Supplementary Information (SI) for Chemical Science.
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Creating Hydrophobic Nanopockets in Metal–Organic Frameworks to Promote Lignin Derivatives Hydrodeoxygenation at Ambient Condition

Yan Liang, Hongru Zhou, Yuanxia Zhao, Xiaoyu Liang, Zhiwei Chen, Min Ji and Min Wang**
State Key Laboratory of Fine Chemicals, School of Chemistry, Dalian University of Technology
Dalian 116024, Liaoning, China
E-mail: wangmin@dlut.edu.cn, jimin@dlut.edu.cn

Keywords: Metal–Organic Frameworks • Nanoconfinement • Enzymes • Hydrodeoxygenation

Contents

Section S1. Materials and methods

Section S2. Characterization

Section S3. Supplementary Figures

Section S1. Materials and methods

S1-1: Chemicals

All the raw chemicals are obtained commercially and used without additional purification. 2-Methyl-1,4-benzenedicarboxylic acid (Sigma-Aldrich, 99%), 2-Aminoterephthalic acid (Sigma-Aldrich, 99%), 1,4-Dicarboxybenzene (Sigma-Aldrich, 99%), Zirconium tetrachloride ($ZrCl_4$, Macklin, 99.5%), Acetic acid (AR, Kemiou Chemical), Methanol (Kemiou Chemical, 98%), Ethanol (Kemiou Chemical, 98%), N, N-Dimethylformamide (DMF, Damao Chemical), Sodium tetrachloropalladate (Aladdin), n-Decane (Macklin), Hexane (AR, Kemiou Chemical), Benzyl alcohol (Damao Chemical), 3-Methoxybenzyl alcohol (bidepharm, 98%), 4-Methoxybenzyl alcohol (Macklin, 98%), 2-Methylbenzyl alcohol (Energy Chemical, 98%), 3-Methylbenzyl alcohol (Energy Chemical, 98%), 4-Methylbenzyl alcohol (Energy Chemical, 98%), 3-Hydroxy-4-methoxybenzyl alcohol (Macklin, 98%), 4-Hydroxy-3-methoxybenzyl alcohol (Macklin, 98%), Benzaldehyde (Energy Chemical, 98%), 4-Hydroxybenzaldehyde (Energy Chemical, 98%), 3-Methylbenzaldehyde (Aladdin, ≥97%), p-Methyl benzaldehyde (Macklin, 97%), 4-Ethylbenzaldehyde (Macklin, 98%), p-Anisaldehyde (Macklin, 99%), Vanillin (Macklin, 99%), O-Vanillin (Macklin, 99%), 2,2,6,6-Tetramethyl-piperidine 1-oxide (TEMPO), Acetonitrile (Damao Chemical).

S1-2: Synthesis of UIO-66-X (-CH_3, -H and -NH_2)

A typical synthesis of UiO-66-CH_3 was obtained by dissolving $ZrCl_4$ (0.053 g, 0.227 mmol), 2-methylterephthalic acid (BDC-CH_3) (0.041g, 0.227 mmol), and 1.2 mL of acetic acid in DMF (10 mL) at room temperature. The obtained mixture was sealed in 50 mL Teflon-lined stainless autoclave and heated in a 120 °C oven for 24 h. After cooling to room temperature, the resulting powder was separated by centrifugation and washed several times with separate aliquots of methanol and DMF. The solvent was removed under vacuum at 150 °C for 12 h. The UiO-66-H and UiO-66-H was synthesized in the same way as above, except that the ligands were replaced by 1,4-dicarboxybenzene (BDC-H) and 2-Amino-1,4-benzenedicarboxylic acid (BDC-NH_2), respectively.

S1-3: Synthesis of Pd@UIO-66-X

50 mg of UIO-66-X powder was activated by heating at 150 °C for 3 h. Then, the powder was suspended in dry n-hexane (10 mL) and 256 µL of $PdCl_2$/HCl solution (56.82 mM) was added dropwise into the MOFs under vigorous stirring. After careful filtration, the powder was washed by water and ethanol for several times and dried in air at room temperature. These

synthesized samples were further dried at 80 °C for 12 h, followed by treating under a 20 mL/min flow of 20% H_2/Ar at 200 °C for 1 hour to obtain Pd@UIO-66-X.

S1-4: General procedure for the hydrodeoxygenation of benzyl alcohol reaction

The catalytic conversion of benzyl alcohol was performed in homemade reactors. Typically, 5 mg of catalyst was added into 1 mL substrate/ethanol solution (10 mM) in a 6.5 mL of quartz tube reactor, then the system was completely replaced with H_2 before sealed with a cap. The quartz tube was then placed in a thermostatic water bath and the reaction temperature was maintained at 25 °C. After the reaction, the suspension was centrifuged and the aliquots were analyzed by gas chromatography-mass spectrometry (GC-MS) using an Agilent 7890A/5975C instrument equipped with an HP-5 MS column (30 m in length, 0.25 mm in diameter), and quantified by gas chromatography using an Agilent 8860 instrument equipped with an HP-5 MS column (30 m in length, 0.25 mm in diameter) and FID detector.

S1-5: Quantitative analysis

The liquid products were quantified based on an internal standard (n-decane) and the effective carbon number (ECN) method.[1] 100 μL (1 mg/100 μL) of n-decane were added into the product as internal. The mixture was filtered through a 0.22 μm nylon syringe filter and analyzed by Agilent 8860 instrument equipped with an HP-5 MS column (30 m in length, 0.25 mm in diameter) and FID detector. The detailed calculation was as follows:

$$n=A/A_{decane} \times n_{decane} \times E_{decane}/E$$

$$conversion=(1-n'_{substrate}/n_{substrate}) \times 100\%$$

$$yield=n/n_{theoretical} \times 100\%$$

where n is the molar number of hydrodeoxygenation product, n_{decane} is the molar number of n-decane added into the reaction systems. $n_{substrate}$ and $n'_{substrate}$ is the molar number of substrate before and after reaction, respectively. $n_{theoretical}$ is the theoretical molar number of hydrodeoxygenation product. A and A_{decane} is the GC area of hydrodeoxygenation products and n-decane, respectively. E_{decane} is the effective carbon number (ECN) of decane, E is ECN of substrate.

