Facile synthesis of Pd@MOF catalyst and its application for High Selective Hydrogenation and Hydrodeoxygenation of Biomass-Derived Compounds

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Abstract

High selective hydrogenation and hydrodeoxygenation of biomass-derived compounds are still challenging especially under mild reaction conditions using heterogeneous catalysis. Here, we reported a one-step synthesis method that successfully prepared Pd species immobilized on NH2-MIL-125 (Ti) MOF frameworks which were named Pd@MOF and used as a highly efficient hydrodeoxygenation catalyst for the reduction of vanillin to 2-methoxy-4-methyl phenol in excellent yield with an atm of H2 pressure at room temperature. Pd(PPh3)4 was dispersed in a solvent containing the MOF precursors. Among them, the PPh3 ligand could be oxidized to remove and Pd particles in situ doped in MOF framework during the solvothermal process. Compare to immersed-Pd/MOF and Pd-MOF, Pd@MOF has higher catalytic efficiency because the smaller Pd particles encapsulated in MOF inhibit Pd over oxidation. Moreover, the different reduction products could be obtained selectively by tuning reaction time, and the catalyst realized to catalyze the highly effective transformation of a variety of biomass-derived compounds.

Keywords

MOF, vanillin, hydrodeoxygenation, biomass-derived compounds, time-tuning

1. Introduction

Biomass, the most abundant renewable resource on the planet, has found applications in producing sustainable fuel sources and chemicals.1, 2 Vanillin is widely regarded as one type of platform intermediate for the conversion of lignin biomass into valuable chemicals and fuels due to the presence of –OH, –CHO and benzene ring functional groups. In particular, the selective hydrodeoxygenation of vanillin to 2-methoxy-4-methylphenol (MMP) is highly desired as MMP is an essential chemical applied in fragrances and the synthesis of the pharmaceutical intermediates.3-6 To achieve efficient conversion of vanillin to MMP, considerable catalyst systems have been
investigated for catalytic hydrodeoxygenation (HDO), for example, biochars supported noble metal nanoparticles, \(^7\) Pd/CFR nanocatalyst, \(^4\) nitrogen-doped Co nanoparticles, \(^8, 9\) Cu NPs supported on activated carbon, \(^3\) bimetallic metal-based catalysts, \(^2\) and single atom catalyst \(^10\) have been applied in vanillin hydrodeoxygenation. Among these catalysts, catalytic HDO with effective transformation, however, higher \(H_2\) pressure, high reaction temperature, or complicated catalyst preparation are required in most cases. Thus, developing high-efficiency efficient catalysts for hydrodeoxygenation reactions needed long exploration.

Metal-organic frameworks (MOFs) as high surface area materials are arguably one of the most ideal supports with chemical tunability, insolubility, recyclability, and so on. \(^11-13\) Besides, supported noble metal heterogeneous MOFs have formed a large number of effective catalysts used in practical applications. \(^14\) Recently, progresses in the applications of Pd-supported MOFs to propel catalyze organic transformations have been well documented. \(^15-17\) In addition, several MOFs loaded Pd have been developed to catalyze the reaction of vanillin HDO reaction. For instance, Samy El-Shall’s group prepared palladium nanoparticles encapsulated in \(NH_2\)-UiO-66 MOF and used the Pd@\(NH_2\)-UiO-66 catalyst in the hydrodeoxygenation of vanillin at 90 °C under 0.5 MPa \(H_2\) pressure. \(^18\) Zhang and co-workers fabricated Pd NPs supported on MOFs by an incipient-wetness impregnation method. The as-prepared Pd/\(SO_3\)H-MIL-101(Cr) catalyst has general catalytic activity and selectivity in hydrodeoxygenation reaction of vanillin at 100 °C under 0.5 MPa \(H_2\). \(^19\) Besides, Chang’s group reported the use of synthesized Pd@HPCs by the wet impregnation method derived from MIL-101-NH\(_2\) MOF as a highly active and stable catalyst for hydrodeoxygenation (HDO) or hydrogenation reactions of various biomass-derived organic compounds at 80 °C under 0.5 MPa \(H_2\). \(^20\) Whereas supported noble metal Pd doped MOF were numerously prepared by impregnation, most of the Pd nanoparticles may be loaded on the surface of the frames and small metal nanoparticles (NPs) aggregate easily and lead to poor thermodynamical stability during the reaction, resulting the catalyst’s activity was declined. \(^21, 22\)

