



Accepted Article

Title: An Acid Stable Metal-Organic Framework as an Efficient and Recyclable Catalyst for the O-H Insertion Reaction of Carboxylic Acids

Authors: Li Zhang, Yingxia Wang, Hao Cui, and Cheng-Yong Su

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemCatChem 10.1002/cctc.201800597

Link to VoR: http://dx.doi.org/10.1002/cctc.201800597



WILEY-VCH

www.chemcatchem.org

FULL PAPER

WILEY-VCH

An Acid Stable Metal-Organic Framework as an Efficient and Recyclable Catalyst for the O-H Insertion Reaction of Carboxylic Acids

Yingxia Wang, Hao Cui, Li Zhang* and Cheng-Yong Su*

Abstract: Although metal-organic frameworks (MOFs) can be used in many reactions, their applications in acid involved reactions are limited due to their instability in acid environment. As a stable MOF, the Ir(III)-porphyrin metal-organic framework of the formula [(Hf₆(μ_3 - $O_{8}(OH)_{2}(H_{2}O)_{10})_{2}(Ir(TCPP)CI)_{3}]$ solvents (Ir-PMOF-1(Hf)) can sustain its structure upon treatments in different pH (0-11) aqueous solutions. In this work, Ir-PMOF-1(Hf) has been examined in the O-H insertion reaction of carboxylic acids with diazo compounds. Catalytic results show that as low as 0.042 mol% of Ir-PMOF-1(Hf) can promote the acid O-H insertion with the maximum turn over number (TON) of 1381, and furthermore, it can be recycled and reused for 10 runs, suggesting that Ir-PMOF-1(Hf) is efficient for this acid involved reaction. Ir-PMOF-1(Hf) can also be miniaturized to nano scale (diameter range of 400-500 nm), and a large improvement with regards to TON (8400) can be observed in its catalysis.

Introduction

Metal-organic frameworks (MOFs) have emerged as a kind of modern materials for gas storage, drug delivery, sensing and catalysis, due to their high surface areas, stability and porosity, and modular design.¹ Especially in catalysis, MOFs have been used in a range of reactions, including H₂ production,² CO₂ conversion,³ multiple component coupling,⁴ X-H (X = C, Si, N, O) insertion,⁵ and many other reactions.⁶ However, their applications in acid involved reactions are underdeveloped and only a few papers have been published,^{7,8} but nevertheless, none of these works were related to the application of MOFs in the synthesis of bioactive α-acyloxy carbonyls, which can be prepared through the O-H insertion reaction of carboxylic acids with diazocarbonyl compounds.^{9,10}

Metalloporphyrin complexes of iron, ruthenium, and rhodium, etc. are known to catalyze X-H (X = C, N, Si) bond insertion with high efficiency and selectivity.^{5,11} Our group has recently discovered that irridium(III) porphyrin complexes can efficiently promote the O-H insertion of alcohols and phenols. The incorporation of Ir(TCPP)Cl (TCPP = tetrakis(4-carboxyphenyl)porphyrin) into the framework of PCN-224 results in a porous iridium(III)-

[a] Miss Y. Wang, Dr. H. Cui, Prof. L. Zhang, Prof. C.-Y. Su, MOE Laboratory of Bioinorganic and Synthetic Chemistry, Lehn Institute of Functional Materials, School of Chemistry Sun Yat-Sen University Guangzhou 510275, China E-mail: zhli99@mail.sysu.edu.cn; cesscy@mail.sysu.edu.cn

Supporting information for this article is given via a link at the end of the document.

porphyrin metal-organic framework (Ir-PMOF-1), which possesses two types of open cavities $(1.9 \times 1.9 \times 1.9 \text{ and}$ $3.0 \times 3.0 \times 3.0 \text{ nm}^3$) crosslinked through orthogonal channels $(1.9 \times 1.9 \text{ nm}^2)$ in three directions.^{5a,b} The smaller cavity is surrounded by four Ir(TCPP)CI walls to form a catalytic coordination space, where the reactions can be carried out. Chemical stability study has further disclosed that Ir-PMOF-1(Hf) can sustain its structure in a wide range of pH values (0-11) for more than 24 h, suggesting that its framework can resist acids.