S1-6: Liquid adsorption tests

Pd@UIO-66-X and UIO-66-X (0.02 g) was added into the aimed benzyl alcohol ethanol solutions (1 mL) with different concentrations, respectively. After be continuously stirred for a certain time, the solid was separated and the substrate concentration was calculated from the results analyzed by gas chromatography.

$$C_{MOF}=(n_{before}-n_{after})/V_{MOF}$$

C_{MOF} is the substrate concentration in MOF skeleton. n_{before} is the mole number of added substrate before adsorption. n_{after} is the mole number of substrate in the solution after adsorption which is calculated according to the GC results. V_{MOF} is the space volume of MOF obtained from Nitrogen adsorption.

References

1. S. Li, T. A. Masoud, Y. M. Questell-Santiago, F. Héroguel, Y. Li, H. Kim, R. Meilan, C. Chapple, J. Ralph and J. S. Luterbacher, Formaldehyde Stabilization Facilitates lignin monomer production during biomass depolymerization, *Science*, 2016, **354**, 329-333.

Section S2. Characterization

Transmission electron microscopy (TEM) and the corresponding energy-dispersive X-ray spectrometer (EDS) mapping were recorded by a Tecnai G2 F30 S-Twin and JEOL JEM-F200 high resolution transmission electron microscope operating at 300 kV. Powder X-ray diffraction (XRD) patterns were measured with a Bruker D8 Advance with Cu Kα radiation (λ =1.5406 Å) at a scan rate of 5° min^{-1}. Nitrogen adsorption-desorption isotherms and Brunauer–Emmett–Teller (BET) surface area analysis was performed with a BSD-PS(M) adsorption apparatus at 77 K by Micromeritics ASAP-2425. The water contact angle was measured by the SINDIN SDC 350KS using the sessile drop method. All the samples were dried in the vacuum oven overnight at 100 °C before detecting the water contact angle. Then, a 5 µL droplet of deionized water was positioned on the surface via a microsyringe and images were collected to measure the angle that formed at the liquid/solid interface. Fourier transform infrared (FT-IR) spectroscopy were carried out a Nicolet iS10 IR spectrometer equipped with an MCT/A detector. The in-situ Fourier transform infrared spectroscopy (FT-IR) experiments were conducted on a Thermo Scientific Nicolet iS10 IR spectrometer equipped with an in-situ liquid system and operated at the range of 600-4000 cm^{-1} at a resolution of 4 cm^{-1}. The spectra of the adsorbed benzyl alcohol molecules have subtracted the spectra of the samples before the adsorption. Benzyl alcohol-adsorption FT-IR spectra were conducted as follows: The samples were placed in a homemade IR cell and evacuated ($P < 10^{-3}$ Pa) at 200 °C for 30 min. After the disk cooling to 100 °C, 10 µL of benzyl alcohol was spiked into the cell via the septum. 30 min later, after adsorption equilibrium was reached, the FTIR spectra of the samples were collected. The cell was then evacuated for 20 min ($P < 10^{-2}$ Pa) at 100 °C and the spectra were collected during the desorption process. In situ FT-IR spectra of reaction were also recorded using a Thermo Scientific Nicolet iS10 IR spectrometer. Prior to the experiment, the fresh samples were pretreated at 200 °C for 1 h to remove the adsorbed surface water. After cooled to 100 °C, 10 µL of benzyl alcohol was spiked into the cell and adsorbed for 30 min. After cooling down the reactor to 25 °C, the IR spectrum was collected as the baseline after this step yielding differential spectra. Then, H_2 was introduced into the cell to trigger reaction and the spectra were collected continuously. X-ray photoelectron spectroscopy (XPS) measurements were conducted by Thermo Scientific K-Alpha electron spectrometer. Inductively coupled plasma optical emission spectrometry (ICP-OES) was measured by PerkinElmer Avio 500. Cyclohexane adsorption isotherms was performed on Quantachrome Autosorb IQ. All the samples were vacuum degassed at 200 °C for 8 h. The thermogravimetric analysis measurements were performed on a HITACHI STA200 simultaneous thermalanalyzer with a heating rate of 10 °C/min from room temperature to 600 °C at air atmosphere. The In-situ FT-IR spectra of CO adsorption were recorded using a Thermo Scientific Nicolet iS10 IR spectrometer. Prior to the experiment, the fresh samples were pretreated at 200 °C for 1 h to remove the adsorbed surface water. CO was adsorbed for 30 min, then evacuated at 25 °C, and the spectra were collected during desorption until the final chemisorption peak was almost unchanged.

Section S3. Supplementary Figures

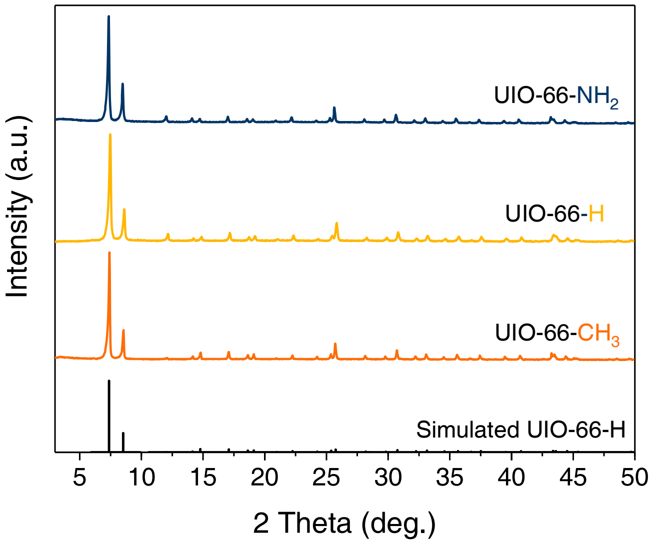

Figure S1. The PXRD patterns of UIO-66-CH$_3$, UIO-66-H, and UIO-66-NH$_2$.

