁷, Copyright 2016 Wiley-VCH Verlag GmbH &Co. KGaA, Weinheim.

Huang's group¹⁰⁶ introduced carbon materials to Pd@ZIF-8, the C@Pd@ZIF-8 catalytic system has good stability in the catalytic hydrogenation of olefins. The catalytic activity of C@Pd@ZIF-8 was estimated in the hydrogenation of unsaturated compounds, including styrene, 1-heptene, cyclohexene, cyclooctene and quinoline. The initial catalytic activities of

C/Pd@ZIF-8 catalyzed hydrogenation of styrene, 1-heptene and cyclohexene were 89.70%, 88.96%, and 79.28%, respectively. After 5 cycles of catalytic activity, the catalytic activity of C/Pd@ZIF-8 decreased only slightly, at 85.3%, 66.9%, and 37.5%, respectively. The skeleton of Pd@MIL-101 was stable and can be used multiple times. In addition, it is important to note the effect of functional group electrons on the catalyst. The conversion of hydrogenation of cyclohexene by Pd@MIL-140 containing phenyl, naphthyl and biphenyl groups, was 63%, 28% and 15%, respectively.¹⁰⁷

3.2.3 Nitroaromatic reduction. Nitroaromatic compounds such as nitrobenzene, nitrophenol and their homologs are widely present in industrial a cutural wastewater.¹⁰⁸ These pollutions need to be degraded from the environment, Pd an be used, and porous Zn-BDC encapsulated Pd NPs is used to catalytically reduce 4-nitrophenol.⁶⁵ Zn-BDC has an d double-sided quadrilateral antiexcellent three-dimensional open frame that form prism cage (Figure 7). Each of its secondary puilding units is connected by BDC²⁻ and trz⁺ cations, and the size of the window in the b-a is direction is ca. 10.9 \times 6.9 Å². Computational aborb a solvent containing no guest molecules of simulations have shown that it approximately 2466.5 $Å^3$. with other supported Pd catalysts, Pd@Zn-BDC formed Pd NPs can efficiently catalyze the hydrogenation of 4by Zn-BDC encaps nitrophenol.



Figure 7. (a) The possible role of the decomposition of 1,3-d(1,2,4-triazole) quinoxaline in the construction of Zn-BDC; (b) Coordination expironment of dimetallic Zn cluster in Zn-BDC; (c) The structural diagram from the b-axit, (c) The three-dimensional open window of ca. 10.9 $\times 6.9$ Å² from the b-axis; (e) The structural diagram from the c-axis. Adapted with permission from ref ⁶⁵, Copyright Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2015.

Zr-MOF (such as UiO-66, UiO-67, etc.) is a kind of MOFs with extremely high thermal stability and chemical stability. As a carrier for noble metal Pd NPs, they have broad application prospects in industrial applications.⁶¹ Recently, a novel Zr-MOF, DUT-67 (DUT, Dresden University of Technology), was used to encapsulate the Pd NPs for catalytic degradation of nitrobenzene.⁵⁰ Pd NPs with different loadings (0.3, 0.5, 1.0 wt.%) were highly dispersed on the microcrystalline interface of DUT-67 by solvent injection methods. Pd NPs have a particle size of about 3.5 nm under the action of the organofunctional group on the organic link of the DUT-67 framework and the micropore limitation. The catalytic effect was best when the

loading of Pd NPs was 0.5 wt.% and 1.0 wt.%, Pd@DUT-67 can exhibit excellent catalytic performance (conversion: 99%; selectivity: 99%) for catalytic degradation of nitrobenzene under the best conditions (ethanol-water mixed solvent, K₂CO₃, 60 °C).

