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# Metal–Organic-Framework-Derived Carbons: Applications as Solid-Base Catalyst and Support for Pd Nanoparticles in Tandem Catalysis

Xinle Li

*Iowa State University and Ames Laboratory*

Biyang Zhang

*Iowa State University and Ames Laboratory, biyangz@iastate.edu*

Yuhui Fang

*Beijing Normal University*

Weijun Sun

*Iowa State University and Ames Laboratory*

Zhiyuan Qi

*Iowa State University and Ames Laboratory*

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## Abstract

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## Keywords

Knoevenagel condensation, metal–organic frameworks, n-doped carbons, palladium, tandem catalysis

## Disciplines

Chemistry | Materials Chemistry | Mechanics of Materials

## Comments

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## Authors

Xinle Li, Biying Zhang, Yuhui Fang, Weijun Sun, Zhiyuan Qi, Yuchen Pei, Shuyan Qi, Pengyu Yuan, Xuechen Luan, Tian Wei Goh, and Wenyu Huang

# Metal-Organic Framework Derived Carbons: Applications as Solid Base Catalyst and Support for Pd Nanoparticles in Tandem Catalysis

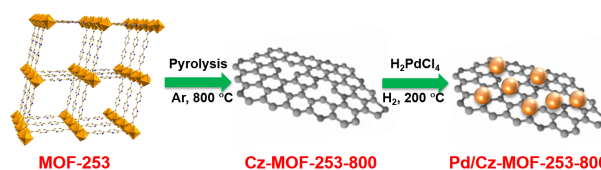
Xinle Li,<sup>[a]</sup> Biying Zhang,<sup>[a]</sup> Yuhui Fang,<sup>[c]</sup> Weijun Sun,<sup>[a]</sup> Zhiyuan Qi,<sup>[a]</sup> Yuchen Pei,<sup>[a]</sup> Shuyan Qi,<sup>[c]</sup> Pengyu Yuan,<sup>[b]</sup> Xuechen Luan,<sup>[a]</sup> Tian-Wei Goh,<sup>[a]</sup> and Wenyu Huang\*<sup>[a]</sup>

**Abstract:** The facile pyrolysis of a bipyridyl metal-organic framework, MOF-253, produces N-doped porous carbons (Cz-MOF-253), which exhibit excellent catalytic activity in the Knoevenagel condensation reaction and outperform other nitrogen-containing MOF-derived carbons. More importantly, by virtue of their high Lewis basicity and porous nature, Cz-MOF-253 supported Pd nanoparticles (Pd/Cz-MOF-253-800) show excellent performance in a one-pot sequential Knoevenagel condensation-hydrogenation reaction.

Porous carbon materials have been recognized as advanced organocatalysts over the past decades due to their exceptional chemical and thermal stability, electrical conductivity, structural diversity, low cost, and low toxicity, etc.<sup>[1]</sup> The nitrogen doped (N-doped) carbon materials emerge as promising solid base catalysts in heterogeneous catalysis<sup>[2]</sup> and extensive efforts have been devoted towards the synthesis of N-doped porous carbons via facile carbonization of a library of nitrogen-rich precursors such as melamine,<sup>[3]</sup> polymer monolith,<sup>[4]</sup> ionic liquids,<sup>[5]</sup> petroleum coke,<sup>[6]</sup> and biomass derivatives,<sup>[7]</sup> etc. Metal-organic frameworks (MOFs), a new class of organic-inorganic hybrid crystalline materials, have sparked intense interest in porous carbon synthesis due to their tailorable structure and porosity, high surface area, and homogeneous heteroatom doping.<sup>[8]</sup> Although plenty of MOFs have been reported as solid base catalysts,<sup>[9]</sup> the low chemical stability of most MOFs limits their further application in harsh reaction conditions. With these in mind, we envision that N-doped MOF-derived carbons could perfectly tackle this challenge by virtue of their superior chemical stability and homogeneous nitrogen doping upon pyrolysis. In addition, it is of importance to investigate whether MOF-derived carbons can preserve/inherit basic catalytic sites of the precedent MOFs since it not only expands the scope of MOF-derived carbons in catalysis but also allows the flexible design of multifunctional catalysts in MOF-

derived carbons. To this end, MOF-253, a prototype Al-based MOF lined with 2,2'-bipyridyl moiety,<sup>[10]</sup> was judiciously selected as the precursor for porous carbon synthesis. The nitrogen dopant in MOF-253 derived carbons can serve multiple functions: (1) nitrogen dopant can readily affect the electronic properties of carbons, thus improving their catalytic performance;<sup>[11]</sup> (2) it functions as catalytically active Lewis basic sites, which has not been studied in MOF-derived carbons to date; (3) it facilitates efficient Pd loading and stabilizes the Pd nanoparticles (NPs).<sup>[12]</sup>