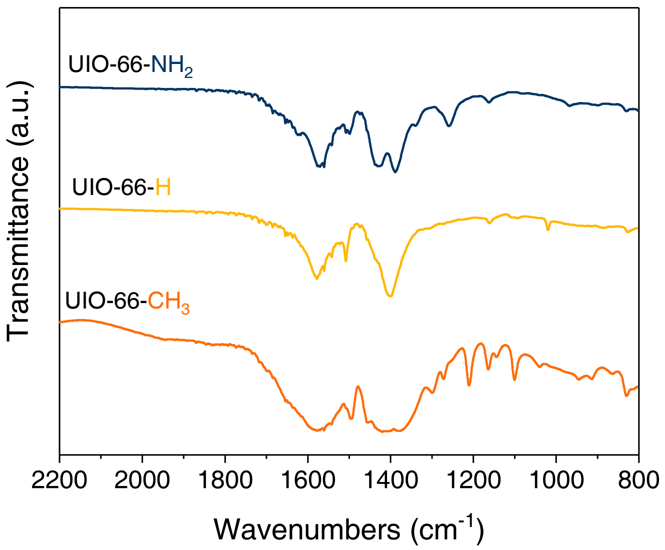

Figure S2. FT-IR spectrums of UIO-66-CH_3, UIO-66-H, and UIO-66-NH_2.

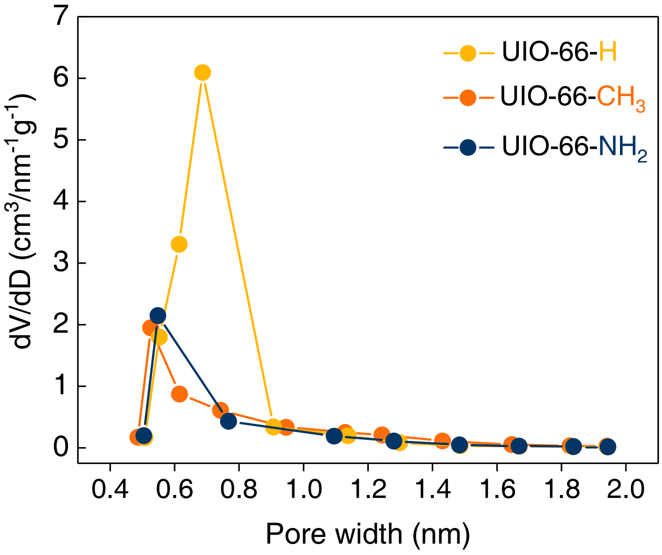

Figure S3. Pore size distribution of UIO-66-CH_3, UIO-66-H, and UIO-66-NH_2.

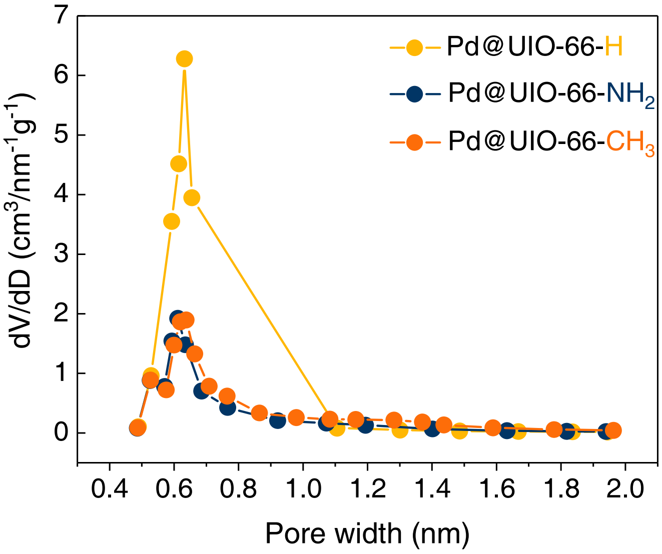

Figure S4. Pore size distribution of Pd@UIO-66-CH$_3$, Pd@UIO-66-H, and Pd@UIO-66-NH$_2$.