Pd@MIL-100(Fe) was synthesized by traditional injection has a uniform pore size, MIL-100(Fe) providing support and space limitations for Pd NPs. In the absence of any surfactant as a stabilizer, the size of the MIL-101(Fe) supported Pd NPs can be maintained in a fine state without aggregation. Their catalytic performance was evaluated for the reduction of 2/3/4nitrophenol.⁶² Taking 4-NP as an example, firstly, through two kinds of forces, (i) 4-NP benzene ring and organic link (H₃BTC) in MIL-100(Fe) have strong or cular π - π stacking interaction, (ii) The coordination effect of the hydroxyl functional excupion 4-NP and the Lewis acid active iron site on MIL-100(Fe), 4-NP was adsorbed v MIL-100(Fe). The active hydrogen and electrons are then efficiently transferred from ydride ions to the Pd NPs, which then attacks the 4-NP molecule and reduces it 4-AP. Meanwhile, the active site of the Pd NPs was maximally exposed to the reactants ince o surfactant was involved in the synthesis. The aly connacted with the Pd NPs by the mass transfer of nitrophenol molecule can be mor tion of millions of nanoreactors at the same time, greatly MIL-100(Fe). This was like improving the catalyt

Besides encapsulating single Pd NPs metal, MOFs are also excellent carriers for alloy Pd NPs metal. The noble metal is doped with some other cheaper metals, which is advantageous to reduce the cost of the catalyst while maintaining catalytic activity. Such as Au, Ni, Cu, and Fe, can be used to modify the Pd metal to manipulate the d-band electronic structure, which can increase the bonding strength of the reactants to the active sites of the metal.⁷⁸ It was important to find the right ratio to optimize the catalytic activity while reducing the cost of the catalyst by adjusting the ratio of Pd metal to other metals. For example, the catalyst activity increases with the ratio of Ni. When the Pd/Ni ratio reaches 24, the catalytic performance was optimal, and

the nitrobenzene can be efficiently catalytically reduced at room temperature.⁷⁸ It is a great hope for the synthesis of new catalysts that the incorporation of metal alloys into functionalized MOFs.

3.3 Pd@MOF catalysts for tandem reactions. In a one-pot tandem reaction, the resulting intermediate does not require separation, purification, and transfer, thereby saving energy.¹⁰⁹ It is a compelling solution in green chemistry that use of multifunctional catalysts to catalyze multi-step tandem reactions. In a tandem reaction, the intermediate product produced in the previous step can be directly used as the reactant of the next reaction.¹¹⁰⁻¹¹² It helps to reduce by-products and waste generated in separate single-step reaction MOF was excellent catalysts for tandem reactions, Pd NPs and MOFs can synergized andem reaction.¹¹³⁻¹¹⁶ For example, Pd@UiO-66-NH₂ has higher catalytic activity and higher selectivity due to the the oxidation activity of Pd NPs and synergistic effect of Pd NPs and MOFs. Combined the Lewis acidic site of UiO-66-NH₂, PdC JiO-60-NH₂ can efficiently catalyze one-pot acetylation tandem reaction (Conversion 99.%; selectivity: benzaldehyde acetal, 99.9%).⁷⁵ atel from the liquid phase, and can be reused at least 5 Pd@UiO-66-NH₂ can be quickly times in subsequent continu fter simple centrifugation. In another excellent example, (BDC)₂ DABCOMOF) was synthesized by MOFs-derived Pd@Cu-MOF (Cu-MOF carbon (Cz-MOF-253) supported Pd NPs, which has excellent catalytic performance for catalyzing one-pot tandem reaction.¹¹⁶ The bimetallic Pd NPs-containing catalytic system supported by MOFs was a new choice for catalyzing one-pot tandem reaction.

In the bimetallic Pd NPs-containing catalytic system supported by MOFs, in addition to the synergy between Pd NPs and MOFs, there was also a synergy between Pd NPs and other metals (such as Au, Ag, Pt, Ni, and so on). This synergistic effect makes the bimetallic Pd-containing catalysts likely to be superior to the single metal Pd-containing NPs catalysts. Xu's group¹¹⁷ using DPISM prepared Ag-Pd@MIL-101 can efficiently catalyze the multi-step tandem

