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## Pd Nanoparticles Supported on MIL-101: An Efficient Recyclable Catalyst in Oxidation and Hydrogenation Reactions

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Pd nanoparticles supported on the chromium terephthalate metal organic framework MIL-101 (Pd/MIL-101) in different loadings (0.9 and 4.5 wt%) have been successfully prepared through a simple Pd-acetate adsorption and reduction in acetone, and tested as catalyst for selected liquid phase oxidation and hydrogenation reactions. The materials were characterized by XRD, N<sub>2</sub> adsorption–desorption isotherm, TEM, SEM-EDX and ICP analysis. The parent MIL-101 structure was found well preserved after formation of Pd nanoparticles and after catalytic reaction runs. The present catalyst afforded good activity and selectivity for the oxidation of benzyl alcohol to benzaldehyde with 85% conversion and 97% selectivity using air (1 atm) at 85 °C after 14 h. The catalyst also showed good activity in the hydrogenation of the C=C bond in alkenes to corresponding alkanes and also benzaldehyde to benzyl alcohol at room temperature using H<sub>2</sub> (1 atm). Rigorous test results confirmed that Pd-nanoparticles supported on MIL-101 are responsible for the catalytic reactions occurred. Pd/MIL-101 was reusable several times without losing the structural integrity and initial activity, and demonstrated significantly higher catalytic activities than those by a commercial Pd catalyst supported on activated carbon.

Keywords: Metal Organic Frameworks (MOFs), Pd/MIL-101, Oxidation, Hydrogenation.

## **1. INTRODUCTION**

The selective oxidation of alcohol to aldehyde, in particular, benzaldehyde from benzyl alcohol is one of the most versatile and important class of organic reactions for laboratory and industrial scale.<sup>1–4</sup> Much attention has been given for the development of ecologically acceptable catalytic systems using molecular oxygen or air as an oxidant, which only produces water as by-product.<sup>5–8</sup>

Recently, heterogeneous catalytic systems having noble metals (Pd, Au, Pt) were reviewed by Hutchings,<sup>9</sup> and among these noble metals, Pd-based catalysts have been more extensively investigated. Surveying on the literatures dealing with alcohol oxidation by Pd, it appears that the catalytic activity and selectivity can be controlled by the size of active phase and also by the nature of the support. Thus several strategies involving formation of Pd nanoparticles on hydroxyapatite,<sup>10</sup> carbon,<sup>11</sup> zeolite,<sup>12</sup> TUD-1 or SBA-16 mesoporous silica,<sup>13–15</sup> and carbon nanotube<sup>16</sup> were reported to afford high catalytic activity

in the oxidation of alcohols. Pd nanoparticles supported on alumina<sup>17</sup> also exhibited good catalytic activity for the aerobic oxidation of alcohols. Supported Pd catalysts are also known to be good for liquid phase hydrogenation reactions.<sup>18, 19</sup> Hydrogenation of unsaturated hydrocarbons or aldehyde is an important organic transformation for the preparation of fine chemicals. A group of scientist reported hydrogenation of 1-hexene over Pd/SiO<sub>2</sub> and Pd/MCM-41, and found that Pd/MCM-41 exhibited higher hydrogenation activity than Pd/SiO2.20 Pinna and co-workers described the hydrogenation of benzaldehyde to benzyl alcohol over various Pd supported catalysts over activated carbon, silica and alumina.<sup>21</sup> They found that Pd/C showed the highest activity for benzaldehyde hydrogenation.<sup>21</sup> Rode et al. reported the effect of the nature of the support and the size of Pd nanoparticles on the activity and selectivity of alkyne hydrogenation.<sup>22</sup> Supported Pd nanoparticles showed higher activity than that of the bulk Pd catalyst in the butyne hydrogenation.<sup>22</sup>

Metal-organic frameworks (MOFs), a new type of crystalline porous materials formed via coordinative bonding

