Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Palladium nanoparticles supported on sulfonic acid functionalized metal-organic framework as catalysts for biomass cascade reactions

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1. General information

1.1 **Chemicals and Materials.** Palladium (II) acetylacetonate ($Pd(acac)_2$)was purchased from Kunming institute of precious metals. N,N-dimethylformamide (DMF, 99.5%), methanol (99.5%), ethanol (99.7%), propanol (99%),hydrofluoric acid (HF, 37wt%), and hydrogen chloride (HCl > 99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Monosodium 2-sulfoterephthalic acid (98%), and terephthalic acid (98%) were purchased from Tokyo Chemical Industry. Chromium (III) nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$, 99%), 2-furoic acid (FA, 98%), 2-tetrahydrofuroic acid (98%), and ethyl 2-furoate (98%) were purchased from J&K Chemicals. All reagents were used without further purification.

1.2 **Characterization of samples.** The morphology of the products was observed by scanning electron microscope (SEM, Hitachi S4800) and transmission electron microscope (TEM, JEOL 2100F) with an accelerating voltage of 200 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray (EDX) spectroscopy were performed with an FEI TECNAI F30 microscope operated at 300 kV. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max X-ray diffractometer (Cu Kα radiation, 0.15418 nm). The actual amounts of Pd were determined by inductively coupled plasma mass spectrometry (ICP-MS, ICP-MS7700x). Fourier transform infrared (FT-IR) spectra were measured using by Nicolet 380.Thermogravimetric (TG) and differential Thermal Analysis (DTA) analyses were conducted on SDT Q600**.** IR spectra of pyridine adsorbed was measured by Thermo Fisher Nicolet 6700.

1.3 **Catalytic performance evaluation of samples.** The catalysts (5 mg) were ultrasonically dispersed in 5 mL of ethanol (propanol, or n-butyl alcohol), and the resulting solution was transferred to a pressure autoclave. 1.8 mmol of the substrate (FA) was added to the above solution. The autoclave was flushed with flowing H_2 for several times to remove the oxygen in the air and then pressurized to 1 MPa. After reaction at 100 °C for 6 h under stirring, the solution was analyzed by gas chromatography coupled with mass spectrometry (GC-MS, QP2010 Plus).

2. Synthesis methods

2.1 **Synthesis of MIl-101.**The MIL-101 was synthesized according to the previously reported procedure with some modifications.[1] In a typical process, 800 mg (2.0 mmol) $Cr(NO_3)_3 \cdot 9H_2O$, 332 mg (2.0 mmol) terephthalic acid were dissolved in 25mL deionized water and 0.4 mL HF aqueous solution. The solution was homogenized by sonication, transferred into a Teflon-lined stainless steel autoclave, and kept in oven at 200 °C for 8 h. The solid product was centrifuged and washed three times with deionized water. The obtained green powder was purified in 100 mL alcohol aqueous at 100 °C for 24 h to remove residual ligand. And the product was finally dried at 110 °C overnight under vacuum for the further use.

2.2 **Synthesis of MIl-101-SO_3H.** The one-pot synthesis of the sulfonic acid-functionalized MIL-101 was based on the reported method.[2] Typically, monosodium 2-sulfoterephthalic acid (5.4 g, 0.02 mol), and $Cr(NO_3)_3 \cdot 9H_2O$ (4.002 g,0.02 mol) were dissolved in 60 mL deionized water. The solution was homogenized by sonication and 0.52 mL HF aqueous solution (37 wt%) was added. The solution was transferred into a Teflon-lined stainless steel autoclave and kept in oven at 190 °C for 48 h. After reaction, the obtained green powder was washed with water and methanol three times. The solid product was purified in 100 mL alcohol aqueous at 100 °C for 24 h to remove residual ligand. Finally the product was dried at 110 °C overnight under vacuum prior to the further use. To acidize the resultant solid and exchange out the Na^+, the product was treated in a mixed solution of diluted HCl (0.08 M) in 50 mL methanol and 100 mL water according to the reported procedure. The product after acidification was washed with alcohol aqueous solution and finally dried at 110 °C overnight under vacuum before use.