On the other hand, Knoevenagel condensation reactions are the valued approach for the production of  $\alpha,\beta$ -unsaturated carbonyl compounds which are widely used in pharmaceutical, cosmetic and agrochemical industries.<sup>[13]</sup> Conventionally, Knoevenagel condensation reactions are catalyzed by homogeneous basic catalysts, which are hurdled by the limited recyclability. Therefore, it is highly desirable to develop heterogeneous catalysts that realize those reactions from the viewpoints of economy and green chemistry. To achieve more economic and environmental benefits, tandem catalysis, which enables a series of reactions to take place in one pot, have attracted substantial attention since it avoids the need for the isolation of intermediates and reduces the production of wastes.<sup>[14]</sup> Recently, significant advances have been made in tandem catalysis by porous aromatic frameworks,<sup>[15]</sup> and metal NPs encapsulated within MOFs.<sup>[12a,16]</sup> In addition, metal NPs supported on MOF-derived carbons have also been exploited as catalysts recently.<sup>[17]</sup> However, minimal studies have been done on metal NPs stabilized within MOF-derived carbons for tandem catalysis thus far.<sup>[18]</sup>



**Scheme 1.** Schematic illustration of the synthesis of Cz-MOF-253 and Pd/Cz-MOF-253 for tandem catalysis.

Herein we report the synthesis of N-doped porous carbon (termed Cz-MOF-253) by a facile pyrolysis of bipyridyl MOF-253 (Scheme 1). The as-prepared Cz-MOF-253 solid base catalyst exhibits excellent catalytic efficiency in the Knoevenagel condensation reaction and surpasses the other nitrogen-containing MOF-derived carbons. Furthermore, recycling and leaching tests show that Cz-MOF-253 is a true heterogeneous

[a] X. Li, B. Zhang, W. Sun, Z. Qi, Y. Pei, X. Luan, T. W. Goh, Prof. W. Huang  
Department of Chemistry, Iowa State University, Ames, Iowa 50011, United States  
Ames Laboratory, U.S. Department of Energy, Ames, Iowa 50011, United States  
E-mail: whuang@iastate.edu

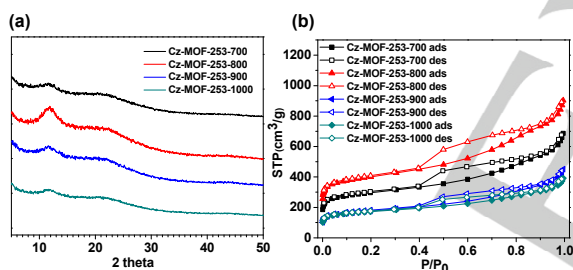
[b] P. Yuan  
Department of Mechanical Engineering, Iowa State University, Ames, Iowa 50011, United States

[c] Y. Fang, S. Qi  
Department of Chemistry, Beijing Normal University, Haidian, Beijing 100875, People's Republic of China

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catalyst. For a proof-of-concept, Pd NPs stabilized within Cz-MOF-253 (Pd/Cz-MOF-253) were evaluated in a one-pot stepwise tandem reaction in which Knoevenagel condensation and subsequent hydrogenation were combined to demonstrate their integrated catalytic properties and high catalytic efficiency. To the best of our knowledge, this represents the first work that demonstrates the applications of N-doped MOF-derived carbons as solid base catalysts and support for Pd NPs in tandem catalysis.