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of metal ions or clusters with polyfunctional organic molecules to form an infinite one-, two- or threedimensional frameworks, have received much interest in recent years for potential applications in gas storage, separation, heterogeneous catalysis, and as a template for new materials.<sup>23–29</sup> In particular, the robust framework of the chromium terephthalate MOF, MIL-101 developed by Férey et al.<sup>30</sup> has shown very high gas storage capacity for  $CO_2$  and  $CH_4$ ,<sup>31</sup> and also were effective as a catalyst or catalyst support<sup>32–36</sup> due to its high surface area, large pore windows (12 Å and 16 Å × 14.5 Å), mesopores (29 Å and 34 Å), accessible coordinative unsaturated sites (CUS), and excellent chemical and solvent stability.<sup>37</sup>

Reports dealing with Pd nanoparticles on MOFs as catalytic species, however, are rather limited.<sup>36, 38-41</sup> Recently, Fischer and co-workers reported Pd-loaded catalysts on MOF-5<sup>42-44</sup> and MOF-177<sup>45</sup> via metal organic chemical vapor deposition (MOCVD) and subsequent decomposition/reduction by photo-assisted method. The sample was only weakly active in the hydrogenation of cyclooctene.<sup>43</sup> Kaskel et al. also prepared a Pd-loaded MOF-5 catalyst via the incipient wetness and subsequent reduction by hydrogen at 150–200 °C.<sup>38</sup> The prepared Pd-loaded catalysts were tested in hydrogenation reaction of styrene<sup>38</sup> and ethyl cinnamate.<sup>45</sup> However, the reported catalysts were not stable in air.<sup>43</sup> Clearly, stability and robustness of the MOF should be considered in selecting a support for catalytically active species.

Among the Pd-supported MOF catalysts, Pd/MIL-101had demonstrated high stability against thermal treatment, chemical agent and moisture for several reactions such as Heck coupling,<sup>36</sup> styrene hydrogenation,<sup>34</sup> Suzuki-Miyaura coupling,<sup>39</sup> and synthesis of methyl isobutyl ketone.<sup>40</sup> These findings prompted us to test the efficacy of Pdsupported MIL-101 catalyst for oxidation of alcohols using air at atmospheric pressure as an oxidant. For this purpose, we have successfully prepared a Pd-supported MIL-101 catalyst by a simple method of Pd-acetate adsorption and reduction/decomposition without using H<sub>2</sub>.

In this paper, we describe the one-step preparation of Pd nanoparticles on MIL-101 and report their catalytic activity in benzyl alcohol oxidation using air at atmospheric pressure. The catalyst was also tested for hydrogenation of several industrially important alkenes and aldehyde using  $H_2$  at atmospheric pressure. We also conducted a rigorous test on catalyst stability, and the catalytic activity of Pd/MIL-101 was compared with a commercially available Pd-supported catalyst on activated carbon.

## 2. EXPERIMENTAL DETAILS

### 2.1. Materials

Chromium (III) nitrate nonahydrate (99%, Sigma-Aldrich), 1,4-benzene dicarboxylic acid (99%, Sigma-Aldrich), hydrofluoric acid (Duksan, 48%), palladium (II) acetate (98%, Sigma-Aldrich), Pd-supported activated carbon

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(5 wt% Pd) (Aldrich), styrene (99%, Aldrich), cyclooctene (TCI), benzaldehyde (99%, Sigma-Aldrich) and benzyl alcohol (99%, Sigma-Aldrich) were obtained commercially and used without further purification.

## **2.2. Catalyst Preparation**

MIL-101 was hydrothermally prepared from chromium (III) nitrate nonahydrate, hydrofluoric acid and 1,4benzene dicarboxylic acid by the literature method.<sup>30</sup> Dried MIL-101 (0.01 g) was pre-treated in 2 cm<sup>3</sup> of acetone for 30 min.  $Pd(O_2CMe)_2$  (0.011 g) was then dissolved in 3 cm<sup>3</sup> of acetone and added to the above mixture with stirring. The resulting mixture was sealed tightly in a capped vial and heated at 45 °C for 24 h. The supernatant was colorless. The solid was filtered off, washed with acetone and treated with N,N-dimethylformamide (DMF, 5 cm<sup>3</sup>) at 100 °C for 12 h. The solid was filtered off, washed with DMF and dried under vacuum at 140 °C for 4 h. The metal loading achieved was 4.53 wt% determined by ICP analysis. The Pd sample with weight loading of 1.0% was also prepared by the same method. The Pd loading on the sample was 0.91 wt% based on ICP analysis. The samples are denoted as Pd,,/MIL-101 in this work, where n stands for the actual Pd wt% of the catalyst.

