Electronic Supplementary Information (ESI)

Surfactant-free Pd nanoparticles immobilized to metal-organic framework with size- and location-dependent catalytic selectivity

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1. Materials and instrumentation

All chemicals were commercial and used without further purification. Palladium chloride ($PdCl_2$, 99.9%, Kishida Chemical Co. Ltd), chromic nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$ 99%, Sigma-Aldrich), terephthalic acid ($HOOCC_6H_4COOH$ 99%, Tri Chemical Laboratories Inc.), vanillin ($C_8H_8O_3$, >98.0%), aqueous hydrochloric acid (HCl, >35.0%), aqueous hydrofluoric acid (HF 46%, Kishida Chemical Co. Ltd) and *n*-hexane (Sigma-Aldrich) were used as received. Ultrapure water was used for sample preparation and catalytic reactions.

Powder X-ray diffraction (XRD) was performed on a Rigaku Ultima IV X-ray diffractometer with Cu Kα source (40 kV, 40 mA). The surface area measurements were performed with N_2 sorption isotherms at liquid nitrogen temperature (77 K) using automatic volumetric adsorption equipment (Belsorp max) after activation under vacuum at 150 ^{o}C for overnight. The pore volume was calculated by a single point method at $P/P_0 = 0.99$. X-ray photoelectron spectrometry (XPS) analyses were carried out on a Shimadzu ESCA-3400 X-ray photoelectron spectrometer using an Mg Kα source (10 kV, 10 mA). Scanning transmission electron microscopy (STEM), transmission electron microscopy (TEM) images and energy-dispersive X-ray (EDX) spectra were recorded on Tecnai G^2 F20 (FEI) with operating voltages of 200 or 120 kV quipped with energy-dispersive X-ray detector. High resolution STEM images, showing lattice fringes of Pd for Pd@MIL-101, were performed on Titan3 G2 60-300 (FEI) with operating voltage of 300 kV. Tomographic experiments were performed on TECNAI G^2 F20 equipped with a −59.6° to +59.6° tomography tilt stage and holder operated at 120 kV to minimize the beam damage with punctual resolution ~0.27 nm. Images for tomographic reconstruction were taken using a 2° interval over the largest possible angle (preferably 100°). A reference image taken at 0° tilt was taken before and after image acquisition to ensure no changes in the sample structure due to beam damage during acquisition. Tomographic reconstruction was performed using the INSPECT 3D software package. For all techniques low-intensity beam conditions were used as far as possible to minimize the electron dose and possible beam damage of the MOF crystals. The contents of products and reactant were determined based on authentic samples by GC-FID (SHIMADZU GC-2014, 250 ^{o}C) assembled with DB-FFAP 30 m column.

2. Synthesis of MIL-101

MIL-101 was synthesized using the reported procedure.[1] Terephthalic acid (1.66 g, 10.0 mmol), $Cr(NO_3)_3 \cdot 9H_2O$ (4.00 g, 10.0 mmol), aqueous HF (0.5 mL, 46 wt%) and de-ionized water (70 mL) were placed in a 100 mL Teflon-liner autoclave and heated at 220 °C for 8 h. After cooling, the resulting green powders of MIL-101 with formula $Cr_3F(H_2O)_2O[(O_2C)C_6H_4(CO_2)]_3 \cdot nH_2O$ ($n \leq 25$) were doubly filtered off using two glass filters with pore sizes between 40 μm to remove the unreacted crystals of terephthalic acid, and then further purified by solvothermal treatment in ethanol at 80 ^{o}C for 24 h. The resulting green solid was soaked in NH_4F (1 M) solution at 70 ^{o}C for 24 h to eliminate the terephthalic acid inside the pores of MIL-101 and immediately filtered, washed with hot water several times, dried at room temperature, and used for further experiments.

3. Synthesis of H_2PdCl_4

A solution of tetrachloropalladinic acid (H_2PdCl_4) was prepared by mixing 500 mg of $PdCl_2$ into 20 mL of 10% v/v HCl aqueous solution under stirring at room temperature until complete dissolution.