Figure 1. Chemical stability of Ir-PMOF-1(Hf) in different pH (0-11) media and the application in the reaction of carboxylic acids and diazocarbonyl compounds.

Herein, we report the catalytic activities of Ir-PMOF-1(Hf) in carbene insertion reactions into carboxylic acids, another important group of compounds containing O-H bonds (Figure 1). Catalytic results show that Ir-PMOF-1(Hf) is a powerful catalyst for the reactions of diazo compounds and carboxylic acids, which is efficient with as low as 0.04 mol [Ir]% of Ir-PMOF-1(Hf) being required in the acid O-H insertion with the maximum TON of 1381 and recyclable for ten runs. Remarkably, the catalyst amount can be cut down to 0.005 mol [Ir]%, and the TON can be increased by 6 times, reaching 8400, when the crystallite of Ir-PMOF-1(Hf) is in nano scale (diameter range of 400-500 nm). For comparison, most of the acid involved reactions are catalyzed by Uio-66^{7b,g,h} or MOF-199 (HKUST-1)^{7e}, in which

WILEY-VCH

the MOF catalyst amount was more than 10 mol%, the catalysts can be reused for less than 5 runs.

Results and Discussion

Reaction of benzoic acid and ethyl diazoacetate (EDA) with the molar ratio of 2:1 and in the presence of 0.8 mol [Ir]% of Ir-PMOF-1(Hf) was chosen as the model reaction for solvent optimization. A range of solvents, including dichloromethane (DCM), 1,2-dichloroethane (DCE). acetonitrile (CH₃CN), toluene, n-hexane and acetone, have been examined. Before test, the chemical stability of Ir-PMOF-1(Hf) in these solvents has been studied. After Ir-PMOF-1(Hf) was immersed in these solvents for 3-5 days, the solvents are still colourless and the powder X-ray patterns of the catalyst samples remain (Figures S1 and S2), suggesting that Ir-PMOF-1(Hf) can be used as a heterogeneous catalyst in these solvents.

I able 1. Reaction Optimation."	tion Optimation. ^a
---------------------------------	-------------------------------

C	OH + N2	⊖ EDA	OF-1(Hf)		
Entry	Molar Ratio of	Catalyst	Solvent	Time	Yield
	acid / EDA	([lr] mol%)			(%)
1	2:1	0.8	acetone	3 h	trace
2	2:1	0.8	CH₃CN	12 h	trace
3	2:1	0.8	<i>n</i> -hexane	12 h	0
4	2:1	0.8	toluene	10 min	60
5	2:1	0.8	DCE	1.5 h	31
6	2:1	0.8	DCM	10 min	73
7	2:1	0.4	DCM	0.5 h	68
8	2:1	0.042	DCM	20 h	58
9	2:1	2.4	DCM	8 min	66
10	1:1	0.8	DCM	15 min	45
11	3:1	0.8	DCM	9 min	72
12	4:1	0.8	DCM	9 min	80
13 ^b	2:1	0.16	DCM	5 h	55

[a] In each reaction, the amount of EDA is 22.8 mg, and EDA has been completely consumed. The yields are based on the conversions of diazoacetates to the O-H insertion products. [b] The amount of EDA is enlarged to 1.14 g.

Catalytic results show that, in polar solvents such as acetone and CH₃CN, the reactions were sluggish and only a trace amount of O-H insertion product 2-ethoxy-2oxoethyl benzoate (1a) has been produced (Table 1, entries 1 and 2). It is found that in nonpolar solvent n-hexane, no product can be detected even after 12 h (entry 3). To our delight, the reaction in toluene can give rise to 60% yield after 10 min (entry 4). We then explored halogenated solvents such as DCE and DCM, and found that the reaction in DCE has moderate yield (31%) in 1.5 h whereas the reaction in DCM can be largely promoted and the yield is up to 73% in 10 min (entries 5 and 6). When the catalyst amount was decreased to 0.4 and 0.042 [Ir] mol%, the yield is cut down to 68 and 58%, respectively, whereas the reaction time is much longer (entries 7 and 8). For comparison, when the catalyst amount is increased to 2.4 mol [Ir] %, the reaction can be finished in 8 minutes, but however, the yield hasn't increased (68%, entry 10). Based on these data, the maximum turn over number (TON) is calculated to be 1381. Tuning the molar ratio of benzoic acid and EDA from 1:1, 2:1, 3:1 to 4:1, the best yield of 80% can be obtained with the 4 times excess of benzoic acid (entries 6, 10-12). A scale up reaction (up to 1.14 g of EDA) in the presence of 0.16 [Ir] mol% of Ir-PMOF-1(Hf) has been set up, and the yield is 55% in 5 h (entry 13). It is noted that, in addition to the O-H insertion products, the self-coupling reaction products of EDA, i.e. diethyl fumarate and maleate, accounted for all initial EDA.9