## ch2.3. Catalyst Characterization

X-ray powder diffraction patterns were recorded on a Rigaku diffractometer using CuK $\alpha$  ( $\lambda = 1.54$  Å) at 0.5 °/min. The BET surface areas were determined on a Micromeritics ASAP 2020 surface analyzer at -196 °C. Prior to the measurement, the samples were degassed at 150 °C under vacuum for 12 h. TEM micrographs were obtained on a JEOL JEM-2100F instrument and the samples were dispersed in ethanol in an ultrasonic bath, and a drop of supernatant suspension was placed onto a holey carbon coated grid and dried at 60 °C. SEM-EDX data were obtained on a Hitachi S-4200 instrument. Pd and Cr contents in MOF were measured using inductively coupled plasma spectrometry (ICP-OES, Optima 7300DV).

## 2.4. Catalytic Reaction

The oxidation reaction was carried out in a one-necked round bottom glass reactor equipped with a condenser. In a typical run, 1 mmol of benzyl alcohol, 3 cm<sup>3</sup> of *o*-xylene and 0.020 g of catalyst (4.53 wt% Pd) were heated at 85 °C under open air at atmospheric pressure. The hydrogenation reaction was carried out under atmospheric pressure of hydrogen at room temperature. The reaction vessel was refilled with hydrogen three times. In a typical run, 1 mmol of substrate, 2 cm<sup>3</sup> of methanol and 0.010 g of catalyst (4.53 wt% Pd) were stirred at room temperature, and hydrogen at atmospheric pressure was introduced to the reaction vessel. After completion of the reaction, the catalyst was filtered off and the conversion was measured using a GC (Acme 6000, Younglin, Korea) fitted with a high performance HP-5 capillary column and a FID.

A hot filtering experiment was carried out by separating the catalyst quickly from the reaction mixture after 8 h reaction time, and the filtrate was then maintained at 85 °C for an additional 6 h.

## 3. RESULTS AND DISCUSSION

## 3.1. Synthetic Aspect of Pd<sub>n</sub>/MIL-101

Earlier, Pd nanoparticles-supported catalysts on MIL-101 were usually prepared in a two-step process; for example, Pd impregnated into MOF from a Pd(NO<sub>3</sub>)<sub>2</sub> containing DMF solution at room temperature followed by reduction in H<sub>2</sub> at 200 °C.<sup>39</sup> An alternative synthetic procedure of introducing Pd nanoparticles onto MIL-101 in liquid phase was applied for the first time in this work. Dilute acetone solution of  $Pd(O_2CMe)_2$  was added into the MIL-101 and heated at 45 °C for 24 h, followed by treatment with DMF to produce an active Pd<sub>n</sub>/MIL-101. The experimental observation indicated that the reduction of Pd<sup>II</sup> to Pd<sup>0</sup> took place due to the presence of framework functionalities and acetone as reaction medium; we found that the color of  $Pd(O_2CMe)_2$  gradually disappeared in the presence of MOF and acetone. DMF was used just as a washing solvent. The resultant material was stable in air or in organic solvents at high temperature. Similar thermal reduction of Pd(O<sub>2</sub>CMe)<sub>2</sub> impregnated MOF-5 in vacuum was reported earlier but at substantially higher 150 to 200 °C.<sup>38</sup>

## 3.2. Characterization of Catalyst

MIL-101 before and after Pd deposition was characterized by XRD, N<sub>2</sub> adsorption-desorption isotherm, TEM, SEM-EDX and ICP-OES. XRD patterns of both MIL-101 and Pd<sub>n</sub>/MIL-101 (Fig. 1) show identical peaks at  $2\theta$  values of 4-15° to previously reported characteristic peaks of MIL-101, confirming that the structure of MIL-101 was maintained with high phase purity even after the postsynthetic Pd deposition process.<sup>36</sup> In addition, the XRD of Pd/MIL-101 having 4.53 wt% (Fig. 1(c)) exhibited a new weak broad peak at  $2\theta = 39.5^{\circ}$ , corresponding to Pd<sup>0</sup>. Similar observation was reported earlier for Pd<sup>0</sup>-containing mesoporous silica or carbon, which was interpreted as a consequence of small and relatively well-dispersed Pd nanoparticles formed.<sup>46</sup> Pd<sub>0.9</sub>/MIL-101, on the other hand, did not show any additional reflection of  $Pd^0$  (Fig. 1(c)) due to its low Pd concentration.<sup>38</sup>