reaction to synthesize diarylamine. Ag-Pd@MIL-101 carries three catalytically active sites, MIL-101 provides a catalytically active site for Lewis acids, Pd NPs provide hydrogenation activity, and Ag NPs can significantly increase selectivity for the desired product (Figure 8). In the work, a comparative study of Ag-Pd@MIL-101 with commercial catalyst Pd@C shows that the former has higher catalytic selectivity than the latter.¹¹⁷ This demonstrates the superiority of MIL-101 as a carrier and alloy system. In another excellent example, we briefly mention an uncommon MOF, Mn(II)-MOF[(MnL₂) 2CH₃OH] used as a support carrier containing Pd alloy. The catalytic performance of Pd-Au@Mn(II)-MOF was detected based on a one-pot tandem reaction of benzyl alcohol and benzylamine or benzyl alcohol and antline.⁷⁰ In the work, the conversion of imine benzyl alcohol having an electron withdowing can reach 93-99%. 01 The yield of amines with electron-withdrawing groups can reach 93-99%, but the yield of amines with electron-donating groups was only 59-93% Although many examples demonstrate fical in reducing catalyst costs while that MOFs-loaded Pd-containing alloys a maintaining or even increasing catalyst any alloy forms have not been tried. This ity. program deserves further study.



Figure 8. (a) Synergistic catalytic multi-step tandem reaction of each component of the Pd-Ag@MIL-101 catalyst; (b) Synthesis of secondary arylamines through hydrogenation of nitrobenzene and reductive amination of benzaldehyde; (c) **i**) TEM images showing the

ultrafine PdAg NPs in Pd₂Ag₁@MIL101, **ii**) TEM images for Pd₂Ag₁@MIL101 catalyst after three runs of the reaction; (d) Recycling performance for the conversion of **A** and selectivity to the target **D** after the two-step reaction over Pd@MIL-101; (e) Recycling and filtration tests as well as the control experiment with introduction of pyridine during the reaction process over Pd₂Ag₁@MIL-101 catalyst. Adapted with permission from ref ¹¹⁷, Copyright 2015 American Chemical Society.

4. PHOTOCATALYSIS APPLICATION OF PD@MOF

In 1972, Japan's Fujishima and Honda¹¹⁸ discovered that the semiconductor material TiO₂ single crystal electrode can photocatalytic decompose water. See aemly, scientists began extensive research on photocatalysis technology.¹¹⁹⁻¹²⁰ Photocatalytic technology has many advantages,¹²¹⁻¹³⁰ (i) the operating conditions are mild and simple; (ii) the reaction matrix and intermediate products will be completely minerali ut secondary pollution; (iii) solar zec. energy was a clean and sustainable energy source. Many materials with semiconductor ¹³¹⁻¹³⁵ MOFs are one of the most promising properties can exhibit photocatalytic a vivity The band gap of MOFs material was strictly materials for photocatalytic appli related to the HOMO-LU and the energy absorbed by the MOFs material can be anic link to the metal oxygen cluster, and the energy conversion directly transferred from efficiency was high. In addition, other photocatalytically active materials can be introduced into the framework of the MOFs material.¹⁴¹⁻¹⁴⁴

4.1 Pd@UiO for photocatalysis. Pd@MOF has higher surface area and catalytic active sites. Meanwhile, it can quickly and stably accept photogenerated electrons from the MOFs skeleton and promote photogenerated electrons due to the famous plasma effect of Pd NPs. The hole pairs are separated, thereby greatly improving the photocatalytic efficiency of the photocatalyst (Figure 9a). UiO-66-NH₂ was a photoresponsive material with excellent properties. In the structure of UiO-66-NH₂, the zirconium oxygen cluster was surrounded by a terephthalic acid ligand in the form of quantum dots, and the NH₂ group acts as an auxiliary color group. Terephthalic acid ligands can absorb light energy like an antenna and efficiently transfer energy to the inorganic zirconium oxide cluster (Figure 9b). Meanwhile, UiO-66-NH₂ was an excellent carrier for encapsulating Pd NPs. Pd@UiO-66-NH₂ has higher photocatalytic activity and stability than Pd NPs or UiO-66-NH₂ alone.⁷² The excellent performance of Pd@UiO-66-NH₂ may be due to the following three aspects: (i) the tight structure between the highly dispersed Pd NPs and the MOFs main body enhances the light trapping effect; (ii) the photogenerated electrons generated by the MOFs main body, it was transferred to Pd NPs and rapidly consumed, which effectively inhibits photogenerated electron-hole recommation; (iii) the porous structure of MOFs and highly dispersed Pd NPs provide more calent to redox reactions. Based on the excellent photocatalytic properties of Pd@CiO-66-NH₂, it can be used in various fields such as environmental remediation (Figure 1) and organic conversion (Figure