Figure 2. Catalytic results with different catalysts.

Catalytic results of the model reactions in the presence of different isostructural MOF catalysts such as Ir-PMOF-1(Hf), Ir-PMOF-1(Zr), Ru-PMOF-1(Hf), Rh-PMOF-1(Zr), PCN-224(Hf) and PCN-224(Zr) are shown in Figure 2 and Table S1.^{3,5,12} In PCN-224(Hf) and PCN-224(Zr), there is no metal in the center of the porphyrin ring. The reactions can be

Ir(III) porphyrins.

FULL PAPER

WILEY-VCH



accomplished in around 10 min using Ir-porphyrin-based

MOF catalysts (e.g. Ir-PMOF-1(Hf) and Ir-PMOF-1(Zr)),

which are competent to the corresponding homogeneous

catalyst of IrCl(TPP)(CO) and much better than IrCl₃·3H₂O.

For comparison, Ru-PMOF-1(Hf), Rh-PMOF-1(Zr) and

PCN-224 are all inefficient for this reaction, and the yields

are less than 20% even after 16 h. This group of catalytic

data confirm that the active centers are mainly based on

[a] Reaction conditions: 0.8 mol [Ir]% of the catalyst, 2 mL DCM, and 2:1 molar ration of acid and diazocarbonyl compounds. The yields are based on the conversions of diazocarbonyl compounds to the O-H insertion products. In each reaction, diazocarbonyl compounds have been completely consumed.

This protocol can be further applied to other carboxylic acids (Table 2). As for functionalized benzoic acids, the yields of the reactions with 4-methylbenzoic acid and 2hydroxybenzoic acid are 79 and 57%, respectively (entries 2 and 3). It is noted that the substrate 2-hydroxybenzoic acid contains two kinds of O-H groups, i.e., from phenols and carboxylic acids, whereas the insertion reaction selectively occurs with carboxyl group rather than phenol group. Similar to benzoic acid, the aromatic acid of thiophene-2-carboxylic acid can give rise to 74% yield, although the reaction need much longer time (50 min, Table 2, entry 4). As for the reactions with alkyl acids such as trifluoroacetic acid (TFA), propionic acid and hexa-2,4dienoic acid, they are efficient and the yields are up to 91, 60 and 64%, respectively (entries 6-7). The fast rate (6 min) and an excellent yield (91%) with regards to TFA may be due to the electron withdrawing effect of fluorine atom which makes it more easily for O-H insertion. When the diazocarbonyl compound was changed from EDA to propyl diazoacetate (PDA), tert-butyl diazoacetate (BDA), or benzyl diazoacetate (BnDA), the reactions with benzoic acid can also occur easily and the yields were in the range of 63-69% (entries 8-10). These results show a good tolerance of Ir-PMOF-1(Hf) in the synthesis of bioactive aacyloxy carbonyls through the O-H insertion reaction of carboxylic acids with diazocarbonyl compounds. Preliminary attempts to expand this catalysis to chiral acids such as N-sulfonyl prolines and thiazolidine-4-carboxylic acids have been carried out, and catalytic results disclose that these chiral acids derived from natural amino acids can react with EDA in the presence of Ir-PMOF-1(Hf), but unfortunately, the yields are very low (around 10%, Table S2).

A plausible reaction mechanism is shown in Figure 3. The diazocompound EDA firstly reacted with the iridium(III)porphyrin within the MOF catalyst of Ir-PMOF-1(Hf) to generate iridium carbene A,^{13a} which then inserted into the O-H bonds of carboxylic acids through the ylide intermediates **B** or **C** followed by a 1,2-H shift process.^{13b}



This article is protected by copyright. All rights reserved.