4. Synthesis of Pd@MIL-101

Pd nanoparticles within MIL-101 were prepared via double-solvents method. Typically, 100 mg of activated MIL-101 (150 ^{o}C for overnight under vacuum) was suspended in 20 mL of dry *n*-hexane as hydrophobic solvent and the mixture was sonicated for few min until it became homogeneous. With constant vigorous stirring 0.15 mL of aq. H_2PdCl_4 solution was added dropwise over a period of 15 min. The resulting solution was continuously stirred for 2 h. After careful filtration, the green powder was dried in air at room temperature. These synthesized samples were further dried at 150 ^{o}C for overnight, followed by treating in a stream of H_2/He (50 mL min^{-1}/50 mL min^{-1}) at 200 ^{o}C for 5 h to yield Pd@MIL-101.

5. Synthesis of Pd/MIL-101

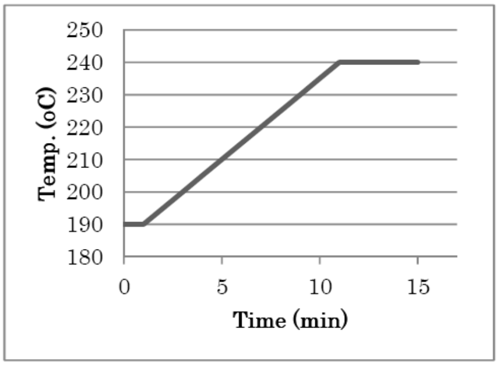
Pd nanoparticles onto MIL-101 were prepared via deliberately chosen precursor deposition method. Typically, 100 mg of as-synthesized MIL-101 was mixed with 0.5 mL aq. H_2PdCl_4 with constant stirring. The resulting composite was continuously stirred for 2 h and then dried in air at room temperature. These synthesized samples were further dried at 150 ^{o}C for overnight, followed by treating in a stream of H_2/He (50 mL min^{-1}/50 mL min^{-1}) at 200 ^{o}C for 5 h to yield Pd/MIL-101.

6. Catalytic vanillin reduction

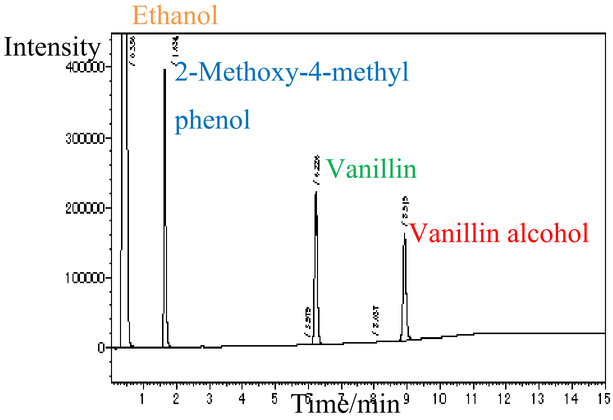
In a typical reaction under, 100 mg (0.656 mmol) vanillin and 100 mg 2% Pd@MIL-101 or Pd/MIL-101 catalyst were added into a stainless steel reactor, and 5 mL ultrapure deionized water was added as solvent. After closing the cylinder and complete removal of air and O_2 from it, the reactor was pressurized with molecular H_2 at a desired pressure. The hydrodeoxygenation of vanillin was carried out at a temperature of 75 ^{o}C or mentioned temperatures with magnetic stirring at a speed of ~500 rpm. After reaction, the contents of products and reactant were extracted with ethyl acetate and determined by GC-FID.