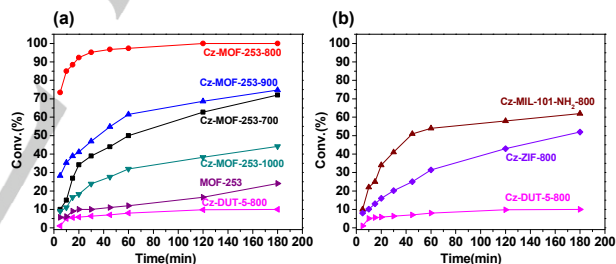
MOF-253 was synthesized via a solvothermal reaction of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  and 2,2'-bipyridine-5,5'-dicarboxylic acid.<sup>[19]</sup> PXRD profiles of the as-synthesized sample coincide well with the simulated pattern (Figure S1). The  $\text{N}_2$  sorption and pore size distribution analysis reveal that MOF-253 possesses a large surface area of  $1940 \text{ m}^2/\text{g}$  and major micro-pores at  $\sim 11 \text{ \AA}$  (Figure S2 and S7a). To investigate the effect of carbonization temperatures on the formation of carbons, MOF-253 was carbonized at 700, 800, 900 and 1000 °C in an argon atmosphere, giving rise to various MOF-derived carbons (denoted as Cz-MOF-253-n, n refers to the pyrolysis temperature in Celsius). It is noted that higher carbonization temperature leads to more weight loss (Table S1). To remove  $\text{Al}_2\text{O}_3$ , the Cz-MOF-253 was treated with 20% HF and washed with deionized water.<sup>[20]</sup> PXRD patterns of Cz-MOF-253 carbons exhibit broad and weak peaks around  $24^\circ$  and  $44^\circ$ , which can be indexed to the diffraction peaks of (002) and (101) of graphitic carbon.<sup>[21]</sup> The peak around  $12^\circ$  presumably corresponds to the peak of (001) of graphene oxide, and its intensity decreases as the pyrolysis temperature increases after 800 °C.<sup>[22]</sup>



**Figure 1.** (a) PXRD patterns of Cz-MOF-253 derived from the pyrolysis of MOF-253 at different temperatures; (b)  $\text{N}_2$  sorption isotherms of the Cz-MOF-253 obtained at different pyrolysis temperatures.

X-ray photoelectron spectroscopy (XPS) analysis indicates the atomic percentage of N in Cz-MOF-253-700, 800, 900 and 1000 are 9.4, 8.5, 7.0, and 3.7 %, respectively (Table S2). The XPS survey indicates that four elements exist in these Cz-MOFs (C, N, O, and F) in the absence of Al peaks (Figure S3). The XPS analysis for N 1s implies four types of nitrogen species: graphitic-N ( $401.1 \pm 0.3 \text{ eV}$ ), pyrrolic-N ( $400.5 \pm 0.3 \text{ eV}$ ), pyridinic-N ( $398.5 \pm 0.2 \text{ eV}$ ) and oxidized nitrogen  $\text{N}^+\text{O}^-$  ( $404.4 \pm 0.1 \text{ eV}$ ) in all Cz-MOF-253 samples prepared at different pyrolysis temperatures (Figure S4).<sup>[23]</sup> For all Cz-MOF-253 samples, pyrrolic-N (36-42%) and pyridinic-N (34-38%) are the main constituents of N, while the graphitic-N (16-22%) and oxidized N (4-8%) contents are relatively low. With the increase of pyrolysis temperature, pyrrolic-N and pyridinic-N were partially converted into graphitic-N species (Figure S5a). The Raman spectrum for Cz-MOF-253 indicates that higher pyrolysis temperature (i.e., 900, 1000 °C) leads to the higher degree of graphitization with the lower  $I_D/I_G$  values (Figure S6). It is worth