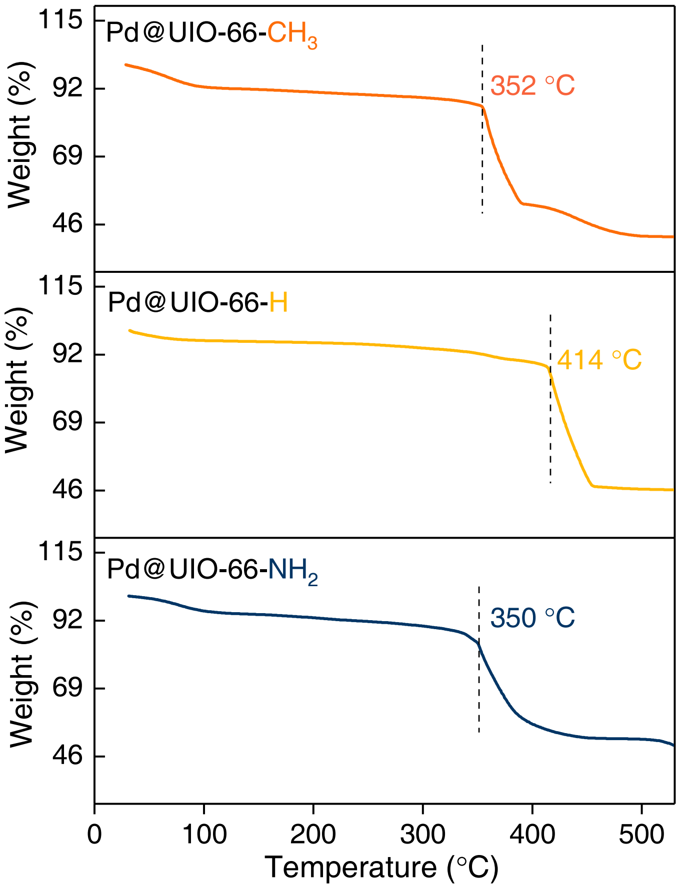

Figure S5. TGA curves of Pd@UIO-66-CH_3, Pd@UIO-66-H, and Pd@UIO-66-NH_2.

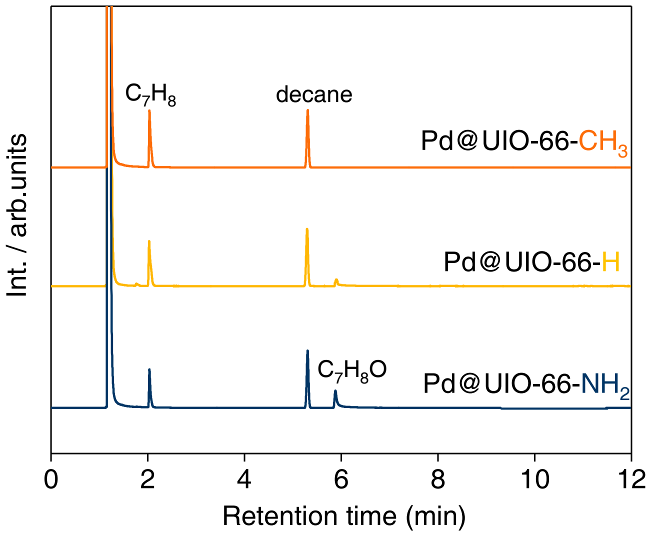

Figure S6. The GC analysis of the products after benzyl alcohol hydrodeoxygenation by Pd@UIO-66-CH_3, Pd@UIO-66-H, and Pd@UIO-66-NH_2, respectively. Reaction conditions: 5 mg of catalyst, 1 mL of substrate solution (10 mM), 1 atm of H_2, 25 °C, 2 h.

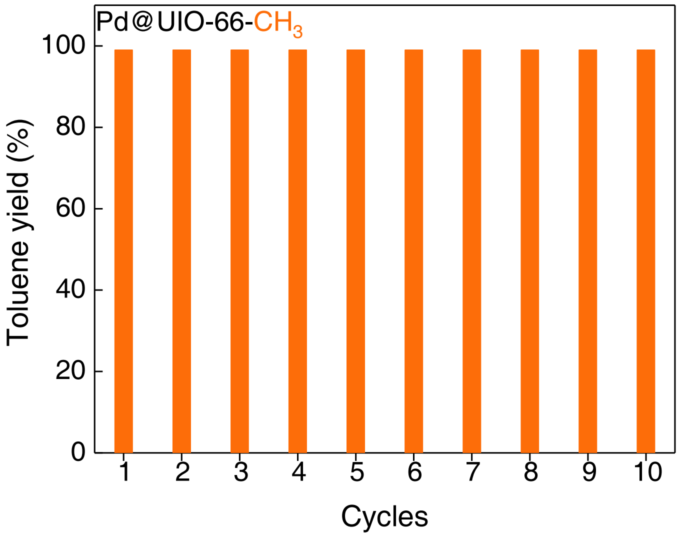

Figure S7. The recycle tests over Pd@UIO-66-CH_3.

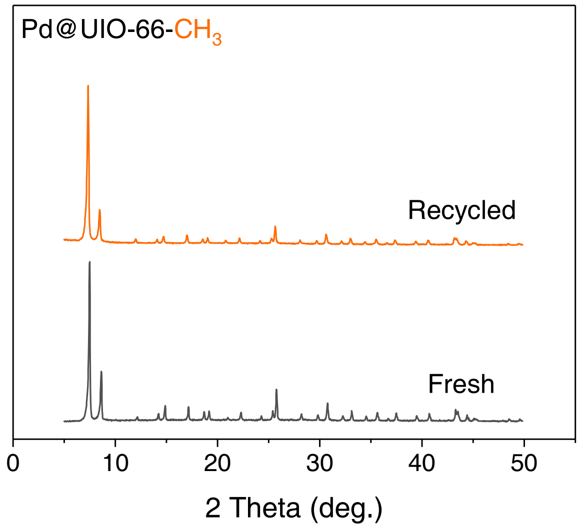

Figure S8. The PXRD patterns of Pd@UIO-66-CH$_3$ after recycled.