7. Analysis of Vanillin by GC-FID

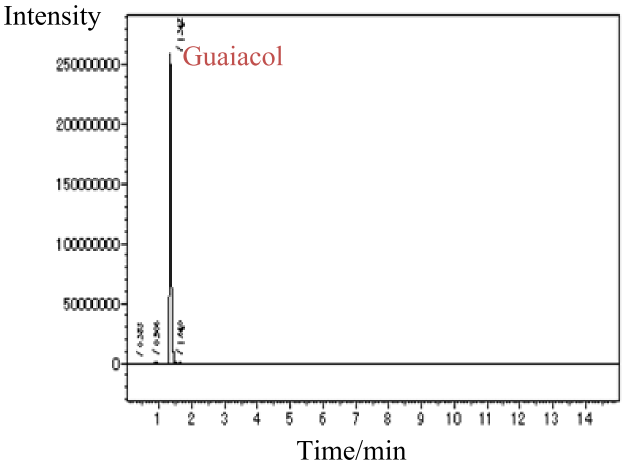
Conditions: 1 min hold at 190 ^{o}C, heating rate 5 ^{o}C/min from 190 to 240 ^{o}C, 4 min hold at 240 ^{o}C; Injector: 250 ^{o}C; Detector: FID



Temperature profile for GC analysis.



GC-FID chromatogram of standard samples



GC-FID chromatogram of standard guaiacol sample

Reference:

(1) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science*, 2005, **309**, 2040.

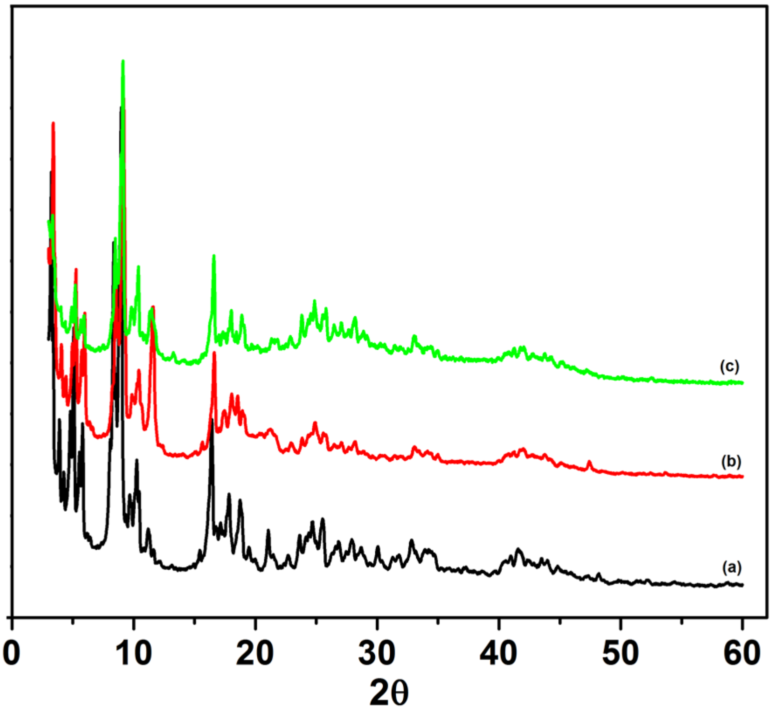


Figure S1. Powder XRD patterns of (a) MIL-101, (b) 2% Pd@MIL-101 and (c) 2% Pd/MIL-101.