2.3 **Synthesis of Pd/MIl-101-SO_3H.** According to the thermal decomposition characteristics of palladium acetylacetonate, the MIL-101-SO_3H was activated at

110 °C overnight under vacuum. 100 mg MIL-101-SO_3H and different amounts of ($Pd(acac)_2$) (e.g., 40, 60, and 120 mg)were added in 30mL alcohol aqueous solution. After stirred for 10h at room temperature, the product was collected by centrifugation and dried at 60°C under vacuum. Finally, the solid powder was heated in muffle furnace at 200 °C for 90 minutes. The Pd content in the composites were determined to be 5.2, 8.5, and 19.7 wt %, respectively.

3. Supplementary Results

Table S1. Catalytic results of the cascade reactions with different catalysts under 1MPa H_2 at 100 ℃.

Catalyst	Conversion%	Sel. EF%	Sel. TFA%	Sel. ETF%
blank	trace			
MIL-101	0.17	>99.9		
MIL-101-SO_3H	9.6	>99.9		
Pd/MIL-101-SO_3H	100		0.8	99.2
Pd/MIL-101	100		35.2	64.8
Pd/C	100		64	36
Pd black+MIL-101-SO_3H	16.1		13.6	86.4
MIL-101-SO_3H@Pd/MIL-101-SO_3H	90.59		59.4	40.6

Table S2. Catalytic results of the cascade reactions with different alcohols.

Substrate	Alcohol	Conversion%	Sel. %
FA	methanol	100	99.2
FA	n-propanol	100	99.5
FA	butanol	100	98.5

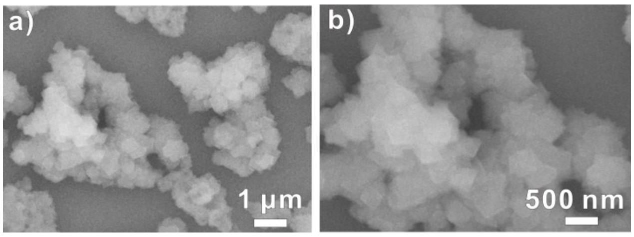


Fig. S1 SEM images of MIL-101-SO_3H matrices.

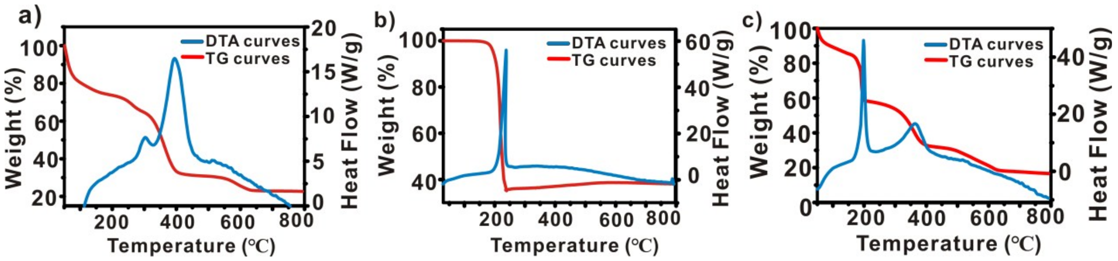
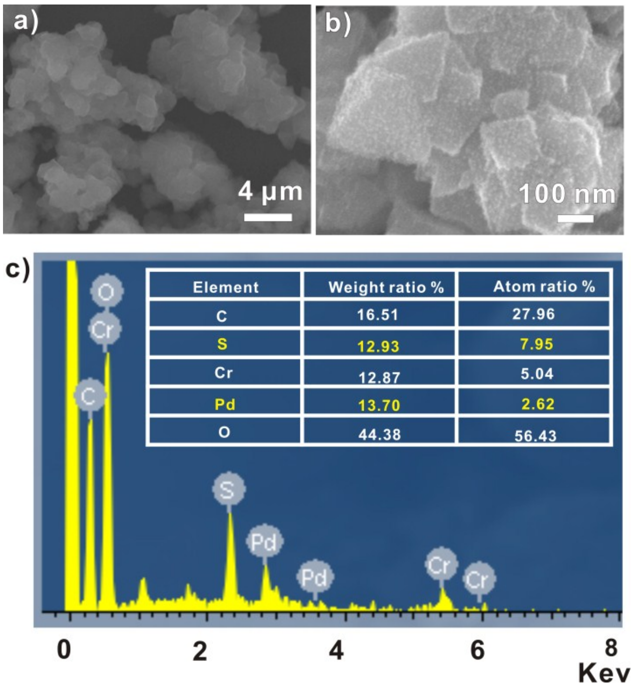