Figure 9. (a) Possible roles of incorporated Pd NPs as synergistic catalyst in photocatalytic applications by acting as electron reservoirs. (b) A diagram drawing of the structure of UiO-66-NH₂ based on the structure of UiO-66. Zirconium-oxygen clusters (green part); N of the free amino groups (blue dots); Possible mechanism of the photocatalytic application by Pd@UiO-66-NH₂, (c) reduction of Cr(VI) over Pd@UiO-66-NH₂. Adapted with permission from ref ⁷², Copyright the Royal Society of Chemistry 2013; (d) Visible-Light Promoted Suzuki Coupling Reaction over Pd@UiO-66-NH₂. Adapted with permission from ref ⁴⁸, Copyright 2016 American Chemical Society.

It is two important issues that the treatment heavy metal polluti tewater containing organic dyes in the environmental field.¹⁴⁵⁻¹⁵⁴ Fortunately, Pd@MQV research has shown it to be one of the most promising photocatalysts in this fiel. The photogenerated electrons and holes generated by Pd@UiO-66-NH2 under visible iation are respectively transferred to oxidation and reduction active sites to caplyze oxidation and reduction reactions. For example, the generated holes are used to atal ze the degradation of organic dyes such as MO re consumed for the reduction of Cr(VI).⁷² In the single and MB, and the generated electrated pollution system, the reduc on ra f Cr(VI) was 70% under continuous irradiation of visible degradation rates of MO and MB were 5% and 38%, respectively.⁷² light for 60 minutes, and b In the composite pollution system where Cr(VI), MB and MO coexist, there may be mutual promotion effects between the pollutants. For example, in Cr(VI)/MO and Cr(VI)/MB binary systems, the degradation rates of Cr(VI) are 79% and 100%, respectively,⁷² which significantly higher than the degradation rate of a single system. Meanwhile, the presence of Cr(VI) may also promote photocatalytic oxidation of MO and MB.

In addition, Pd@UiO-66-NH₂ can use solar energy instead of heat to drive the Suzuki reaction. Pd@UiO-66-NH₂ catalyzes excellent results due to combined with UiO-66-NH₂ high light responsiveness and catalytic activity of Pd NPs. Pd@UiO-66-NH₂ catalyzed conversion

of iodobenzene and phenylboronic acid can be as high as 99%, the conversion number was as high as 2514 h⁻¹ under the optimal reaction conditions (photocatalyst: 5 mg, iodobenzene: 0.8 mmol, phenylboronic acid: 1.6 mmol, TEA: 2.4 mmol, N₂, DMF/H₂O: 1/1, 16 mL, visible light irradiation, reaction time 5 h).⁴⁸ Compared with other Pd-containing photocatalysts,¹⁵⁵⁻¹⁵⁹ Pd@UiO-66-NH₂ photocatalytic Suzuki coupling reaction was one of the best.

MOF-encapsulated alloyed Pd NPs can be used in the energy field.^{81, 160} For example, UiO-66 (Zr_{100-x}Ti_x) (Full name: Titanium-doped zirconium amine functionalized MOFs) encapsulated Au/Pd can catalyze the hydrogen production of formic acid at room temperature.¹⁶¹ The catalytic activity of Au/Pd@UiO-66 was nu igner than that of the corresponding UiO-66 supported single metal catalyst due to the gy between Au, Pd and MOF. Au/Pd@UiO-66 can increase hydrogen producion by a factor of 1.5 and achieve ¹⁾ (Figure 10).¹⁶¹ Au@Pd@UiO-66 hydrogen yield (42000 mL h⁻¹g⁻¹) at high TOF catalyzes the reaction pathway to produce hydrogen hom formic acid as shown in Figure 10b. When the Pd bond dissociates, many wakly pasic amino groups will have a positive effect, poisible for promoting the C–H bond cleavage to form and the Pd catalytic active site was CO₂. Finally, molecular hyp produced by the action of -⁺HNH₂.