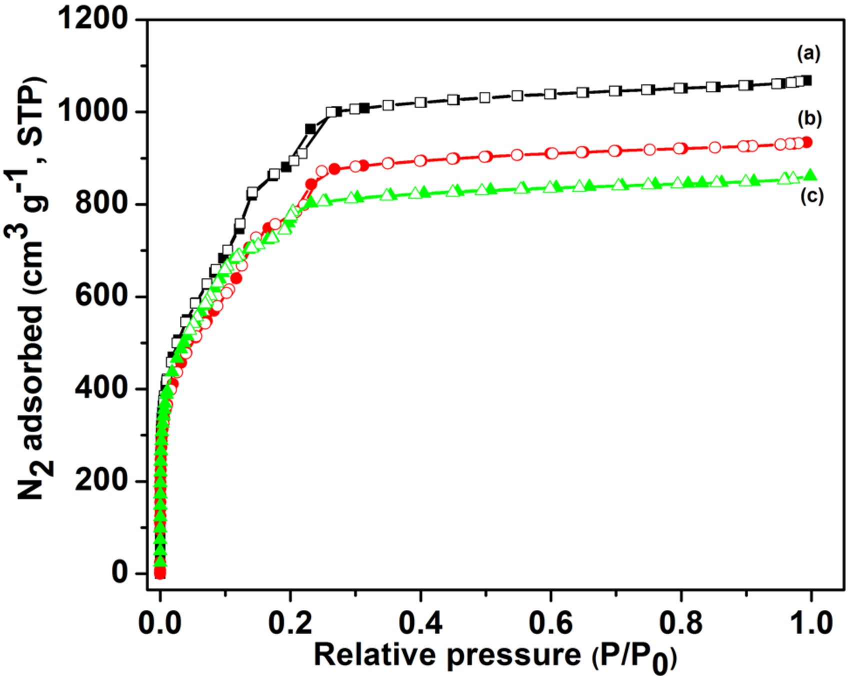


Figure S2. N_2 sorption isotherms of (a) MIL-101, (b) 2% Pd@MIL-101 and (c) 2% Pd/MIL-101 at 77 K (filled and open symbols represent adsorption and desorption branches, respectively).

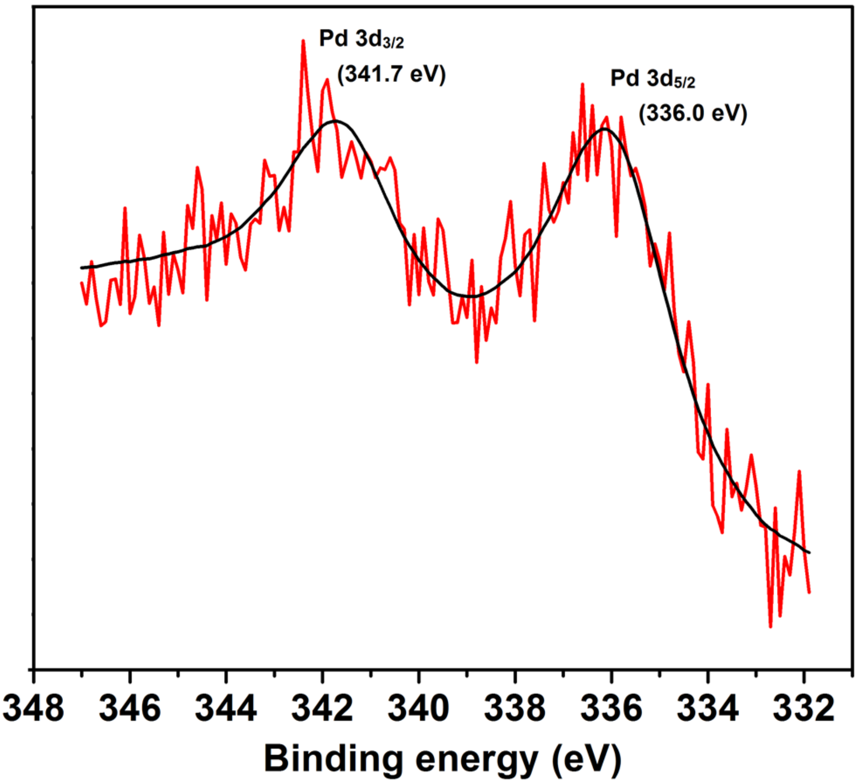


Figure S3. XPS of 2% Pd@MIL-101 at Pd 3d levels.