One of the biggest advantages for Ir-PMOF-1(Hf) catalyzed O-H insertion of carboxylic acids lies in that the catalyst can be isolated easily and reused for more than 10 runs with little loss of its catalytic activity (Figure 4). Before being reused for the next run, the catalyst only need be washed with DCM for several times and dried under air. The longer reaction time after the 7th run is needed (Table S2), which may due to the residue of benzoic acid or products in the pores, preventing the approach of reactants to the active sites and the transmission of products through the crossing channels. As a result, the smaller substrate EDA transferred easier into the cavities of Ir-PMOF-1(Hf) and carried out the the unpleasant dimerisation reaction there. This hypothesis has been confirmed by the smaller N₂ uptake (328 cm³ g⁻¹) and reduced BET surface area (1162 m²g⁻¹) of Ir-PMOF-1(Hf) after catalysis (Figures S3 and S4). The integrity of the catalyst after catalysis was showed by the similarity of the PXRD patterns with the simulated ones of the as-synthesized samples (Figures S5 and S6).



To make sure whether the valence state of Ir in Ir-PMOF-1(Hf) has remained after the catalytic reaction, we have measured the energy-dispersive X-ray spectroscopy (XPS) of Ir-PMOF-1(Hf) before and after catalysis. Two intense peaks around 65.3 and 62.3 eV, which are assignable to Ir 4f_{5/2} and Ir 4f_{7/2}, respectively, appear in the XPS spectrum of Ir-PMOF-1(Hf) after the reaction (Figure S7).¹⁴ It suggests that the valence of Ir is still +3. The XPS result shows the atomic ratio of Hf : Ir : CI after catalysis is 0.96 : 0.25 : 0.27 (Table S4), which closely matches the ratio of 4 : 1: 1 determined from the single-crystal data. Moreover, a negligible amount of iridium (less than 0.18% of the total Ir content in Ir-PMOF-1(Hf)) leaching into the reaction solution was detected by inductively coupled plasma optical (ICP-OES) spectroscopy emission analysis. These

experiments confirm the heterogeneous nature of Ir-PMOF-1(Hf)-catalyzed reactions.

The charming advantages (e.g. high external surfaces and fast diffusion rate) of nanoscale MOFs inspire us to reduce the sizes of Ir-PMOF-1(Hf) into nano scale, and then employ the nanocrystalline PMOF in the O-H insertion of acids.¹⁵ The purity and crystallinity of nano Ir-PMOF-1(Hf) are related to the concentration of the modulator (e.g. benzoic acid) and the reaction temperature. When the molar amount of benzoic acid is 467 (or bigger than 467) times higher than that of the metalloporphyrin ligand Ir(TCPP)CI, microcrystals in the diameter range of 30-50 µm were obtained. On the other hand, when the temperatures are in the range of 100-120℃, only microcrystals can be gotten. Through the optimization, we found that a 435 : 1 molar ratio of benzoic acid and Ir(TCPP)CI as well as 90 °C are the optimized reaction conditions for the formation of nano Ir-PMOF-1(Hf). The scanning electron microscopy (SEM) (Figure 5a, b) discloses that the prepared Ir-PMOF-1(Hf) nanocrystals are block-shaped, whose diameters are in the range of 400-500 nm. The powder X-ray patterns of the as-synthesized nanocrystals match with those of the simulated ones, confirming the phase purity (Figure S1). In the presence of 0.005 mol% of the nanoscale Ir-PMOF-1(Hf) (400-500 nm), the yield for the reaction of benzoic acid and EDA can be 42% after 47 h. Based on this, the turn over number (TON) can be calculated to be 8400, which is much higher than the maximum TON (1380) of normal Ir-PMOF-1(Hf)catalyzed reaction. The morphology and crystallinity of nano Ir-PMOF-1(Hf) can be maintained during catalysis, which can be confirmed by SEM (Figure 5), PXRD pattern (Figure S5) and IR spectra (Figure S8) before and after the catalytic reaction.



Figure 5. SEM of nano Ir-PMOF-1(Hf) before catalysis (a, b) and after catalysis (c, d).