Fig. S2 TG and DTA curves of (a) MIL-101-SO_3H, (b) Pd(acac)$_2$, and (c) MIL-101-SO_3H loading with Pd(acac)$_2$.

TG analysis of Pd(acac)$_2$ revealed that the decomposition of Pd(acac)$_2$ began at 175 °C and finished at 240 °C. And the TG curve of MIL-101-SO_3H particles embedded with Pd(acac)$_2$ was similar with that of the blank MIL-101-SO_3H particles. However, the DTA analysis indicated that an exothermic reaction occurred at 200 °C, which should be corresponding to the decomposition of Pd(acac)$_2$. Therefore, the synthetic process of Pd/MIL-101-SO_3H via thermal decomposition of palladium precursors in MIL-101-SO_3H was conducted at 200 °C.



Element	Weight ratio %	Atom ratio %
C	16.51	27.96
S	12.93	7.95
Cr	12.87	5.04
Pd	13.70	2.62
O	44.38	56.43

Fig. S3 (a, b) SEM images and (c) EDX spectrum of as-prepared Pd/MIL-101-SO_3H composites.

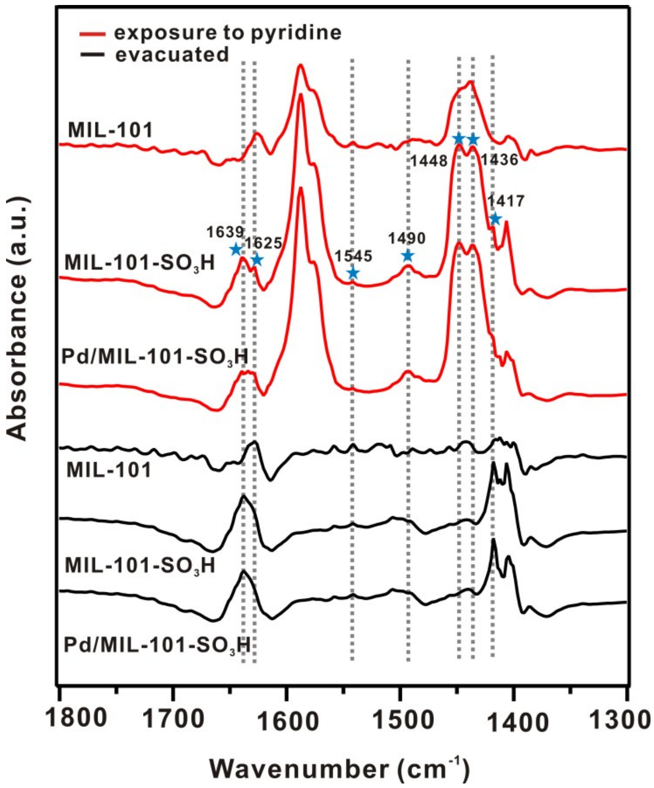


Fig. S4 IR spectra of pyridine adsorbed on MIL-101, MIL-101-SO$_3$H and Pd/MIL-101-SO$_3$H.