Figure 10. (a) Plasmonic Au@Pd Nanoparticles Supported on a Basic Metal–Organic Framework; (b) A possible mechanism of hypogenereduction from formic acid catalyzed by Au@Pd@UiO-66 in visible light; (c) Low-magnification TEM image and size distribution diagram of the Au@Pd/UiO66(2r₈ fir₅), (d) Amount of H₂ produced through FA dehydrogenation in the dark (block blrs) or under visible light irradiation (gray bars, $\lambda > 420$ nm, 320 mW cm⁻²) over different catalysts. Adapted with permission from ref ¹⁶¹, Copyright 2016 American Chemical Society.

4.2 Pd@MIL for photocatalysis. The porous structure of MIL-101(Fe) provides an additional channel for the migration of photogenerated electrons. Photogenerated electrons rapidly migrate from MIL-100(Fe) to Pd NPs for reaction after MIL-100 (Fe) encapsulation of Pd NPs, which was beneficial to the separation of photogenerated electron-holes.¹⁶² In addition, the ultra-high surface area of Pd@MIL-100(Fe) provides more catalytically active sites, which facilitates contact of the reactants with the catalytically active sites. Because of its excellent photocatalytic properties, Pd @ MIL-100 (Fe) can also be used for environmental remediation,

such as degradation of organic dyes (Figure 11a), reduce heavy metal ions (Figure 11b), remove pharmaceutical and personal care products (PPCPs) (Figure 11c), and organic conversion (Figure 11d).



Figure 11. Schematic diagram of the proposed methalism for photocatalytic by Pd@MIL-100(Fe) under visible-light irradiation (λ) 420 nm). (a) and (b) The photocatalytic degradation of MO and reduction of Cr(VI). A larted with permission from ref ¹⁶², Copyright Tsinghua University Press and Springe-Veltag Berlin Heidelberg 2015. (c) The photocatalytic degradation of PPCIC over Pd@MIL-100(Fe) under visible light irradiation. Adapted with permission from ref ⁷¹, Copyright 2015 Elsevier B.V. (d) Photocatalysis for N-alkylation of aniline with benzyl alcohol via hydrogen auto-transfer process. Adapted with permission from ref ¹⁶³, Copyright 2016 Elsevier Inc.

Prior to the advent of Pd@MIL-100(Fe), photocatalytic technology was used for the degradation of PPCPs.¹⁶⁴⁻¹⁶⁸ To date, TiO₂ with semiconducting properties was still one of the most commonly used photocatalysts for environmental remediation.¹⁶⁹ However, further photocatalytic applications of TiO₂ are greatly limited due to the low surface area and lack of visible light responsiveness. Pd@MIL-100(Fe) was the most promising alternative to TiO₂. For

example, due to the visible light responsiveness of MIL-100(Fe), Pd@MIL-100(Fe) can effectively degrade PPCPs under visible light.⁷¹ In addition, Pd@MIL-100(Fe) has high stability and retains its original photocatalytic activity after four consecutive cycles of operation.

Pd@MIL-100(Fe) was also a green photocatalyst for catalyzing organic synthesis. In 2016, Pd@MIL-100(Fe) was first reported for the catalytic alkylation of amines and alcohols under visible light.¹⁶³ Similar to conventional semiconductor photocatalysts, MIL-100 (Fe) is excited by photons under visible light to produce photogenerated electron-hole pairs. The photogenerated electrons are then rapidly transferred to Pd NPs with lower Fermi levels. The benzyl alcohol was activated after being introduced into the cuastic system and produces electrons that have formed an alkoxide intermediate. Next, the end of the alkoxide intermediate was cleaved to form benzaldehyde. Manwhile, hydrogen molecules are transferred to electron-rich Pd NPs to form Pd hydrogen compounds. Finally, hydrogenation under the catalysis of the Lewis acid sites of Min 100(Fe) and Pd hydrogen compounds produces N-alkylamines.