WILEY-VCH

Conclusions

In summary, we have discovered an acid stable MOF catalyst, Ir-PMOF-1(Hf), for the O-H insertion reaction of carboxylic acids with diazo compounds. Catalytic results show that Ir-PMOF-1(Hf) can be simply recycled and reused for at least 10 runs. Furthermore, it can sustain its framework after the catalytic reactions. We have further prepared nanoscale crystallite Ir-PMOF-1(Hf) with diameters in the range of 400-500 nm and employed it into the O-H insertion reaction, finding that as high as 8400 of TON was achieved. The further researches to explore the properties and catalytic applications of nanoscale PMOFs are in the process.

Experimental Section

General.

All the reagents in the present work were obtained from commercial sources and used directly without further purification. Synthesis of $(Hf_6(\mu_3-O)_8(OH)_2(H_2O)_{10})_2(Ir(TCPP)CI)_3$ -solvents (Ir-PMOF-1(Hf)) was according to the procedure of our published work (Figure S1).5 ¹H NMR were recorded on Bruker AVANCE III 400MHz. ¹³C NMR were recorded on Bruker AVANCE III 101MHz. HRESI-MS was performed by using a Bruker Daltonics ESI-Q-TOF maxis4G. PXRD patterns were recorded on Smartlab X-ray powder diffractometer (Rigaku Co.) at 40 kV and 30 mA with a Cu target tube. Thermogravimetric (TG) analyses were performed under an air atmosphere at a heating rate of 2°C min⁻¹ by using a NETZSCH TG 209 system. X-ray photoelectron spectroscopy (XPS) was performed on a ULVAC PHI Quantera microprobe. Binding energies (BE) were calibrated by setting the measured BE of C 1s to 284.65 eV. ICP spectroscopy was conducted on a Spectro Ciros Vision ICP-OES spectrometer that is equipped with vacuum optics covering the spectral range from 175-777 nm, plasma power, 1300 w; coolant flow, 15.00 L/min; auxiliary flow, 0.80 L/min; nebulizer 0.70 L/min. The sorption isotherms for N₂ (77K) gas were measured with an Autosorb-iQ2-MP gas sorption analyzer (Quantachrome USA).

Caution! Although we have not experienced any problem in the handling of the diazo compounds, extreme care should be taken when manipulating them due to their explosive nature.

Typical procedure for the reaction of carboxylic acid and diazocarbonyl compound

Prior to gas adsorption or catalysis, Ir-PMOF-1(Hf) was activated via the following procedure: The as-synthesized crystals were immersed in acetone for 2 days, and then the solvent was changed with fresh solvent for 3 times. Afterwards, the sample was heated at 120°C under vacuum for 12 h to remove the adsorbed solvents in the cavities.

A mixture of benzoic acid (48.8 mg, 0.4 mmol, 2 eq) and activated Ir-PMOF-1(Hf) (3.1 mg, 0.0016 mmol [Ir], 0.8 mol [Ir]%)

was stirring in DCM (1 mL), and then EDA (22.8 mg, 0.2 mmol, 1 eq) was added slowly into the above mixture through syringe. The resulting reaction mixture was stirring at room temperature for 10 min, until no EDA was detected by TLC. The catalyst was centrifuged, washed with DCM (5 mL × 5), and dried under air before being reused in the consecutive runs. The combined supernatant was evaporated to dryness and the conversion (73%) of the reaction was tested by ¹H NMR spectroscopy. The crude residue was purified by flash chromatography to afford pure product 2-ethoxy-2-oxoethyl benzoate (1a), ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, 2H, *J* = 7.5 Hz), 7.62 (t, 1H, J = 7.4 Hz), 7.49 (t, 2H, J = 7.7 Hz), 4.87 (s, 2H), 4.29 (q, 2H, J = 7.1 Hz), 1.31 (m, 3H). HRMS ([M+Na]) Calcd. for C₁₁H₁₂O₄: 231.0627; Found: 231.0628.