noting that the pyrolysis temperature also significantly affects the BET surface area of the resultant carbon materials. BET surface areas of Cz-MOF-253-700, 800, 900, and 1000 are respective 1090, 1490, 640 and  $630 \text{ m}^2/\text{g}$ .  $\text{N}_2$  sorption isotherms display a type-IV curve with an apparent hysteresis loop for these MOF-derived porous carbons (Figure 1b). These results clearly indicate the presence of mesopores, which is further verified by the pore size distribution analysis (Figure S7b). To gain a clear insight into the basic properties of MOF-derived porous carbons, we resort to  $\text{CO}_2$  temperature programmed desorption (TPD), an efficient tool to probe the basicity of nanocomposites including MOF-derived carbons.<sup>[24]</sup> Cz-MOF-253-800 shows several obvious peaks in  $\text{CO}_2$ -TPD in the temperature range of 100-450 °C (Figure S8). This implies that the carbon materials contains medium to strong basic sites upon pyrolysis, which is consistent with the reported guidelines of weak (50-180 °C) and medium to strong (180-500 °C) basicity groups.<sup>[25]</sup> On the basis of the combined results from  $\text{CO}_2$ -TPD and  $\text{N}_2$  sorption measurement, the Cz-MOF-253 sample possesses strong Lewis basicity and porous nature as anticipated. The  $\text{CO}_2$  desorption temperatures are similar for the sample prepared at 800 and 1000 °C (Figure S8), indicating the similar basic strength of the carbonized MOFs prepared at different temperatures. This agrees with our XPS results that the relative percentages of the four different surface N sites are similar for Cz-MOF-253 carbonized at different temperatures (Figure S5a). Additionally, the percentage area decrease (63%) of the  $\text{CO}_2$  desorption peak for the samples prepared at 800 and 1000 °C (Figure S8) is close to the percentage decrease in the N content measured by XPS (57%) as shown in Table S2.



**Figure 2.** (a) Time-dependent analysis of the Knoevenagel condensation reaction by Cz-MOFs at different pyrolysis temperatures and pristine MOF catalysts; (b) Time-dependent analysis of the Knoevenagel condensation reaction by control catalysts. Reaction condition: 0.1 mmol of benzaldehyde, 0.3 mmol of malononitrile, 2 mL of toluene, and 10 mg of Cz-MOF, stir at 600 rpm, 90 °C.

With the above characterization results in hand, we set out to evaluate the Lewis basicity of Cz-MOF-253 by Knoevenagel condensation. It is noteworthy that pyrolysis temperature has significant effects on the catalytic activity. As shown in Figure 2a, Cz-MOF-253-800 gave the highest activity among the catalysts from different pyrolysis temperatures at 700, 800, 900 and 1000 °C, which could be due to the largest surface area and high N content for the solid base carbon catalyst pyrolyzed at 800 °C. To further confirm the origin of Lewis basicity, we synthesized DUT-5, which is isorecticular to MOF-253 but possesses no nitrogen contents due to the chemical tunability endowed by MOFs.<sup>[26]</sup> Subsequent nitrogen-free carbon materials (designed as Cz-DUT-5-800) were prepared by the same pyrolysis and acid treatment of DUT-5. As expected, Cz-DUT-5-800 shows much lower activity under the identical

conditions, revealing that the nitrogen served as catalytic sites in Knoevenagel condensation. For a comparison, another nitrogen-containing prototype MOFs (i.e., ZIF-8,<sup>[17a]</sup> and Al-MIL-101-NH<sub>2</sub><sup>[27]</sup>) were selected as precursors under the identical pyrolysis temperature and post-acid treatment conditions. As shown in Figure 2b, both Cz-ZIF-8 and Cz-MIL-101-NH<sub>2</sub> exhibits inferior performance in Knoevenagel condensation, highlighting the superiority of using MOF-253 as carbon precursors. Remarkably, Cz-MOF-253-800 exhibits much higher activity than pristine MOF-253. This enhancement is presumably due to the higher density of basic sites and larger pores after pyrolysis (Figure S7), which is beneficial to the diffusion/transportation of reactants to access the active basic sites.

To demonstrate the general applicability of MOF-derived carbon catalyst in the Knoevenagel condensation reaction, the scope of the most active catalyst, Cz-MOF-253-800, was investigated by conducting the Knoevenagel condensation with a variety of substituted benzaldehyde. As illustrated in Table S3, different substituted benzaldehyde was converted to corresponding benzylidenemalononitriles with high yield. Benzaldehyde derivatives involving electron-rich groups (e.g., 2-methoxy, 4-methoxy, 4-hydroxyl), electron-withdrawing substituents (4-nitro) and halide groups (e.g., 4-Br, and 4-Cl) were converted to the desired products in an efficient fashion. These results clearly demonstrate that Cz-MOF-253-800 is a highly efficient solid base catalyst for Knoevenagel condensation reaction.