 $N_2$  adsorption–desorption isotherms at 77 K for fresh MIL-101 and Pd/MIL-101 are shown in Figure 2. The isotherms of both samples show a type I pattern. The characteristic two-step adsorption–desorption isotherm of MIL-101 in relative pressure range of  $0.1 < P/P_0 < 0.3$  is due to the two-types of microporous windows (12 Å, and 16 Å × 14.5 Å) connected to mesoporous cages of 29 Å and 34 Å.<sup>37</sup> The textural property values of Pd/MIL-101 (2400 m<sup>2</sup>/g of BET surface area and 0.66 cm<sup>3</sup>/g of



Figure 1. X-ray powder diffraction patterns of (a) MIL-101, (b)  $Pd_{0.9}/MIL$ -101 and (c)  $Pd_{4.5}/MIL$ -101.

total pore volume) were lower than those of fresh MIL-101 (3100 m<sup>2</sup>/g of BET surface area and 1.88 cm<sup>3</sup>/g of total pore volume). The average pore size of Pd/MIL-101 (17 Å) also became narrower than that of MIL-101 (21 Å), due to incorporated Pd nanoparticles as shown in the inset of Figure 2.

The TEM images of Pd/MIL-101 before the catalytic reaction are shown in Figure 3. The images show that Pd particles are well dispersed over the MOF surface in a nanometer size range of 2–10 nm, and the size distribution remained almost constant after the catalytic reaction runs. Pd particles tended to appear along the edges of the MOF crystallites with near spherical morphology. The sizes of Pd nanoparticles shown in Figures 3(a) and (c) are uniform (ca. 10 nm) and larger than the pore diameter of MIL-101, which indicates that Pd particles are formed on the external surface of MIL-101. However, closer inspection of



**Figure 2.**  $N_2$  adsorption-desorption isotherms of (a) MIL-101 and (b)  $Pd_{4.5}$ /MIL-101: adsorption (filled) and desorption (blank). The inset shows the BJH pore-size distribution curves of (a) MIL-101 and (b)  $Pd_{4.5}$ /MIL-101.

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**Figure 3.** Transmission electron micrographs of ((a), (b)) fresh  $Pd_{4,5}/MIL-101$ , ((c), (d)) reused  $Pd_{4,5}/MIL-101$  catalyst after fifth run and (e) fresh  $Pd_{0,9}/MIL-101$ .

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Figures 3(b) and (d) also show smaller uniform Pd nanoparticles (ca. 2 nm) that can be accommodated inside the pore system. TEM images thus indicate that the metallic Pd particles of dual size distribution are formed during the synthesis, while maintaining the host crystalline structure of MIL-101. Decrease of Pd loading in Pd<sub>0.9</sub>/MIL-101 resulted in a similar size distribution. H<sub>2</sub> reduction of Pd(O<sub>2</sub>CMe)<sub>2</sub> on MIL-101, on the other hand, was reported to produce smaller Pd particles of ca. 1.5 nm.<sup>34</sup> We determined the metal loading values of the supported catalysts by SEM-EDX (Fig. 4) and ICP analysis. The values of Cr/Pd ratio observed from SEM-EDX (Table I) and the bulk ICP were in agreement and 5.33 and 5.70, respectively.

# 3.3. Catalytic Performances Over the Pd/MIL-101 Catalyst

To test the catalytic performance of Pd/MIL-101 catalyst in alcohol oxidation, we carried out the oxidation of benzyl alcohol using open air at atmospheric pressure. The results are summarized in Table II. Blank test reactions were carried out under the same reaction conditions in the presence of parent MIL-101 and in the absence of Pd/MIL-101. No reaction products were occurred in both cases, indicating that the presence of active metal supported on MIL-101 is essential for the oxidation reaction. As expected, benzyl alcohol conversion increased with time, and Figure 5 shows the conversion values of benzyl alcohol at different reaction time. At 85 °C, benzyl

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Figure 4. SEM-EDX of fresh Pd<sub>4.5</sub>/MIL-101.