Recycling experiments

EDA (182.4 mg, 1.6 mmol, 1 eq) was added slowly to the mixture of benzoic acid (390.4 g, 3.2 mmol, 2 eq) and activated Ir-PMOF-1(Hf) (24.8 mg, 0.013 mmol, 0.8 mol [Ir]%) in DCM (16 mL). The resulting suspension was stirred at room temperature until all EDA was completely consumed. The undissolved catalyst was removed through centrifugation, and washed with fresh DCM (8 mL x 4). The combined supernatant was evaporated to dryness, and the residue was dissolved in CDCl₃ and analyzed by ¹H NMR to determine the yield of **1a**. The recycled catalyst was collected, air-dried and then used for the successive runs.

ICP Spectrometric Evaluation

After the catalytic reaction was complete, the catalyst was separated by centrifugation and washed with fresh DCM (5 mL × 5). The combined solution was further filtered with membrane filter (0.22 µm) for 3 times, and then the filtrate was concentrated to around 1 mL by heating. Afterwards, 30 mL of aqua regia was added, and the resulting solution stayed at room temperature for 1 day. After that, the mixture was heated at 150°C to remove most of the solvent, and the residue was treated with hydrochloric acid (21 mL) and nitric acid (7 mL). After standing at room temperature for another 4 h, the resulting solution was heated at 150 °C again until only 1 mL mixture was left. This digestion procedure was repeated until the residue solution was transparent after H₂O was added. The resulting mixture was diluted volumetrically with an aqueous solution of nitric acid (2%) to 25 mL, to obtain a colorless solution, which was then measured by inductively coupled plasma optical emission spectrometer (ICP-OES) for the Ir and Hf contents. The measured Ir and Hf contents were 0.09 ppm and 0.16 ppm, corresponding to 0.18% and 0.07% leaching, respectively.

Synthesis of nanoscale Ir-PMOF-1(Hf)

Ir(TCPP)CI (5 mg, 4.9×10^{-3} mmol), HfCl₄ (15 mg, 4.7×10^{-2} mmol), benzoic acid (260 mg, 2.12 mmol) and dimethylformamide (DMF, 3 mL) were placed in a 20 mL glass vial, which was then sealed and stirred at 90 °C for 14 h, after that the suspension was cooled to room temperature and centrifuged at 12000 rpm for 15 minutes. Afterwards, the upper transparent solvent was transferred to another 10 mL glass vial and heated at 120°C in an oven. After 3 h, red block crystallites of 400-500 nm

FULL PAPER

size were obtained (about 20% yield based on Ir(TCPP)CI). FT-IR

(KBr) v 3402 (br), 1710 (w), 1634 (w), 1604(s), 1549 (s), 1422 (s), 1371 (m), 1354 (m), 1176 (w), 1016 (s), 821 (w), 791 (m), 774 (m), 715 (s), 668 (m), 597 (w), 550 (w), 503 (w) cm⁻¹.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21773314, 21720102007), Natural Science Foundation of Guangdong Province (S2013030013474) and the Fundamental Research Funds for the Central Universities (16lgjc68, 17lgjc12).

Keywords: Iridium Porphyrin Metal-Organic Framework • Heterogeneous Catalysis • O-H Insertion • Nano Crystallite