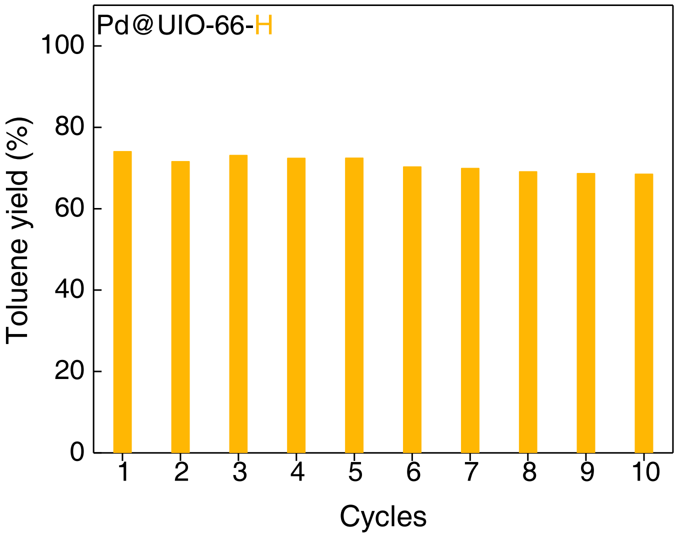

Figure S9. The recycle tests over Pd@UIO-66-H.

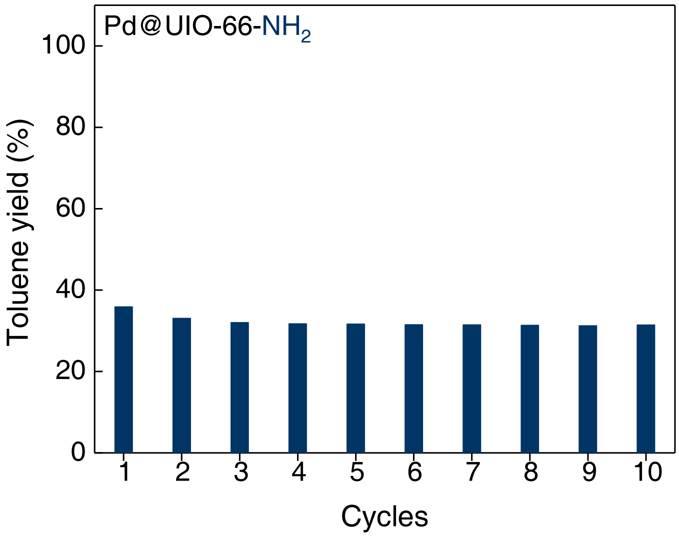

Figure S10. The recycle tests over Pd@UIO-66-NH_2.

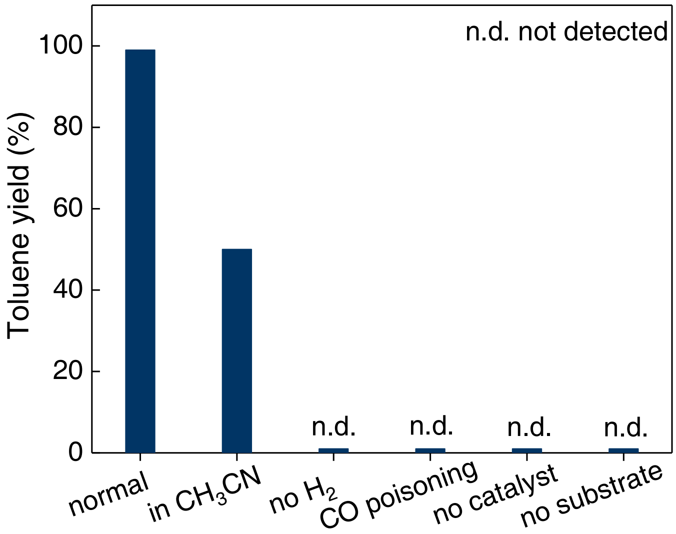

Figure S11. Control experiments over Pd@UIO-66-CH_3 after 2 h.

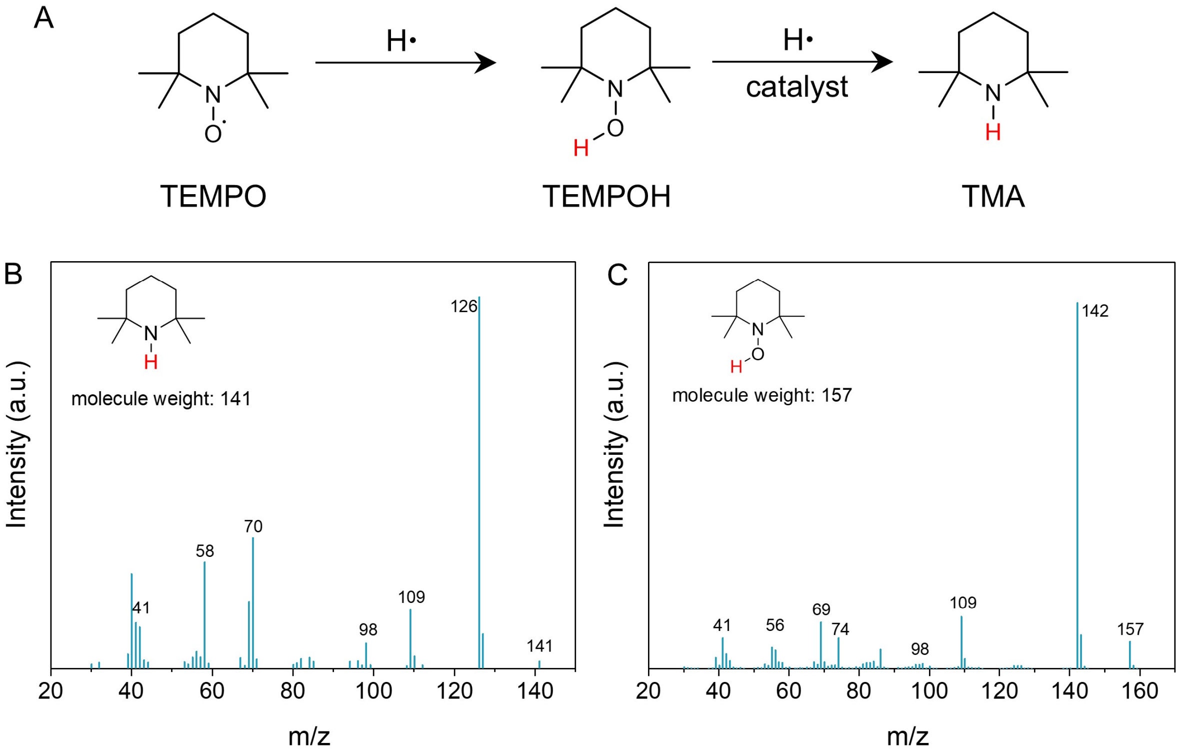

Figure S12. (A) Radical trapping experiment. (B) MS spectra in GC-MS pattern at a retention time of 5.2 min and 8.1 min, respectively.