The heterogeneous catalyst-Cz-MOF-253-800 can be readily reused in the Knoevenagel condensation reaction. There was no obvious loss in the yield of benzylidenemalononitrile in five runs at complete conversion (Figure S9). To probe for deactivation of the catalyst under our reaction conditions, we evaluated the reusability of Cz-MOF-253-800 in Knoevenagel condensation run to approximately 50% conversion. As shown in Figure S10, the Cz-MOF-253-800 catalyst can be used at least five times without a significant decrease in the yield, indicating the good stability of Cz-MOF-253-800 in the recycle test. A leaching test was employed to further confirm the heterogeneity of the Cz-MOF-253-800 (Figure S11). The catalyst was isolated by centrifugation when the conversion reached ca. 50%. Only a slight increase in conversion of benzaldehyde was observed upon removal of the catalyst, due to the background reaction in the absence of catalysts (5% conversion of benzaldehyde was observed in blank test in 1 h). Also, no obvious changes were observed according to the PXRD patterns of the used catalysts (Figure S12). We also did CO<sub>2</sub>-TPD study of the catalyst after catalysis, and the used Cz-MOF-253-800 still shows several obvious peaks in CO<sub>2</sub>-TPD in the temperature range of 100-450 °C, which is comparable with Cz-MOF-253-800 before catalysis (Figure S13). This result along with PXRD analysis unambiguously demonstrates the robust nature of Cz-MOF-253-800 during catalysis.

Given the highly porous nature and intrinsic Lewis basicity, Cz-MOF-253-800 would be a suitable host for stabilizing Pd NPs, allowing the flexible design of bifunctional catalyst for tandem catalysis. Bearing these in mind, we proceeded to explore the potential of MOF-derived carbons in tandem catalysis. The as-prepared carbon was utilized as host to load Pd NPs by a simple solution impregnation method (designed as Pd/Cz-MOF-253-800).<sup>[17a]</sup> TEM images show the presence of highly dispersed and ultrafine Pd NPs with sizes of ~1 nm (Figure S14). To examine the bifunctional nature of Pd/Cz-MOF-253-800, a successive Knoevenagel condensation-hydrogenation reaction

was utilized as a proof-of-concept.<sup>[28]</sup> As indicated in Table 1, Pd/Cz-MOF-253-800 was effective in facilitating Knoevenagel condensation-hydrogenation reactions to afford the corresponding benzylmalononitrile based on various substituted benzaldehyde in a stepwise manner. The heterogeneity of Pd/Cz-MOF-253-800 was assessed by a filtration test. We did not observe any further increase in the yield of benzylmalononitrile upon the removal of the solid catalyst at 50% conversion (Figure S15a). We also evaluated the reusability of the Pd/Cz-MOF-253-800 in the hydrogenation of benzylidenemalononitrile at ca. 30% conversion. The Pd/Cz-MOF-253-800 catalyst can be readily recycled for five consecutive runs without a significant decrease in the yield of benzylmalononitrile (Figure S15b), indicating the robustness of the catalyst. To our knowledge, this is the first demonstration to apply metal NPs/Cz-MOF as bifunctional catalysts in tandem Knoevenagel condensation-hydrogenation reactions.

**Table 1.** Knoevenagel condensation-hydrogenation of substituted benzaldehyde with malononitrile catalyzed by Pd/Cz-MOF-253-800.

Entry	Product	Time (h)	Conv. (%)	Sel. (%)
1		17	99	99
2		17	99	99
3		17	99	99

Reaction conditions: first step, 0.1 mmol of benzaldehyde, 0.3 mmol of malononitrile, 2 mL of toluene, and 5 mg of Pd/Cz-MOF-253-800, 80 °C, 5 h, stir at 600 rpm; Second step, 150 psi H<sub>2</sub>, 80 °C, 12 h, stir at 600 rpm.

In conclusion, we have developed the N-doped porous carbons by the facile pyrolysis of MOF-253, and the obtained mesoporous Cz-MOF-253 exhibited high efficiency in Knoevenagel condensation reaction as a solid base catalyst. In comparison, the analogous nitrogen-free catalyst-Cz-DUT-5-800, and another nitrogen-containing MOF-derived carbons showed inferior performance. The robust Cz-MOF-253-800 can be reused up to five times without the loss of activity, and there were no observable leaching active species during catalysis. Moreover, the intrinsic Lewis basicity and high porous nature enable the design of bifunctional catalyst, Pd/Cz-MOF-253-800, which readily facilitated tandem Knoevenagel condensation and hydrogenation reactions in a stepwise and heterogeneous manner. This work delineates the first attempt that demonstrates the applications of MOF-derived carbons as solid base catalysts and support for Pd NPs in tandem catalysis. Future work on exploring new catalytic reactions based on such porous Lewis basic MOF-derived carbons is currently underway.