Tetrakis(triphenyl phosphine) palladium (Pd(PPh\(_3\))\(_4\)) is a well-known homogeneous coordination catalyst and demonstrates extensive applications in organic reductive and cross-coupling transformations. \(^23-25\) However, Pd(PPh\(_3\))\(_4\) is an air-sensitive homogeneous catalyst that not only suffers from difficulties of separation and recyclability but also often causes catalyst deactivation in the process of reaction. \(^26, 27\) In the past, using a simple one-pot method to obtain generation of palladium nanoparticles from Pd(PPh\(_3\))\(_4\) and make recyclable palladium catalysts through removing PPh\(_3\) ligands and subsequent (MeO)\(_4\)Si or (i-PrO)\(_4\)Ti supporter gelation by treatment with water. \(^28, 29\) However, the palladium catalysts often suffers from problems such as low reactivity, palladium uneven distribution, and poor recyclability.

In this context, we used tetrakis (triphenyl phosphine) palladium (Pd(PPh\(_3\))\(_4\)) as a precursor in a
simple solvothermal step and successfully obtained a MOFs structure with highly dispersed Pd, which has been investigated for application in high selective vanillin hydrodeoxygenation under super mild reaction conditions of room temperature and one atm of H₂. Specially, we used an as-prepared Pd@MOF catalyst in selectively hydrogenation or HDO of lignin-derived aldehyde and ketone compounds to obtain the corresponding chemicals by controlling the reaction conditions. In addition, the nitrobenzene derivatives can also achieve the reductive transformation to obtain the corresponding amines under mild reaction conditions (RT, 1 bar H₂). Notably, Pd@MOF is prepared by a one-step solvothermal method and wraps super small Pd particles, and the Pd particles are homogeneously distributed on the NH₂-MIL-125 (Ti) MOF support leading to the excellent catalytic efficiency.

2.1. Materials and instrumentation

Unless otherwise stated, all reagents for synthesis were purchased from commercial suppliers and used without further purification. Gas Chromatography (GC) data were obtained from a GC-2014C (Shimadzu, Japan) column with HP5 (30 m × 250 mm × 0.25 μm) and an FID detector. GC-MS of products was determined by TRACE 1300ISQ GC-MS (Thermo Fisher Scientific, America) with TG-5MS column (30 m × 250 mm × 0.25 μm). Powder X-ray diffraction (XRD) patterns are recorded by an X’Pert Pro system, using Cu-Kα radiation with a Δ2θ = 5° to 80° 2θ range. X-ray photoelectron spectroscopy (XPS) is recorded with an AXIS Ultra DLD (Kratos, Britain).

2.2. Catalyst preparation

**Synthesis of NH₂-MIL-125 (Ti):** Using a simple solvothermal reaction obtain NH₂-MIL-125 (Ti) MOF catalyst referring to our previously reported procedure. 2-aminoterephthalic acid (H₂ATA) (2.178 g, 12 mmol) and Ti(OC₄H₉)₄ (1 ml, 3 mmol) were dissolved in 18 ml of N, N-dimethylformamide (DMF) and 2 mL of MeOH to give a brown solution. Then it was transferred into a 50 mL of Teflon-lined autoclave and heated at 150 °C for 48 h before it was naturally cooled down to room temperature. The yellow precipitate was washed with MeOH and dried in a vacuum at 80 °C for 12 h.

**Synthesis of Pd@MOF:** The load of Pd in NH₂-MIL-125 was prepared by the same procedure as that for pure NH₂-MIL-125, except that 0.3 mmol Pd(PPh₃)₄ was added into the mixture during hydrothermal process. Triphenylphosphine was oxidized into triphenylphosphine oxide, which was mostly removed by filtration. The Pd loading of Pd-doped NH₂-MIL-125 (Ti) was measured to be 2.8 wt% based on ICP-AES testing.