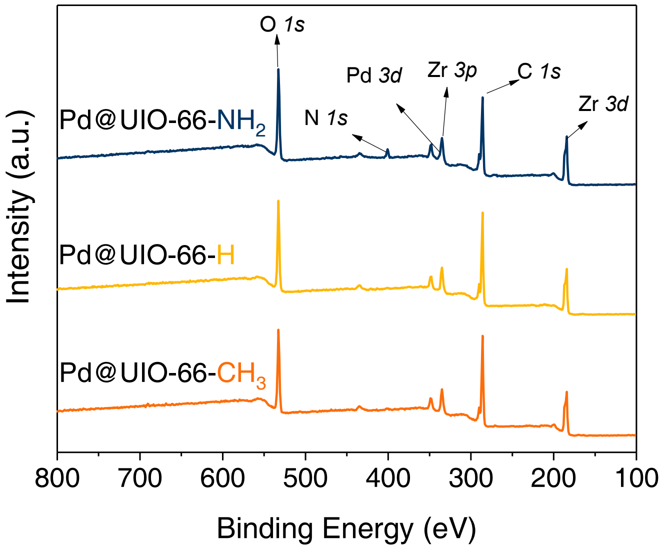

Figure S13. XPS survey spectra of Pd@UIO-66-CH_3, Pd@UIO-66-H, and Pd@UIO-66-NH_2.

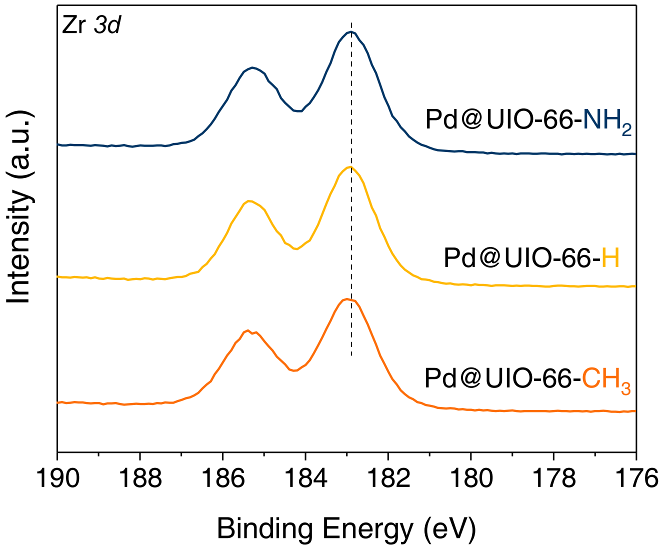

Figure S14. Zr 3d XPS spectra of Pd@UIO-66-CH_3, Pd@UIO-66-H, and Pd@UIO-66-NH_2.

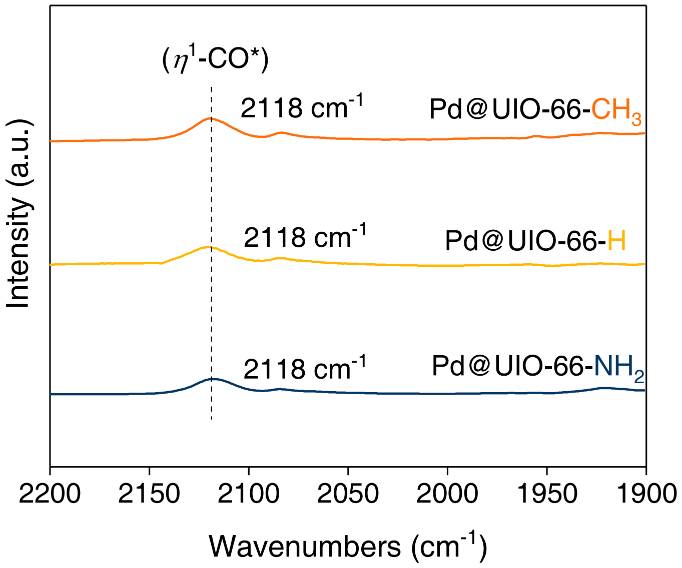

Figure S15. The In-situ FTIR spectra of CO adsorption on Pd@UIO-66-CH$_3$, Pd@UIO-66-H, and Pd@UIO-66-NH$_2$.

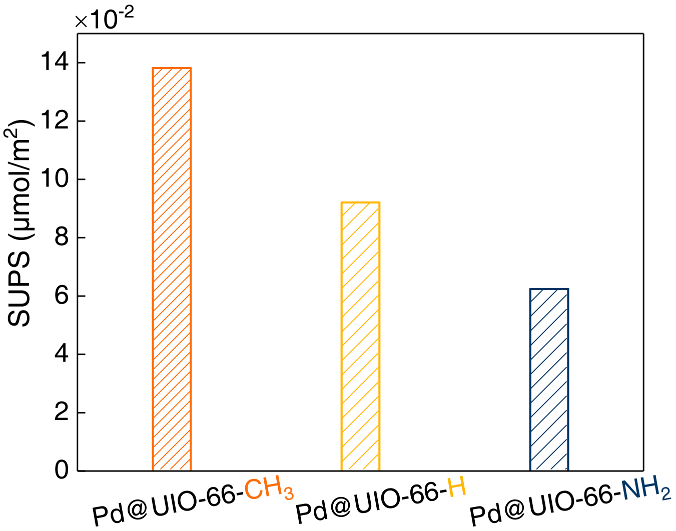

Figure S16. Comparison of the SUPS between Pd@UIO-66-CH_3, Pd@UIO-66-H, and Pd@UIO-66-NH_2.