The exposure of MIL-101 to pyridine appeared some peaks at 1625 and 1448 cm^{-1}, which are mainly attributed to pyridine molecules coordinated with Lewis acid sites (LPy).[3] Compared with MIL-101, MIL-101-SO$_3$ showed additional peaks at 1639, 1490 and 1417 cm^{-1}. Among them 1639 cm^{-1} is attributed to the pyridinium ions ($C_5H_5NH^-$, BPy) formed on Brønsted acid sites, 1490 cm^{-1} is attributed to both BPy and LPy and the peak at 1417 cm^{-1} contributed to ν(S=O).[4] Of note, many peaks disappeared after evacuating at room temperature. MIL-101 only exhibited a peak at 1625 cm^{-1} (LPy). In contrast, MIL-101-SO$_3$ showed significantly higher characteristic peaks of adsorbed pyridine after evacuating, indicating the stronger adsorption with pyridine. And different from MIL-101, MIL-101-SO$_3$ showed an obviously broaden peak at 1639 cm^{-1} (BPy). Pyridine-absorbed IR of Pd/ MIL-101-SO$_3$ was basically the same as that of MIL-101-SO$_3$. In summary, pyridine-absorbed IR indicated both of Pd/ MIL-101-SO$_3$ and MIL-101-SO$_3$ have Brønsted acid sites and Lewis acid sites, while MIL-101 has only Lewis acid sites.

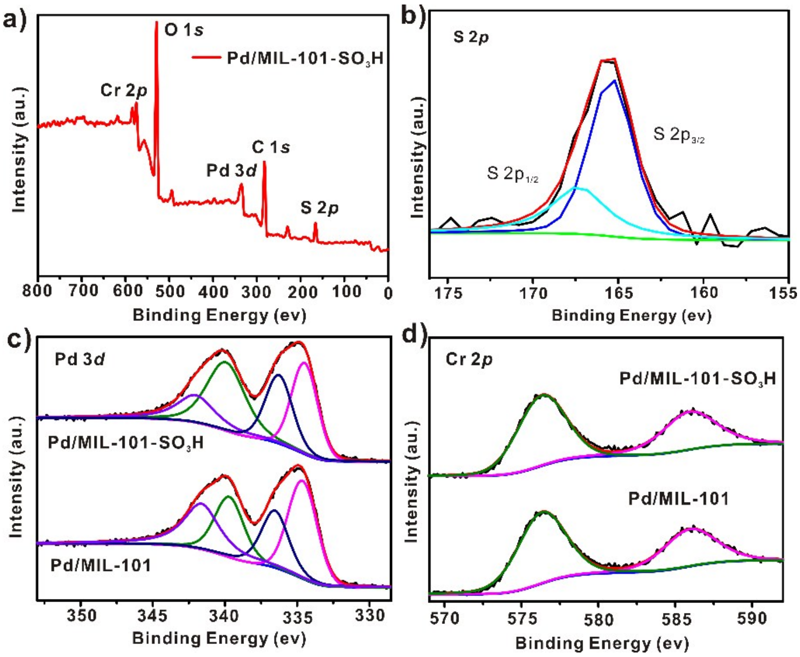


Fig. S5 (a) XPS survey spectrum of Pd/MIL-101-SO$_3$H. High resolution XPS spectra of Pd/MIL-101-SO$_3$H: (b) S 2p, (c) Pd 3d, and (d) Cr 2p.

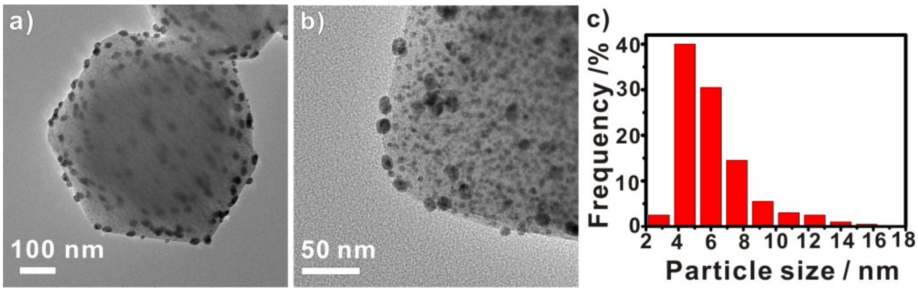


Fig. S6 (a) Low magnification and (b) high magnification TEM images of Pd/MIL-101, (c) Histogram of particle size distribution of Pd NPs supported on the MIL-101.