- (a) J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang, C.-Y. Su, *Chem. Soc. Rev.* 2014, *43*, 6011-6061; (b) A. H. Chughtai, N. Ahmad, H. A. Younus, A. Laypkov, F. Verpoort, *Chem. Soc. Rev.* 2015, *44*, 6804-6849; (c) Y.-B. Huang, J. Liang, X.-S. Wang, R. Cao, *Chem. Soc. Rev.* 2017, *46*, 126-157; (d) S. M. J. Rogge, A. Bavykina, J. Hajek, H. Garcia, A. I. Olivos-Suarez, A. Sepúlveda-Escribano, A. Vimont, G. Clet, P. Bazin, F. Kapteijn, M. Daturi, E. V. Ramos-Fernandez, F. X. Llabrés i Xamena, V. Van Speybroeck, J. Gascon, *Chem. Soc. Rev.* 2017, *46*, 3134-3184; (e) C.-D. Wu, M. Zhao, *Adv. Mater.* 2017, *29*, 1605446.
- [2] A. Dhakshinamoorthy, A. M. Asiri, H. García, Angew. Chem. Int. Ed. 2016, 55, 5414-5445.
- [3] J. Liu, Y.-Z. Fan, X. Li, Z. Wei, Y.-W. Xu, L. Zhang, C.-Y. Su, Applied Catalysis B: Environmental 2018, 231, 173-181.
- [4] (a) T. Yang, H. Cui, C. Zhang, L. Zhang, C.-Y. Su, *Inorg. Chem.* 2013, 52, 9053-9059; (b) T. Yang, H. Cui, C. Zhang, L. Zhang, C.-Y. Su, *ChemCatChem* 2013, 5, 3131-3138.
- [5] (a) H. Cui, Y. Wang, Y. Wang, Y.-Z. Fan, L. Zhang, C.-Y. Su, *CrystEngComm* **2016**, *18*, 2203-2209; (b) Y. Wang, H. Cui, Z.-W. Wei, H.-P. Wang, L. Zhang, C.-Y. Su, *Chem. Sci.* **2017**, *8*, 775-780; (c) L. Chen, H. Cui, X. Liang, L. Zhang, C.-Y. Su, *Dalton Trans.* **2018**, *47*, 3940-3946.
- [6] (a) C. Freire, D. M. Fernandes, M. Nunes, V. K. Abdelkader, *ChemCatChem* 2018, *10*, 1703-1730; (b) Y. Cui, M. Rimoldi, A. E. Platero-Prats, K. W. Chapman, J. T. Hupp, O. K. Farha, *ChemCatChem* 2018, *10*, 1772-1777; (c) F. Pitzalis, C. Carucci, M. Naseri, L. Fotouhi, E. Magner, A. Salis, *ChemCatChem* 2018, *10*, 1578-1585; (d) R. Ma, P. Yang, Y. Ma, F. Bian, *ChemCatChem* 2018, *10*, 1446-1454; (e) R. Oozeerally, D. L. Burnett, T. W. Chamberlain, R. I. Walton, V. Degirmenci, *ChemCatChem* 2018, *10*, 706-709; (f) S. Feng, X. Li, J. Huo, Q. Li, C. Xie, T. Liu, Z. Liu, Z. Wu, S. Wang, *ChemCatChem* 2018, *10*, 796-803; (g) L. Huang, F. Qin, Z. Huang, Y. Zhuang, J. Ma, H. Xu, W. Shen, *ChemCatChem* 2018, *10*, 381-386.
- [7] (a) C. Huang, R. Ding, C. Song, J. Lu, L. Liu, X. Han, J. Wu, H. Hou, Y Fan, Chem. Eur. J. 2014, 20, 16156-16163; (b) Y. Liu, S. Liu, D. He, N. Li, Y. Ji, Z. Zheng, F. Luo, S. Liu, Z. Shi, C. Hu, J. Am. Chem. Soc. 2015, 137, 12697-12703; (c) L. T. M. Hoang, L. H. Ngo, H. L. Nguyen, H. T. H. Nguyen, C. K. Nguyen, B. T. Nguyen, Q. T. Ton, H. K. D. Nguyen, K. E. Cordova, T. Truong, Chem. Commun 2015, 51, 17132-17135; (d) L. Yang, G. L. Ruess, M. A. Carreon, Catal. Sci. Technol. 2015, 5, 2777-2782; (e) S. L. Ho, II C. Yoon, C. S. Cho, H.-J. Choi, J. Organomet. Chem. 2015, 791, 13-17; (f) M. Albert-Soriano, I. M. Pastor. Eur. J. Org. Chem. 2016, 5180-5188; (g) Y. Kuwahara, H. Kango, H. Yamashita, ACS Sustainable Chem. Eng.

2017, *5*, 1141-1152; (h) D. Azarifar, R. Ghorbani-Vaghei, S. Daliran, A. R. Oveisi, *ChemCatChem* **2017**, *9*, 1992-2000.