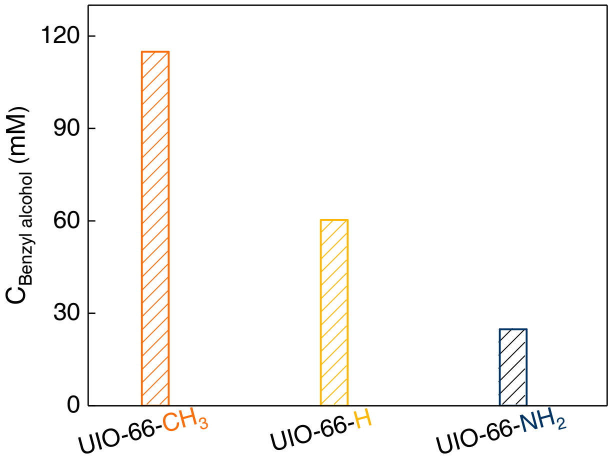

Figure S17. The pre-concentration effect of UIO-66-CH$_3$, UIO-66-H, and UIO-66-NH$_2$ on benzyl alcohol in 2 h, respectively.

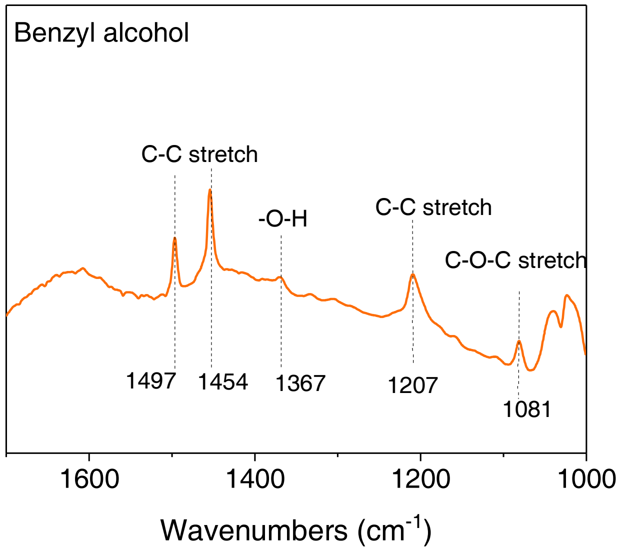

Figure S18. FT-IR spectrum of benzyl alcohol.