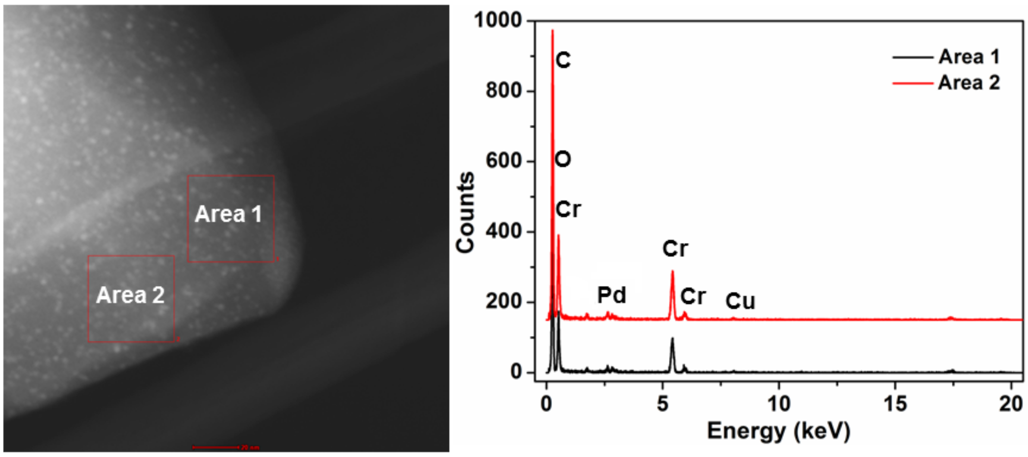


Figure S4. HAADF-STEM image (left) and corresponding area EDX spectra (right) of Pd@MIL-101.

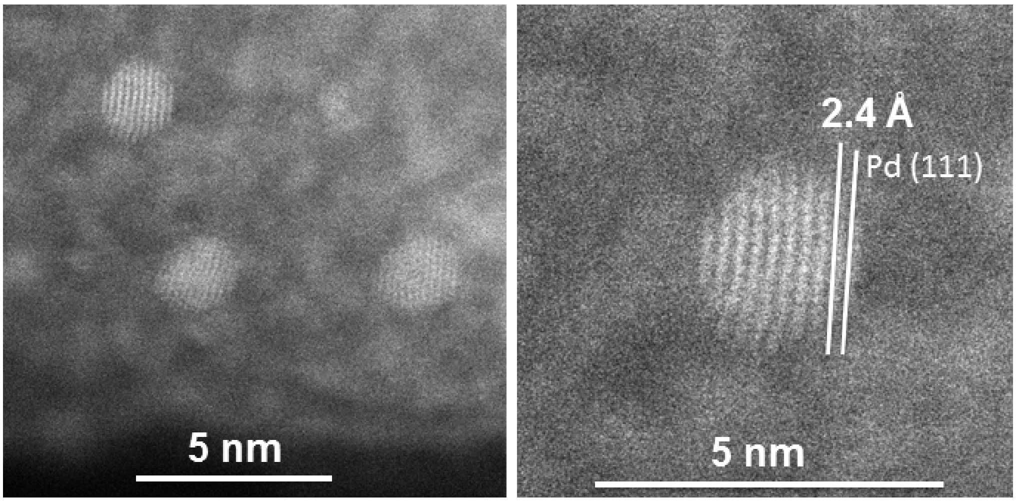


Figure S5. High-resolution STEM (HRSTEM) images of Pd@MIL-101 showing the fringes of the crystalline palladium nanoparticles with interlayer distance of 2.4 Å associated with the (111) lattice planes.