**Synthesis of Pd-MOF:** Using a simple one-pot method obtain Pd-MOFS. Firstly, the Pd precursor was prepared through the generation of palladium nanoparticles from Pd(PPh₃)₄. Pd(PPh₃)₄ (347 mg, 0.3 mmol), tetra(ethylene glycol) (570 mg, 3 mmol), Ti(OC₄H₉)₄ (1 ml, 3 mmol), and 1-butanol (3 mL, 32.7 mmol) were added a 50 mL of Teflon-lined autoclave and stirred at 120 °C for 8 h to give a black suspension. Secondly, 2-aminoterephthalic acid (H₂ATA) (2.178 g, 12 mmol) was dissolved in 18 ml of N, N-dimethylformamide (DMF), and 2 mL of MeOH to give a brown solution. Then it was mixed
with Pd precursor and then heated at 150 °C for 48 h before it was naturally cooled down to room temperature. The green precipitate was washed with MeOH and dried in a vacuum at 80 °C for 12 h. Synthesis of immersed-Pd/MOF: In a typical impregnation and chemical reduction procedure,32 5.8 mg of Pd(acac)₂ was dissolved into 500 μl of MeOH with ultrasound and the solution was then added dropwise into 100 mg of NH₂-MIL-125 (Ti). The formed slurry catalyst was stirred overnight at room temperature, then filtered and dried at 100 °C for 2 h. Finally, the dried precursor catalyst was reduced by an aqueous NaBH₄ solution (2 mL, 0.05 M), and thoroughly washed with deionized water and MeOH. then vacuum drying Afterwards, the sample was put into a vacuum drying at 80 °C for 12 h.

2.3. Catalytic test

The catalytic reactions were performed by employing 10 mL Schlenk glass vessel tubes with an H₂ balloon (1 atm H₂). For hydrodeoxygenation of vanillin, 200 μmol (30.43 mg) of vanillin and 5 mg of catalyst were dispersed in 5 mL of ethanol in a vessel tube and the reaction was performed at room temperature with a stirring speed of 300 rpm. Over the course of the reaction, the conversion of reactant and the selectivity of product were analyzed by a gas chromatograph (GC, GC-2014C) with an HP5 column (30 m × 250 mm × 0.25 μm) and an FID detector. Besides, the products were further confirmed by GC-MS.

3. Result and discussion

3.1. Synthesis and characterizations of the Pd@MOF catalysts

Here we describe a one-step synthetic approach to construct NH₂-MIL-125 (Ti) MOF encapsulated with highly dispersed palladium particles (Pd@MOF). In a facile synthesis, take Pd(PPh₃)₄ as Pd sources, P-ligand could be oxidized to remove. And Pd-MOF was constructed by a one-pot solvent-thermal method through in situ formative MOF to encapsulate Pd particles.32 Immersed-Pd/MOF was synthesized by a simple impregnation method. Unlike yellow colored NH₂-MIL-125 (Ti) MOF, Pd@MOF, and Pd-MOF exhibit green but immersed-Pd/MOF exhibit gray color.

The low-angle powder XRD pattern of the prepared Pd@MOF (Figure 1b, black line) matches well with that of the pristine NH₂-MIL-125 reported by Li et al.33 After the incorporation of Pd particles, the structure of NH₂-MIL-125(Ti) is well preserved for the 2.8 wt% Pd@MOF catalyst (Figure 1b, red line). Additionally, no significant diffraction peak ascribed to Pd species is observed for the Pd@MOF and Pd-MOF catalyst from the wide-angle XRD pattern (Figure 1a). The Pd@MOF was characterized using X-ray Photoelectron Spectroscopy (XPS) technique, and the Pd₃d results are displayed in Figure 1b and Figure S1. All the measured data are corrected based on C1s (284.80 eV) peak. It can be seen from the XPS spectra of Pd@MOF that two peaks of the typical Pd₃d spectrum (Figure 1b) centered at 335.5 and 340.5 eV root in the Pd₃d5/2 and Pd₃d3/2 bands, respectively, which reveals Pd⁰ of Pd species. XPS spectra of Pd-MOF can see two-pair peaks in 335.5 eV, 340.5 eV, 337.6 eV, and 342.7 eV (Figure 1c), which reveals Pd⁰ and Pd¹⁺ of Pd species, which is due to
the partial oxidation of Pd nanoparticles. Interestingly, the XPS spectra of immersed-Pd/MOF (Figure S3b) also reveals mixed oxidation states (Pd$^0$ and Pd$^{II}$) for Pd species. XPS results indicated that encapsulated Pd particles could inhibit Pd oxidation. As they are clearly shown in Figures 2c and 2d, the TEM images demonstrate that the Pd species are too small and dispersed within the NH$_2$-MIL-125 (Ti). Compared with NH$_2$-MIL-125 (Ti), the appearance of Pd@MOF is not changed. EDS analyses also confirm that the Pd species are evenly dispersed within MOF as shown in Figure 3. Compared with Pd@MOF, the palladium nanoparticles aggregate and clump on the surface of immersed-Pd-MOF (Figure S2a), and Pd elemental mapping is also performed to confirm the uneven distribution of Pd species as shown in Figure S3. As to Pd-MOF, the TEM image results indicate that most Pd nanoparticles have not been immobilized on MOF but leaching as shown in Figure S5.