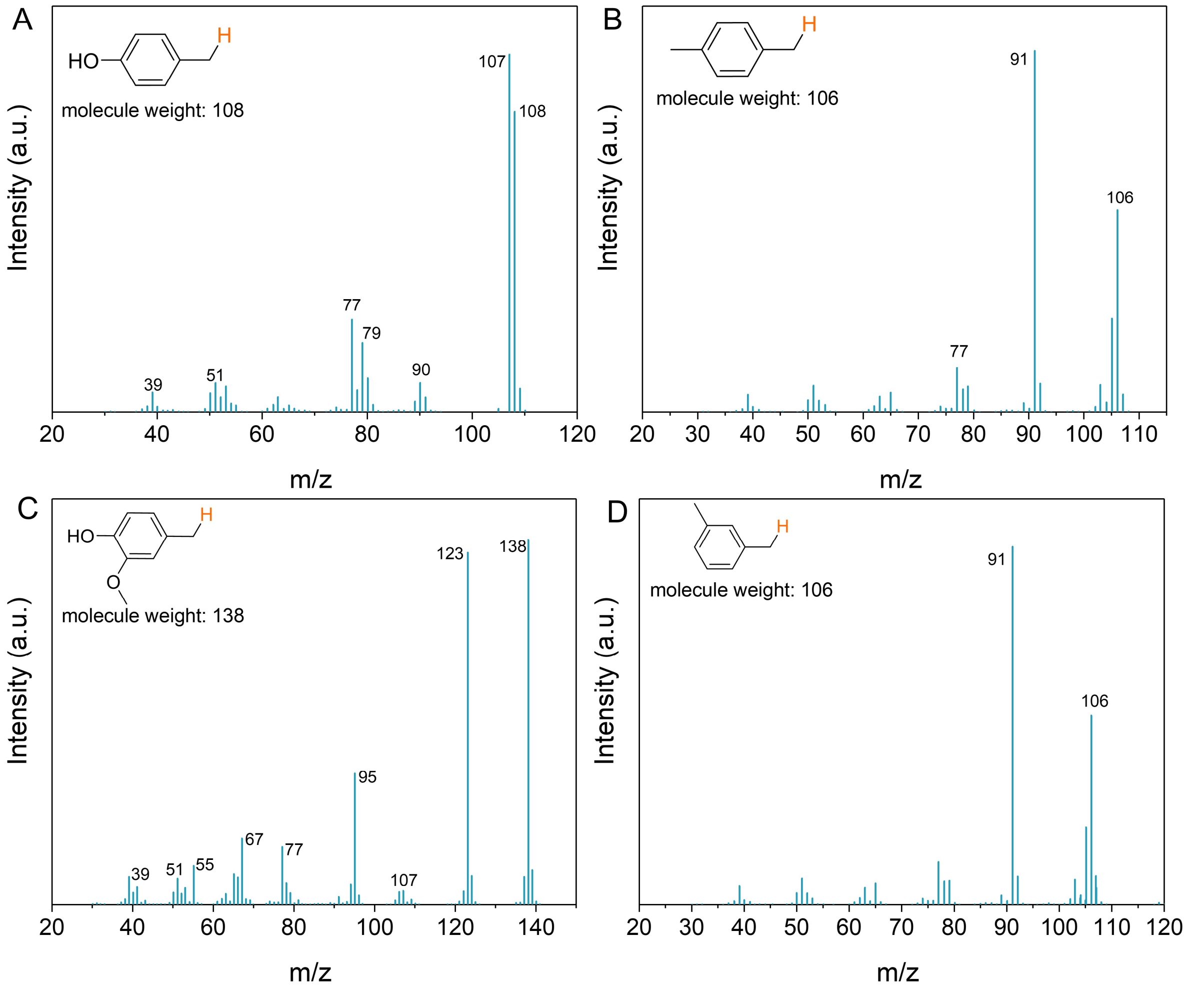

Figure S19. The mass spectra of the hydrodeoxygenation products of various aromatic alcohol/aldehyde substrates.

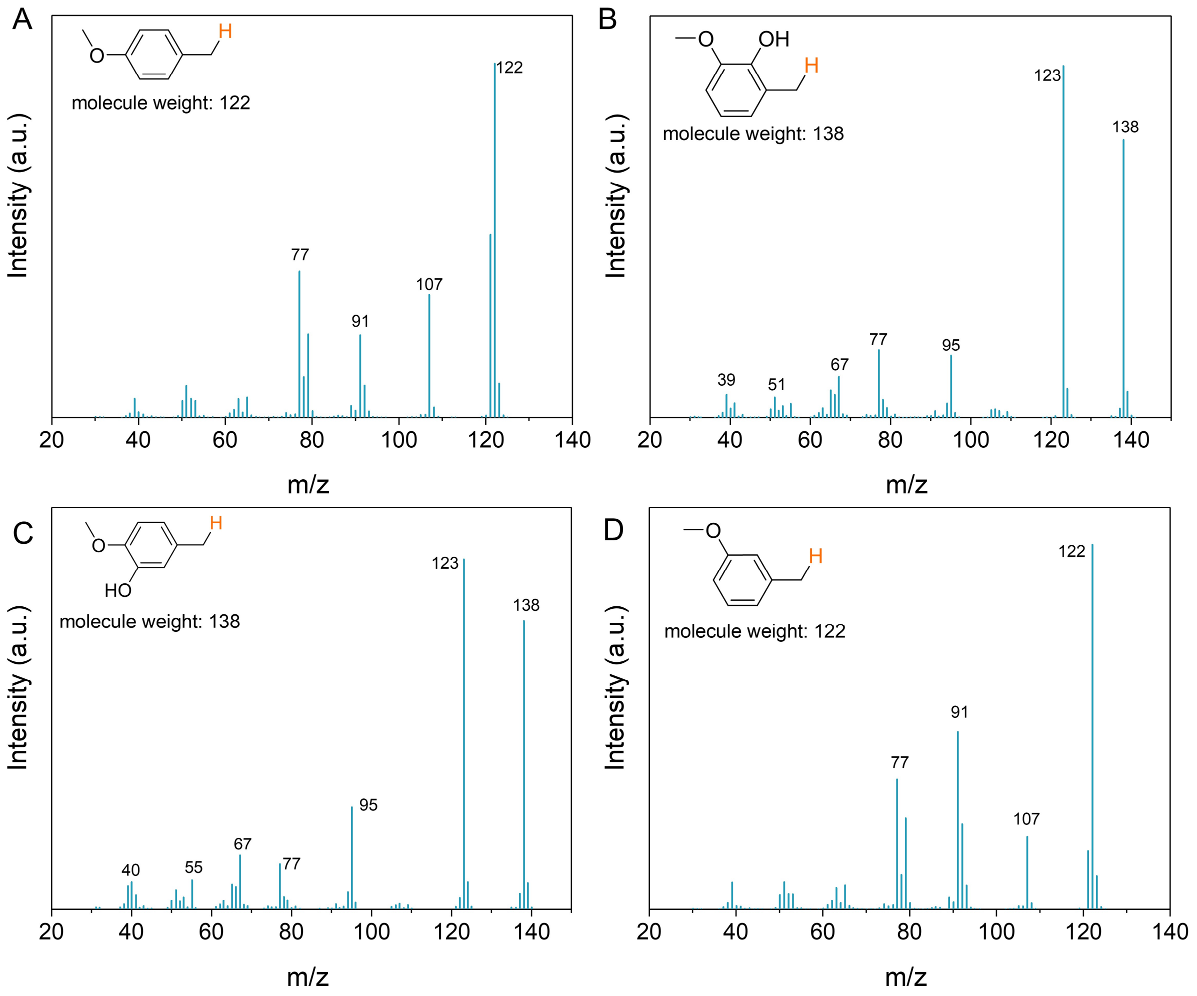

Figure S20. The mass spectra of the hydrodeoxygenation products of various aromatic alcohol/aldehyde substrates.

Table S1. BET and pore volume of samples.

Samples	BET (m^2/g)	pore volume (cm^3/g)
UIO-66-CH_3	826.5	0.537
UIO-66-H	870.5	0.564
UIO-66-NH_2	828.0	0.549
Pd@UIO-66-CH_3	790.8	0.516
Pd@UIO-66-H	786.9	0.503
Pd@UIO-66-NH_2	722.7	0.464

Table S2. The ICP of samples.

Samples	Pd (wt%)
Pd@UIO-66-CH_3	1.81
Pd@UIO-66-H	1.74
Pd@UIO-66-NH_2	1.87