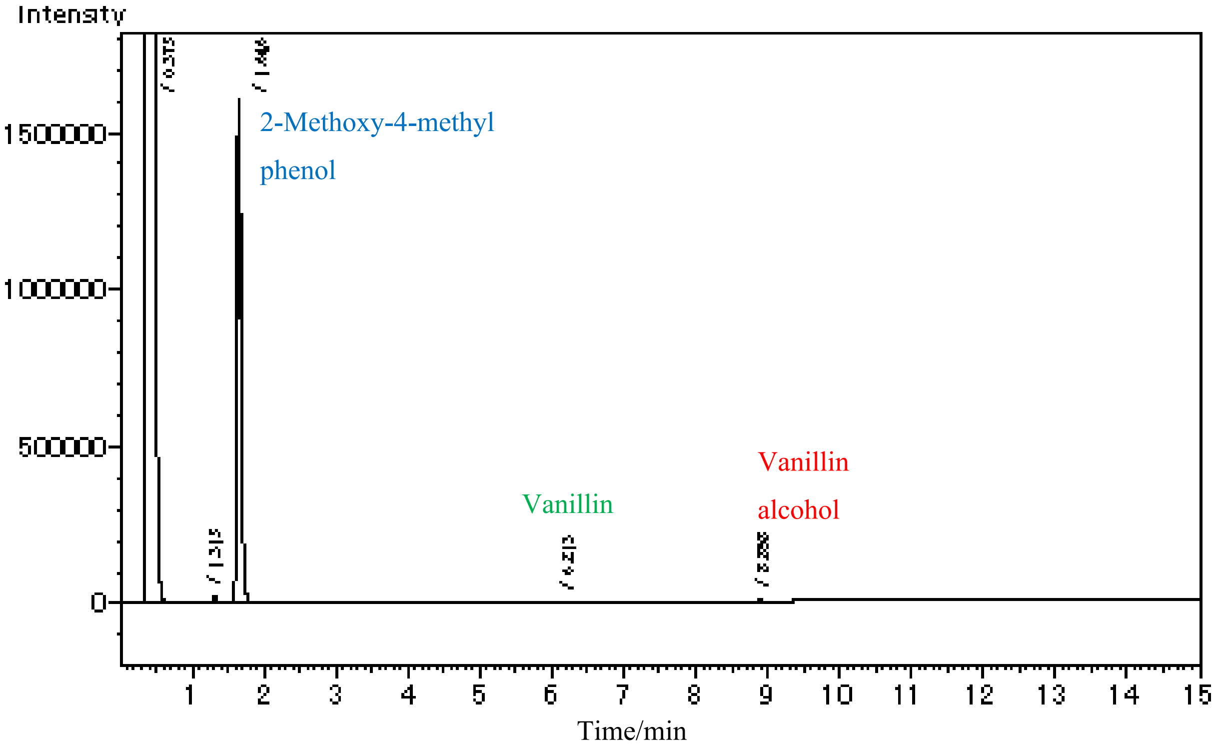


Figure S6. GC-FID chromatogram for complete vanillin hydrodeoxygenation with Pd@MIL-101 catalyst (75 ^{o}C, 7 h, 2 bar H_2) after ethyl acetate extraction.