![Figure 1](image1.png)

**Figure 1.** (a) Power XRD patterns of NH$_2$-MIL-125 (Ti), Pd@MOF and Pd-MOF. (b) High Resolution Pd$_{3d}$ XPS spectrum of Pd@MOF. (c) High Resolution Pd$_{3d}$ XPS spectrum of Pd-MOF.
Figure 2. (a) and (b) TEM images of NH$_2$-MIL-125 (Ti); (c) and (d) TEM images of Pd@MOF.
3.2. Optimization of reaction conditions

Subsequently, we used p-Anisaldehyde (1a) as a model compound to explore the hydrogenation and hydrodeoxygenation reaction of biomass-derived compounds under one bar of hydrogen atmosphere. (Table 1). Using ethanol as the solvent, the control experiment indicated that the aldehyde could selectively be reduced hydrogenation or hydrodeoxygenation at room temperature in different time sections (Table 1, entry 1-2). Besides, the time-dependent transformation image also clearly shows that the aldehyde is first hydrogenated and reduced to the corresponding alcohol, and then is further hydrodeoxygenated to the corresponding product (Figure 4). These results demonstrated that Pd@MOF catalyzed aldehyde hydrodeoxygenation was a stepwise reaction as shown in Scheme 1. The precursor Pd(PPh₃)₄ for the preparation of Pd@MOF could not catalyze the reaction as well (Table 1, entry 5), even though there will be palladium black precipitation leading to the deterioration of Pd(PPh₃)₄ after the reaction. Additionally, the NH₂-MIL-125 (Ti) MOF could not promote the reaction (Table 1, entries 4), indicating that Pd and MOF frame play a synergistic role in catalytic reactions. Commercial Pd@C as a high activity catalyst could catalyze the HDO reaction as well (Table 1, entry 6), but the effect of selective hydrogenation was very poor (Figure 4). However, the
immersed-Pd/MOF catalysts synthesized by Pd salt impregnation and chemical reduction couldn’t significantly promote the reaction (Table 1, entries 3). Pd@MOF showed the best catalytic performance and the C=O group of p-anisaldehyde was effectively and selectively hydrodeoxygenated affording 4-methylanisole with a yield of up to 99% (Table 1, entry 2). In a contrast, the prepared Pd-MOF by the one-pot two-step method only transformed half of yield, revealing its low catalytic activity due to palladium leaching (Table 1, entry 7). The above results confirmed that the reducibility could be related to Pd particles distribution, the valence state of palladium, and the Pd particle size within the MOF framework. Using other common solvents such as CH₃CN, MeOH, and ethyl acetate instead of ethanol did poor affect the yields of the targeted product and the conversions dramatically decreased. (Table 1, entry 8-10). At last, catalysts and hydrogen are essential in hydrodeoxygenation reactions. (Table 1, entry 11 and 12) The above-mentioned experimental results clearly suggest that Pd@MOF can catalyze the reductive reaction of aldehyde efficiently because of the synergetic effect of the MOF skeleton and highly dispersed Pd particles. In summary, Pd in situ encapsulation during the self-assembly of MOF for avoiding the aggregation and oxidation of palladium, thereby improving the catalytic activity of the loaded metal. This phenomenon is also verified by the TEM and XPS characterization that the Pd species of Pd@MOF compared to immersed-Pd/MOF and Pd-MOF is well-distributed and stable.