Finally, it was worth mentioning that the introduction of other nano-scale semiconductor materials such as phosphitungitic acid (PTA) and TiO₂ in support material can form a multicomponent system to improve photocatalytic activity.^{79, 170} For example, Pd-PTA@MIL-100 (Fe) can achieve higher photocatalytic activity than PTA@MIL-100 (Fe) and MIL-100 (Fe) because of the introduction of PTA.¹⁷¹ With the degradation of PPCPs as a reaction model, there may be two types of charge transfer paths for Pd-PTA@MIL-100(Fe). The photocatalytic activity of Pd-PTA@MIL-100(Fe) may be enhanced by three reasons (i) high conductivity of Pd NPs and PTA; (ii) strong visible light responsiveness of MIL-100(Fe); (iii) The energy level matching between the three components can increase the carrier migration rate.

5. CONCLUSIONS AND PROSPECT

Pd NPs supported by versatile MOFs are used for heterogeneous catalysis, which not only inherits the advantages of a single material but also demonstrates the characteristics of its synergistic catalysis. In the last two decades, although some exciting progresses have been made, the field is still in its infancy and there are still some challenges (Figure 12). In order to further industrialization, it is of great significance to develop excellent synthesis methods, to study the basic mechanism of Pd@MOF in the whole reaction process, and to expand its application range.



Figure 12. Diagram summary of Pd NPs supported by versatile MOFs for heterogeneous catalysis.

Pd NPs highly dispersed in MOFs can be obtained by traditional synthesis methods such as solution injection and chemical vapor deposition. However, excessive consumption of metal precursor solvents is uneconomic and it is difficult to control Pd NPs from fully entering the MOF pores. In this way, some metals will gather on the surface of MOF during the synthesis process, resulting in low activity. The above problems are solved by the method of DSPIM. The complex and energy-intensive operation process forced scientists to develop a one-step synthesis method to achieve the simple one-step synthesis of Pd@MOF. Meanwhile, as mentioned in **chapter 2**, in addition to the simple and low-energy operation process, another issue requiring to be considered in the synthesis process is the structure of Pd@MOF. That is how to prevent the aggregation of Pd NPs and expose Pd NPs to the surrounding environment as much as possible. Pd@MOF sandwich structure is an excellent innovation. It can not only encapsulate Pd NPs well but also control mass transfer through the pore structure of the MOF shell, so that the reaction matrix can be in contact with the catalyst to the greatest extent without worrying about a large amount of Pd NPs aggregation and leaching. In addition, a weak link between Pd NPs and MOFs is of concern, which leads to instability and low activity of the catalyst. This aspect needs further exploration.

As mentioned above, despite great efforts, synthesis & Pd@MOF with high stability, high activity, low cost, and long service life is still very affect to or its wide application in industry and commerce. In the future, it is urgent to find more excellent and efficient synthesis methods:

• Synthesis of better structure, giving full play to the versatile function of MOF and adjustable pore structure, call affectively control mass transfer, and reaction matrix and product diffusion;

• In order to develop better synthesis methods, further exploration of existing synthetic methods is needed. The interface interaction between the metal core and the MOF shell needs to be clarified. The growth and formation mechanism of Pd NPs in MOF wells needs to be clarified.

• All kinds of assisting synthesis methods should be developed, which could solve the shortcomings that are difficult to overcome through complex chemical methods.

Pd@MOF has been widely studied not only in synthesis but also for applications. In fact, it is widely used in fine chemical fields, such as catalytic Suzuki coupling reaction, Heck reaction, Sonogashira reaction, and benzol aerobic oxidation, olefin and nitrobenzene hydrogenation reduction reactions. And high catalytic activity was obtained in these typical C–C coupling reactions and typical redox reactions. However, the mechanism of Pd@MOF as a heterogeneous catalyst for these reactions still need further study. So far, we still can't understand exactly the role of Pd@MOF in the whole catalytic process. Therefore, in the future, on the one hand, we should focus on revealing the catalytic mechanism of Pd@MOF, whether Pd NPs plays a large role or MOFs plays a leading role, or both play a synergistic catalytic role. It is now widely believed that Pd NPs and MOFs play a synergistic catalytic role. Therefore, what is the specific mechanism? The charge interaction between them needs to be studied. How to coordinate the charge interaction between them and apply their subergistic catalysis to some important but challenging reactions is of great significance. In relevance these mechanisms, it is necessary to develop in-situ or ex-situ characterization techniques, and meanwhile, its structure and catalytic mechanism can be further discussed by combining theoretical calculation.