- [8] (a) X. Li, R. V. Zeeland, R. V. Maligal-Ganesh, Y. Pei, G. Power, L. Stanley, W. Huang, ACS Catal. 2016, 6, 6324-6328; (b) D. Sun, Z. Li, J. Phys. Chem. C 2016, 120, 19744-19750.
- [9] A. Ford, H. Miel, A. Ring, C. N. Slattery, A. R. Maguire, M. A. McKervey, *Chem. Rev.* 2015, *115*, 9981-10080.
- [10] (a) L. Dumitrescu, K. Azzouzi-Zriba, D. Bonnet-Delpon, B. Crousse, Org. Lett. 2011, 13, 692-695; (b) Z. Wang, X. Bi, Y. Liang, P. Liao, D Dong, Chem. Commun. 2014, 50, 3976-3978; (d) S. Bertelsen, M. Nielsen, S. Bachmann, K. A. Jørgensen, Synthesis 2005, 2234-2238; (e) T. Shinada, T. Kawakami, H. Sakai, I. Takada, Y. Ohfune, Tetrahedron Lett. 1998, 39, 3757-3760.
- [11] (a) J. Yoo, N. Park, J. H. Park, J. H. Park, S. Kang, S. M. Lee, H. J. Kim, H. Jo, J.-G. Park, S. U. Son, *ACS Catal.* 2015, *5*, 350-355; (b) C.-M. Ho, J.-L. Zhang, C.-Y. Zhou, O.-Y. Chan, J. J. Yan, F.-Y. Zhang, J.-S. Huang, C.-M. Che, *J. Am. Chem. Soc.* 2010, *132*, 1886-1894; (c) H.-Y. Thu, G. S.-M. Tong, J.-S. Huang, S. L.-F. Chan, Q.-H. Deng, C.-M. Che, *Angew. Chem. Int. Ed.* 2008, *47*, 9747-9751; (d) B. J. Anding, L. K. Woo, *Organometallics* 2013, *32*, 2599-2607.
- [12] D. Feng, W.-C. Chung, Z. Wei, Z.-Y. Gu, H.-L. Jiang, Y.-P. Chen, D. J. Darensbourg, H.-C. Zhou, J. Am. Chem. Soc. 2013, 135, 17105-17110.
- [13] (a) B. J. Anding, A. Ellern, L. K. Woo, Organometallics 2014, 33, 2219-2229; (b) X. Zhao, Y. Zhang, J. Wang, Chem. Commun. 2012, 48, 10162-10173.
- [14] T. V. Voskobojnikov, E. S. Shpiro, H. Landmesser, N. I. Jaeger, G. Schulz-Ekloff, J. Mol. Catal. A-Chem. 1996, 104, 299-309.
- [15] (a) M. L. Kelty, W. Morris, A. T. Gallagher, J. S. Anderson, K. A. Brown, C. A. Mirkin, T. D. Harris, *Chem. Commun.* 2016, *52*, 7854-7857; (b) P. Li, R. C. Klet, S.-Y. Moon, T. C. Wang, P. Deria, A. W. Peters, B. M. Klahr, H.-J. Park, S. S. Al-Juaid, J. T. Hupp, O. K. Farha, *Chem. Commun.* 2015, *51*, 10925-10928; (c) T. He, X. Xu, B. Ni, H. Wang, Y. Long, W. Hu, X. Wang, *Nanoscale* 2017, *9*, 19209-19215; (d) K. Lu, C. He, W. Lin, *J. Am. Chem. Soc.* 2014, *136*, 16712-16715; (e) J. Park, Q. Jiang, D. Feng, L. Mao, H-C. Zhou, *J. Am. Chem. Soc.* 2016, *138*, 3518-3525.

FULL PAPER

WILEY-VCH

FULL PAPER



Yingxia Wang, Hao Cui, Li Zhang* and Cheng-Yong Su*

Page 1. – Page 6.

An Acid Stable Metal-Organic Framework as an Efficient and Recyclable Catalyst for the O-H Insertion Reaction of Carboxylic Acids

Acid-Resistant MOF Catalyst: As a stable MOF in different pH (0-11) aqueous solutions, the Ir(III)-porphyrin metal-organic framework of the formula $[(Hf_6(\mu_3-O)_8(OH)_2(H_2O)_{10})_2(Ir(TCPP)CI)_3]$ -solvents (Ir-PMOF-1(Hf)) can promote the O-H insertion reaction of carboxylic acids with diazo compounds with the maximum turn over number (TON) of 1381. Furthermore, Ir-PMOF-1(Hf) can be miniaturized to nano scale (diameter range of 400-500 nm), and a much higher TON (8400) can be achieved in the catalysis.