**Table 1.** Hydrogenation or hydrodeoxygenation of 4-methoxybenzaldehyde under various conditions.a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Catalyst</th>
<th>t/h</th>
<th>Con.(%)</th>
<th>Yield (2a) (%)</th>
<th>Yield (3a) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EtOH</td>
<td>Pd@MOF</td>
<td>2.5</td>
<td>&gt;99</td>
<td>96</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>EtOH</td>
<td>Pd@MOF</td>
<td>12</td>
<td>&gt;99</td>
<td>0</td>
<td>&gt;99</td>
</tr>
<tr>
<td>3</td>
<td>EtOH</td>
<td>immersed-Pd/MOF</td>
<td>2.5</td>
<td>29</td>
<td>29</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>EtOH</td>
<td>NH₂-MIL-125 (Ti)</td>
<td>2.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>EtOH</td>
<td>(beta-4)-palladiu</td>
<td>2.5</td>
<td>32</td>
<td>32</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>EtOH</td>
<td>Commercial 5%Pd@C</td>
<td>2.5</td>
<td>&gt;99</td>
<td>0</td>
<td>&gt;99</td>
</tr>
<tr>
<td>7</td>
<td>EtOH</td>
<td>Pd-MOF</td>
<td>2.5</td>
<td>57</td>
<td>57</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>MeOH</td>
<td>Pd@MOF</td>
<td>2.5</td>
<td>79</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>9</td>
<td>EA</td>
<td>Pd@MOF</td>
<td>2.5</td>
<td>0</td>
<td>0</td>
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</tr>
<tr>
<td>10</td>
<td>CH₃CN</td>
<td>Pd@MOF</td>
<td>2.5</td>
<td>22</td>
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</tr>
<tr>
<td>11b</td>
<td>EtOH</td>
<td>Pd@MOF</td>
<td>2.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>EtOH</td>
<td>none</td>
<td>2.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
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</table>

a Standard reaction conditions: 5 mg of catalyst and 0.2 mmol of 1a in 4 mL of solvent under a balloon of H₂ at room temperature. Determined by GC-MS

b 1 balloon of Ar
3.3. Reaction study of Pd@MOF for vanillin and biomass-derived compounds hydrogenation/HDO

Under the optimized conditions, we further explored the substrate scope for the hydrogenation and HDO reaction over Pd@MOF. The C=O and -NO₂ bonds of aldehydes, ketones, and derivatives of nitrobenzene were selectively and effectively transformed, affording the corresponding aromatic hydrocarbons in excellent yields (Table 2 and Table 3). Firstly, lignin-derived aldehydes and ketones were selectively hydrogenated, affording corresponding alcohols in good yields (Table 2). For example, the hydrogenation reduction conversion of monosubstituted aldehydes, such as p-hydroxybenzaldehyde and p-anisaldehyde (Table 2, entry 1 and entry 2), afforded the corresponding alcohol products with excellent yields above 95%. As to substituted biomass aldehyde, vanillin transformed to vanillyl alcohol in moderate yields due to the excessive reduction of part of the product alcohol to p-methyl guaiacol (Table 2, entry 3). In addition, 3,5-dimethoxybenzaldehyde can be effectively converted into a hydrogenated product with excellent yields (95%) (Table 2, entry 4). Moreover, we have also tested several bio-based ketones that could be directly derived from lignin (Table 2, entries 5 and 6), and their corresponding products were generated in moderate yields. These results demonstrate our catalyst can be used in the hydrogenation of the lignin-derivatives.

Given the catalytic efficiency of Pd@MOF, we also examined the hydrodeoxygenation reaction scope on a diverse set of biomass derivatives (Table 3). The room-temperature HDO performances of Pd@MOF for lignin-derived aldehyde-, ketone-, and nitro-containing compounds, such as vanillin, p-anisaldehyde, 4′-methoxyacetophenone, and nitrobenzene were systematically investigated. For lignin-derived aldehydes, the substrates achieved complete transformation (>99%). Interestingly, the HDO efficiency and selectivity are only related to the reaction time. In the case of acetophenone derivatives, a relatively longer reaction time is required to completely convert to the desired HDO product (Table 3, entries 4 and 5). The catalytic performance of Pd@MOF for the HDO reaction of nitroarenes is perfect, its hydrodeoxygenated products, and aromatic amines have been widely used as chemical intermediates for pharmaceutical synthesis.²⁴,²⁵ The catalytic activity of Pd@MOF in nitroarenes hydrodeoxygenation was tested (Table 3, entry 6-8). For nitroarenes containing electron-withdrawing group and electron-donating group, such as -CH₃ and -F, above 99% conversion of aromatic amines can be obtained within 3 h (entries 6, 7, and 8 Table 3). Again, the superior catalytic activity of Pd@MOF is confirmed by remarkably high efficiency in the HDO reaction of various substrates (Table 3).
We have tested the lifetime of catalyst for its practical applications. Thus, the used Pd@MOF can be separated from the reaction solution easily by a simple centrifuge and deal with EtOH. The result showed that the p-anisaldehyde catalytic hydrogenation activity of Pd@MOF is almost maintained after 3 cycles (Figure 5). The yield decreased in the subsequent cycle experiment, which was probably due to the loss of catalysts during the recovery process. When we added 2 mg of catalyst, the yield reached the original level in the fourth and fifth runs. In this work, NH$_2$-MIL-125 (Ti) promotes the chemical stability and recyclability of the Pd species from the homogeneous Pd(PPh$_3$)$_4$, and also makes it more convenient to be easily recycled. Furthermore, the XRD patterns (Figure S4) of reused Pd@MOF were consistent with fresh catalyst, indicating its excellent recyclability.