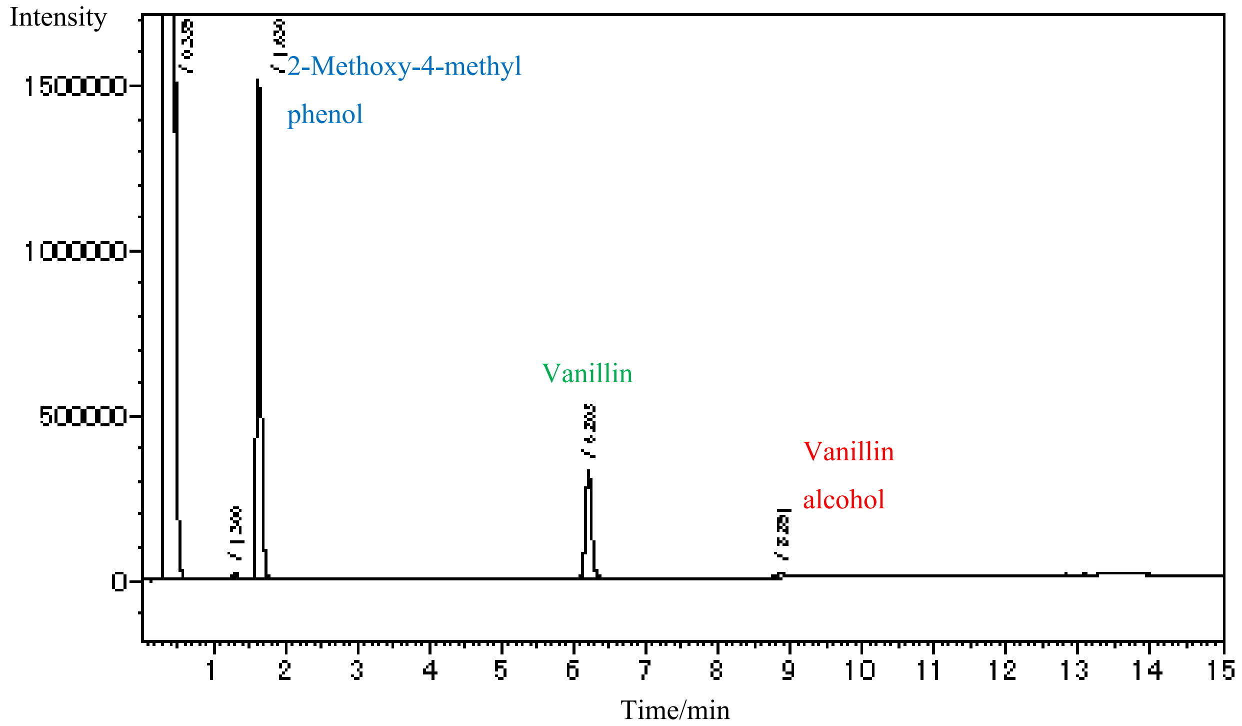


Figure S7. GC-FID chromatogram for vanillin hydrodeoxygenation with Pd@MIL-101 catalyst (75 ^{o}C, 3 h, 2 bar H_2) after ethyl acetate extraction.