On the other hand, as important as the catacytic mechanism of Pd@MOF is the inactivation mechanism of Pd@MOF, which urgentlyneed to be understood. The inactivation of Pd@MOF is a great challenge for its further industrial application. Up to now, few studies have given convincing evidence to proceed activity of Pd@MOF in long-term catalytic processes. Obviously, as most studies have shown, the specific mechanism leading to Pd@MOF inactivation cannot be clearly understood only by XRD and electron microscopy. Now, the things that need to be explored are:

• Changes in the supporting structure of MOF in the catalytic process;

• Studying the influence of base ions on catalytic activity, crystallinity and Pd NPs distribution;

• At different catalytic stages, what are the specific active sites of catalytic, and what is the effect of Pd NPs in different valence states on catalysis.

These studies of the catalyst are very important for the development of catalysts with high stability for industrial catalytic processes. Thus, it is necessary to develop more advanced technologies or combine traditional existing technologies with innovations for further research.

In addition to the highly desirable application of Pd@MOF in fine chemistry, the potential applications related to other fields are urgent to be developed, especially in the field of energy and environment. As mentioned earlier in this review, the synthesis of fine chemical products can be efficiently driven by solar energy by the catalysis of Pd@MOF. Meanwhile, Pd@MOF can also be used for photocatalytic hydrogen production and environmental remediation. As we all know, hydrogen energy is considered as one of the most energy sources for development and application in the 21st century, and Pd NPs, the Remetal supported by the MOF, can play a great role in this field. By contrast, man people do not understand why noble t support the use of noble metals metals are used for environmental remediation. Pe to repair the ecological environment, the main considering the economic cost, but this ason can be solved, in the future:

We can alloy noble metals and non-noble metals, according to a certain proportion, in the case of not reducing catalytic activity, greatly reduce the cost of catalysts;
 It can combine magnetic materials with Pd@MOF to form a core-shell structure, or other better structures, so that expensive catalysts can be more easily separated from the reaction mixture for recycling;

• By studying the mechanism, seek innovative technology, maintain the stability of catalyst in the catalytic process, extend its service life, and indirectly reduce the cost of catalyst.

This composite material can combine the advantages of Pd NPs and the versatility of MOFs to achieve unexpectedly excellent performance. With continued efforts in this field, we believe that more functional applications of Pd@MOF will be discovered. However, there seems to be

some potential harm to human beings and the ecological environment under the bright prospect of such nanomaterials, which also needs to be paid attention to. Relevant detection technologies need to be developed and normative laws and regulations need to be formulated to prevent potential heavy metal pollution caused by the massive application of these nanomaterials.

In summary, MOFs has been proved to have excellent potential to encapsulate Pd NPs for heterogeneous catalysis, and this heterogeneous catalyst has a broad application prospect. However, with the rapid development of technology, we should also keep the original intention of benefiting mankind and avoiding irreparable harm to the ecological environment while developing technology and economy.

AUTHOR INFORMATION

Corresponding Author

Guangming Zeng,*^a Zhifeng Liu,*^a Rong Xia

^a College of Environmental Science and Engineering, Hunan University and Key Laboratory of Environmental Biology and Pollutive Ontice (Hunan University), Ministry of Education, Changsha 410082, P.R. Chira

^b Department of Dermatology, Becond Xiangya Hospital, Central South University, Changsha 410011, P R China.

E-mail: <u>zgming@hnu.edu.cn</u> (G.M. Zeng); <u>zhifengliu@hnu.edu.cn</u> (Z.F. Liu); <u>xiaorong65@csu.edu.cn</u> (R. Xiao).

Author Contributions

† These authors contribute equally to this article.

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