**Figure 4.** Time-dependent transformation from p-anisaldehyde (1a) into (4-methoxyphenyl) methanol (2a) and 1-methoxy-4-methylbenzene (3a).
Table 2. Room-temperature hydrogenation of various substrates by Pd@MOF.\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Time (h)</th>
<th>Con.(^b)</th>
<th>Sel.(^b)</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td><img src="image1.png" alt="Substrate" /></td>
<td><img src="image2.png" alt="Product" /></td>
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<td>96%</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>2</td>
<td><img src="image3.png" alt="Substrate" /></td>
<td><img src="image4.png" alt="Product" /></td>
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<td>97%</td>
<td>98%</td>
</tr>
<tr>
<td>3</td>
<td><img src="image5.png" alt="Substrate" /></td>
<td><img src="image6.png" alt="Product" /></td>
<td>6</td>
<td>90%</td>
<td>86%</td>
</tr>
<tr>
<td>4</td>
<td><img src="image7.png" alt="Substrate" /></td>
<td><img src="image8.png" alt="Product" /></td>
<td>6</td>
<td>95%</td>
<td>&gt;99%</td>
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<tr>
<td>5</td>
<td><img src="image9.png" alt="Substrate" /></td>
<td><img src="image10.png" alt="Product" /></td>
<td>8</td>
<td>83%</td>
<td>94%</td>
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<td>6</td>
<td><img src="image11.png" alt="Substrate" /></td>
<td><img src="image12.png" alt="Product" /></td>
<td>8</td>
<td>56%</td>
<td>89%</td>
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</table>

\(^a\) Reaction conditions: 5 mg Pd@MOF + 0.2 mmol substrate in 4 mL EtOH under one balloon of H\(_2\) at room temperature (25 °C); \(^b\) Determined by GC-MS.
Table 3. Room-temperature selective hydrodeoxygenation of various substrates by Pd@MOF.a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Time (h)</th>
<th>Con. b</th>
<th>Sel. b</th>
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<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="Substrate 1" /></td>
<td><img src="image2" alt="Product 1" /></td>
<td>12</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>2</td>
<td><img src="image3" alt="Substrate 2" /></td>
<td><img src="image4" alt="Product 2" /></td>
<td>12</td>
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<td>&gt;99%</td>
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<td><img src="image5" alt="Substrate 3" /></td>
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<td><img src="image8" alt="Product 4" /></td>
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<td>8</td>
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<td><img src="image16" alt="Product 8" /></td>
<td>3</td>
<td>&gt;99 %</td>
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a: Reaction conditions: 5 mg Pd@MOF + 0.2 mmol substrate in 4 mL EtOH under one balloon of H₂ at room temperature (25 °C); b: Determined by GC-MS.
Conclusion
In summary, a super small Pd particle-loaded MOF was successfully fabricated by choosing Pd(PPh$_3$)$_4$ as the Pd precursor. The obtained Pd@MOF demonstrated dual-functional catalytic property for hydrogenation and HDO of biomass-derived carbonyl compound successfully during tuning reaction time. Additionally, our catalyst can also catalyze the reduction of nitrobenzene derivatives to the corresponding amines. We also prepared immersed-Pd/MOF and Pd-MOF by using different methods from the previous literature. By comparing the catalytic performance of Pd@MOF to both Pd-MOF and immersed-Pd/MOF, confirming the relationship between their reactivity and structure, the size and dispersibility of the Pd particles will directly affect the catalytic efficiency. Notably, Pd@MOF has the potential to upgrade biomass derivatives more than commercial Pd/C because it can tune the reaction time to obtain the corresponding chemicals.

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Author contributions
J. G. L. and L. L. M supervised and designed the research. X.Z.W wrote the original manuscript. J. G. L reviewed and corrected the manuscript. All authors discussed the results and assisted during...
Competing interests
The authors declare no competing financial interests.

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