## Experimental Section



### Preparation of Cz-MOF-253 via Pyrolysis

Activated MOF-253 (100 mg) was spread in a quartz boat, which was placed in a temperature-programmed tube furnace. The heating rate was set at 2 °C /min, and the samples were carbonized at the setting temperature for 4 hours. After cooling to ambient temperature, the obtained black powder was treated with HF (20 wt%) at 60 °C for 12 hours and was washed with deionized water (5X) and methanol (3X). The washed Cz-MOFs samples were dried at 120 °C under vacuum (30 mTorr) for 12 hours. The same procedure was applied to other MOFs samples.

### Preparation of Pd/Cz-MOF-253 via Solution Impregnation Method

Cz-MOF-253-800 (50 mg) was dispersed in 2 mL of H<sub>2</sub>O and sonicated for 30 min to achieve a homogenous dispersion. Afterward, 0.5 mL of 0.04 M H<sub>2</sub>PdCl<sub>4</sub> aqueous solution was added dropwise to the above MOF-derived carbons solution. The mixture was allowed to stir at room temperature for 0.5 hours. The as-prepared Pd<sup>2+</sup>-infiltrated Cz-MOF was washed three times with fresh water and then dried at 80 °C for 1 hour under vacuum. Finally, the sample was reduced at under a 50 mL/min flow of 10 % H<sub>2</sub>/Ar at 200 °C for 4 hours.

### General Procedure for the Knoevenagel Condensation Reaction

Benzaldehyde (0.1 mmol) and malononitrile (0.3 mmol), 8 mg of mesitylene, and 10 mg of Cz-MOF-253 were mixed in toluene (2 mL). The reaction was performed in a 6-dram vial (20 cm<sup>3</sup>) at 90 °C under stirring (600 rpm). Upon completion of the reaction, the product was separated via centrifugation, and the yield was determined by gas chromatography (Hewlett Packard 5890 II, FID detector) and Agilent 6890N/5975 gas chromatograph-mass spectroscopy (GC-MS) equipped with an HP-5ms capillary column (30 m × 0.32 mm × 0.25 μm).

### General Procedure for the Knoevenagel Condensation-Hydrogenation Reaction

Benzaldehyde (0.1 mmol) and malononitrile (0.3 mmol), 8 mg of mesitylene, and 5 mg of Pd/Cz-MOF-253-800 were mixed in toluene (2 mL). The reaction was performed in a 6-dram vial (20 cm<sup>3</sup>) at 80 °C under stirring (600 rpm) for 5 hours. Upon completion of the reaction, the vial was transferred to a Parr 4740 High-Pressure/High-Temperature Pressure Vessel. The autoclave was sealed and flushed five times with 150 psi H<sub>2</sub> (99.995%). The reaction was carried out in 150 psi H<sub>2</sub> at 80 °C with magnetic stirring at 600 rpm. After the reaction was finished, the product was separated via centrifugation, and the yield was determined by gas chromatography (Hewlett Packard 5890 II, FID detector) and Agilent 6890N/5975 gas chromatograph-mass spectroscopy (GC-MS) equipped with an HP-5ms capillary column (30 m × 0.32 mm × 0.25 μm).

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**Keywords:** MOFs • N-doped porous carbons • Knoevenagel condensation • Tandem catalysis • Heterogeneous catalysis

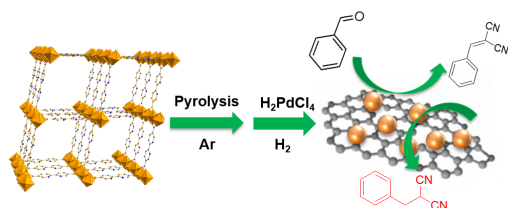
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## COMMUNICATION



Using MOF-derived carbons with high nitrogen contents as solid base catalysts and as the support for Pd nanoparticles in tandem catalysis.

Xinle Li, Biying Zhang, Yuhui Fang,  
Weijun Sun, Zhiyuan Qi, Yuchen Pei,  
Shuyan Qi, Pengyu Yuan, Xuechen  
Luan, Tian-Wei Goh, and Wenyu  
Huang\*

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