Table I. SEM-EDX analysis of fresh Pd<sub>4.5</sub>/MIL-101.

Element	Weight%	Atomic%
СК	25.69	38.54
O K	47.48	53.48
Cr K	19.39	6.72
Pd Logy to: York	CUniversity <sub>7.44</sub>	1.26
Totals Aug 2014	13:07:35 <sub>100.00</sub>	

alcohol was converted to benzaldehyde with 85% conversion and 97% selectivity after 14 h reaction. Aerobic benzyl alcohol oxidation over Pd catalysts can be explained by the dehydrogenation mechanism; the oxidation of the alcohol by dehydrogenation, which results in the formation of the aldehyde and adsorbed hydrogen on the Pd surface,



**Figure 5.** Benzyl alcohol oxidation using air (1 atm) at 85 °C, catalyst amount 20 mg in *o*-xylene: ( $\blacksquare$ ) with Pd<sub>4.5</sub>/MIL-101 catalyst and ( $\Box$ ) filtrate (catalyst filtering off after 8 h reaction).

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Table II.	Summary of th	e catalytic	oxidation/hydrogena	tion activity of
Pd-support	ed catalysts.			

Reaction run	Catalysts	Substrate	Time (min)	Conv. (%)	Select. (%)
1	Pd4.5/MIL-101	Benzyl alcohol <sup>a</sup>	840	84.8	97.1 <sup>b</sup>
2				84.7	97.1
5				84.7	97.0
1	Pd <sub>5.0</sub> /C	Benzyl alcohol <sup>a</sup>	840	50.3	96.7
1	Pd <sub>4.5</sub> /MIL-101	Styrene <sup>c</sup>	60	100.0	$100.0^{d}$
2				100.0	100.0
5				100.0	100.0
1	Pd <sub>0.9</sub> /MIL-101	Styrene <sup>c</sup>	135	100.0	100.0
1	Pd <sub>5.0</sub> /C	Styrene <sup>c</sup>	120	100.0	100.0
1	Pd4.5/MIL-101	Cyclooctene <sup>c</sup>	240	100.0	$100.0^{e}$
5		-		100.0	100.0
1	Pd <sub>4.5</sub> /MIL-101	Benzaldehyde <sup>c</sup>	600	84.5	96.0 <sup>f</sup>
5				84.5	96.0

*Notes*: <sup>*a*</sup>Reaction conditions: 1 mmol substrate, 0.020 g catalyst, 3 cm<sup>3</sup> *o*-xylene, open air (1 atm) and 85 °C; <sup>*b*</sup>Benzaldehyde; <sup>c</sup>Reaction conditions: 1 mmol substrate, 0.010 g catalyst, 2 cm<sup>3</sup> methanol, H<sub>2</sub> (1 atm) and 25 °C; <sup>*d*</sup>Ethyl benzene; <sup>*e*</sup>Cyclooctane; <sup>*f*</sup>Benzyl alcohol.

followed by hydrogen removal from the Pd surface by oxidation with oxygen.<sup>47</sup>

The reaction was also carried out using a commercially available Pd-supported activated carbon (5 wt% Pd), Pd<sub>5.0</sub>/C, under the identical reaction condition as applied for Pd/MIL-101. The results are listed in Table II. Pd<sub>4.5</sub>/ MIL-101 catalyst showed higher activity than Pd<sub>5.0</sub>/C. The origin of the high activity in Pd<sub>4.5</sub>/MIL-101 is not clear at this stage, but may be associated with the uniformly dispersed Pd particles in MIL-101,<sup>48</sup> and also significantly larger pores and pore volume of the support material MIL-101 than in activated carbon, which can contribute towards reducing the mass transfer resistance of reactant/product to the smaller Pd particles located inside the pores.