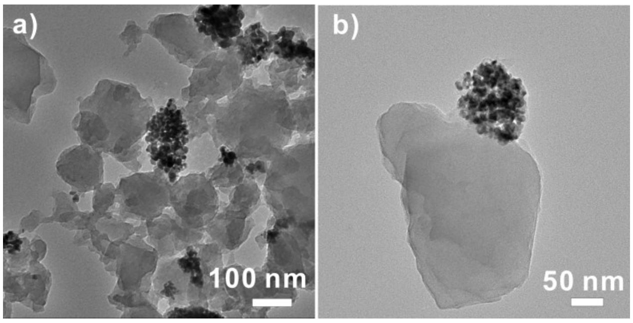


Fig. S7 TEM images of physically mixed catalysts of commercial Pd black and MIL-101-SO$_3$H.

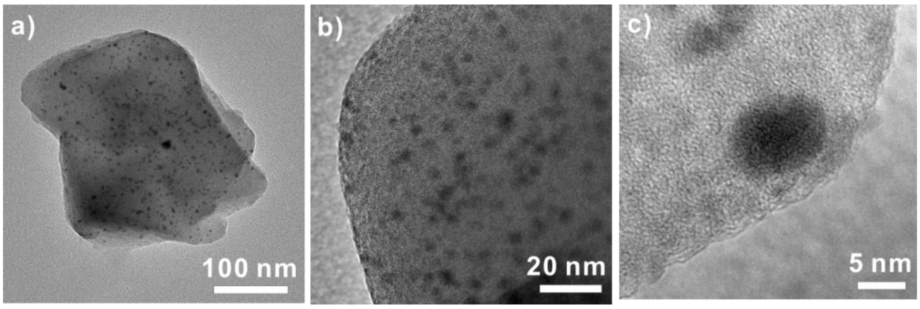


Fig. S8 TEM images of MIL-101-SO_3H@MIL-101-SO_3H/Pd

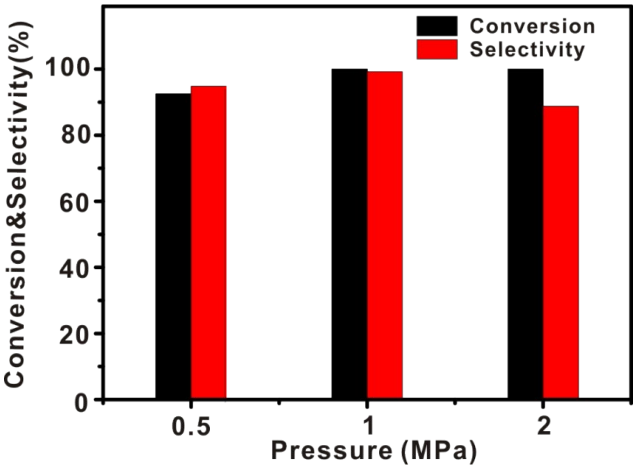


Fig. S9 Catalytic results of cascade reactions under different H_2 pressures.

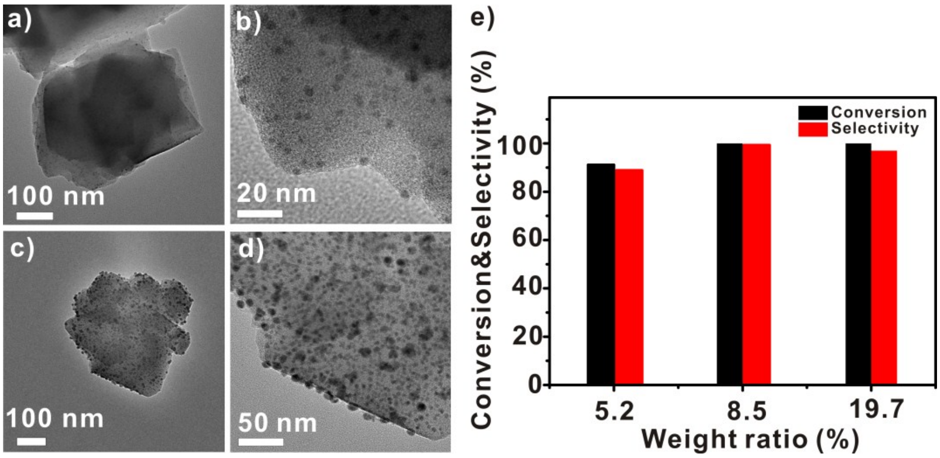


Fig. S10 TEM images of Pd/MIL-101-SO_3H with different contents: (a, b) 5.2 wt %. (c, d) 19.7 wt %. (e) Catalytic results of cascade reactions over the catalysts Pd/MIL-101-SO_3H with different Pd contents.