A series of experiments were also performed for the hydrogenation of alkenes and aldehyde over both Pd<sub>0.9</sub>/ MIL-101 and Pd<sub>45</sub>/MIL-101 catalysts using 1 atm H<sub>2</sub> in methanol at room temperature. The results are also listed in Table II. Blank test reactions were carried out under the same reaction conditions in the presence of parent MIL-101 and in the absence of Pd/MIL-101. No reaction products were occurred in both cases. Figure 6 shows the conversion values of styrene at different reaction time over  $Pd_{4.5}$ / MIL-101. The conversion of styrene gradually increased with time and reached 100% conversion after 60 min. The reaction was then carried out over Pd<sub>0.0</sub>/MIL-101 under the identical conditions. At 100% conversion, styrene was converted to ethyl benzene within 135 min (Table II). These results indicate that the availability of active Pd sites controls the catalytic reaction, which is fundamentally heterogeneous in nature. We then tested the catalytic activity of Pd<sub>4.5</sub>/MIL-101 in the hydrogenation of a model cyclic alkene, cyclooctene. At 25 °C, cyclooctene converted to



**Figure 6.** Conversion profiles for the hydrogenation of styrene: ( $\blacksquare$ ) fresh Pd<sub>4.5</sub>/MIL-101 and ( $\Box$ ) filtered Pd<sub>4.5</sub>/MIL-101 after 20 min reaction time.

cyclooctane with 100% conversion after 220 min under the identical reaction conditions (Table II). The results indicated that the external C=C bond in styrene hydrogenation over Pd<sub>4.5</sub>/MIL-101 catalyst proceeded much faster than in cyclooctene. Alkene conversions with H<sub>2</sub> over Pd catalysts has been extensively studied and generally described by the Horiuti-Polanyi mechanism, which proceeds through a series of successive hydrogenationdehydrogenation steps.<sup>49</sup>5

<sup>CIC</sup>The heterogeneity and reusability of  $Pd_{4.5}/MIL-101$  catalyst in oxidation and hydrogenation reactions were investigated by performing repeated reaction cycles and hot filtering experiments, respectively. In the recycling test, the catalyst was recovered by filtration at the end of each reaction cycle, and washed with solvent, dried, and reused. The results are also included in Table II. The conversion and selectivity were virtually identical, irrespective of the number of reaction cycles performed. No leached Pd was detected in the filtrate by ICP measurements.

The morphology of the reused catalyst in the benzyl alcohol oxidation was also examined by TEM (Figs. 3(c) and (d)). The original near spherical Pd nanoparticles were retained nearly the same as that of the fresh catalyst with good crystalline MIL-101 structure after fifth run. Pd and other nanoparticles supported on MOFs can be classified as three kinds:

(1) those formed inside the pores,

(2) those deposited preferentially on the external surface, and

(3) both formed inside and on the external surface.<sup>41</sup>

Al-Shall et al. also reported 2–6 nm-sized Pd nanoparticles deposited on the external surface of MIL-101 similar to this work.<sup>50</sup> Hydrothermally stable MIL-101 with high surface area offers preferential nucleation sites over the coordinative open metal sites, and also expected to bind the nanoparticles strongly. Particles of ca. 10 nm on MIL-101

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would be expected to have little possibility of leaching considering their lower radius of curvature than those among the smaller Pd nanoparticles. Further confirmation on the heterogeneous nature of Pd/MIL-101 was provided by hot filtering experiments. The catalyst was filtered-off (after 8 h of reaction and conversion reached 49.5% for benzyl alcohol (Fig. 4), and after 20 min of reaction and conversion reached 55.6% for styrene (Fig. 5)) and the filtrates were then stirred for an additional duration. No further reaction product was observed after catalyst separation. These results indicated that catalysis reactions occurred on the Pd nanoparticles supported on MIL-101 and Pd/MIL-101 is behaved truly as a heterogeneous catalyst.

## 4. CONCLUSIONS

Pd nanoparticles supported on the chromium terephthalate metal-organic framework MIL-101 were prepared via a simple Pd-acetate adsorption-reduction procedure. The structure of the hosting MIL-101 was unchanged after post-synthetic Pd introduction or after catalytic runs. The Pd<sub>4.5</sub>/MIL-101 catalyst showed high activity and found to be a true heterogeneous catalyst for oxidation of alcohols using open air at atmospheric pressure, which also produced good activity for the hydrogenation of alkenes and aldehyde. The present Pd-supported MOF catalyst exhibited higher activity than Pd supported on activated carbon. The catalyst could be separated quantitatively by simple filtration and reused several times without losing the initial high catalytic activity.

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