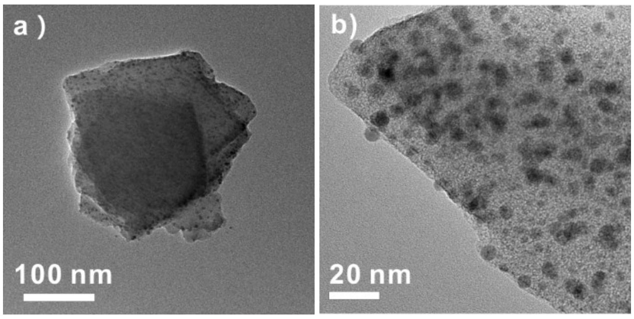


Fig. S11 TEM images of Pd/MIL-101-SO$_3$H after reaction.

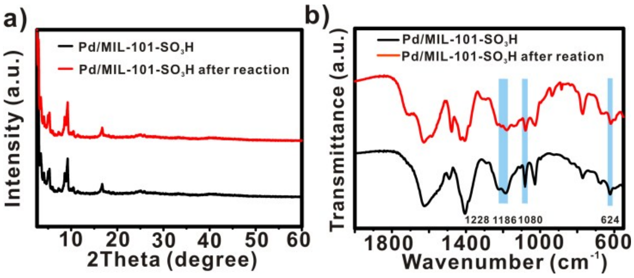


Fig. S12 (a) XRD patterns and (b) FT-IR spectra of Pd/MIL-101-SO$_3$H before and after reaction.

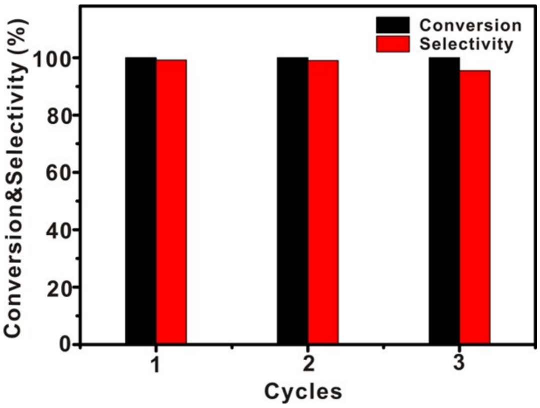


Fig. S13 Recycling test of Pd/MIL-101-SO$_3$H catalyst. Reaction condition: 1.8 mmol 2-furoic acid, 5 mL alcohol, stirred reaction for 6 hours in 1 MPa H$_2$ atmosphere at 100 °C.

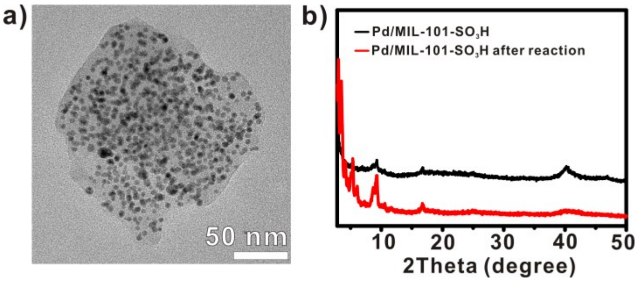


Fig. S14 (a) TEM image and (b) XRD pattern of Pd/MIL-101-SO$_3$H after the three cycling catalytic reaction.

References

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2. G. Chang, M. Huang, Y. Su, H. Xing, B. Su, Z. Zhang, Q. Yang, Y. Yang, Q. Ren, Z. Bao and B. Chen, *Chem Commun.*, 2015, **51**, 2859-2862.
3. M. J. Kim, S. M. Park, S. J. Song, J. Won, J. Y. Lee, M. Yoon, K. Kim and G. Seo, *J Colloid Interface Sci*, 2011, **361**, 612-617.
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