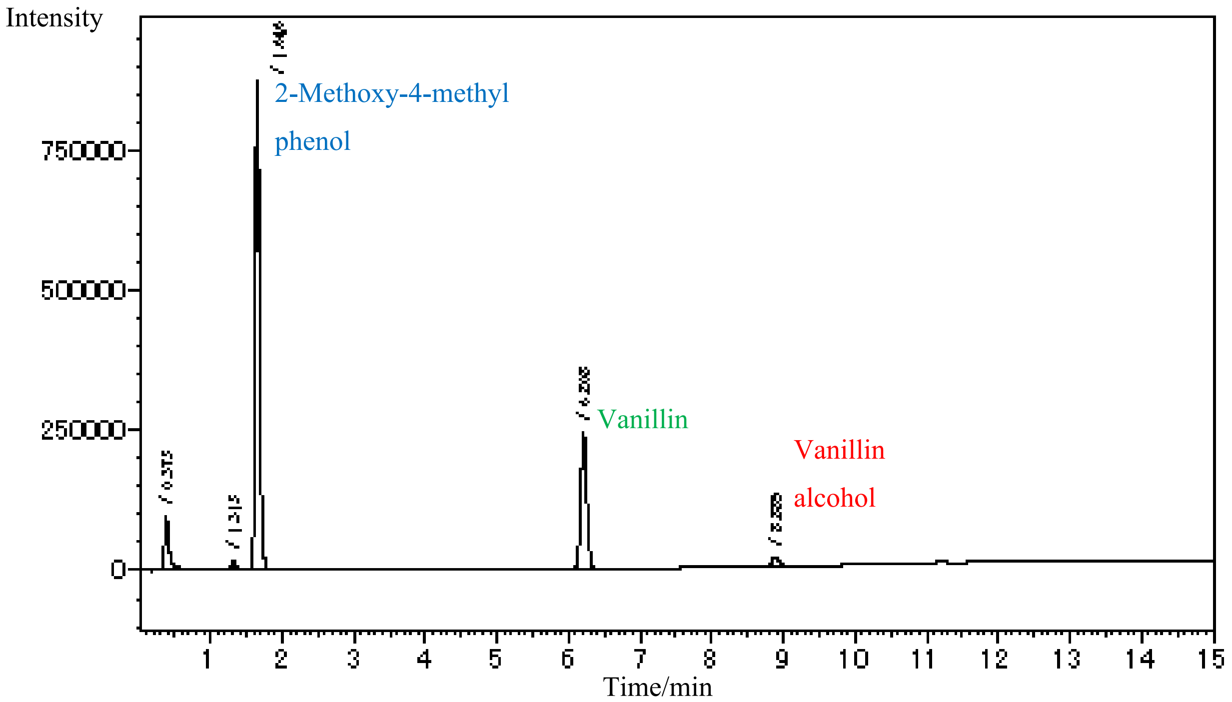


Figure S8. GC-FID chromatogram for vanillin hydrodeoxygenation with Pd@MIL-101 catalyst (75 ^{o}C, 3 h, 2 bar H_2) before ethyl acetate extraction (aqueous phase).

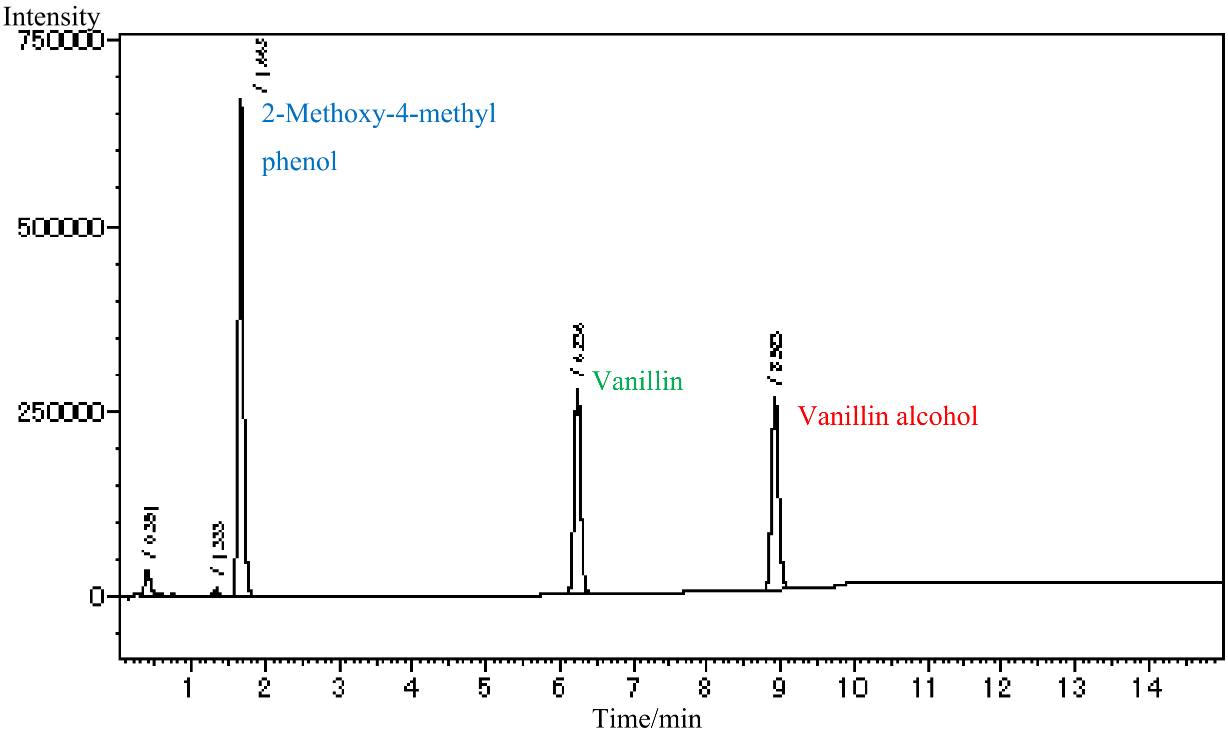


Figure S9. GC-FID chromatogram for vanillin hydrodeoxygenation with Pd/MIL-101 catalyst (75 ^{o}C, 3 h, 2 bar H_2) after ethyl acetate extraction.

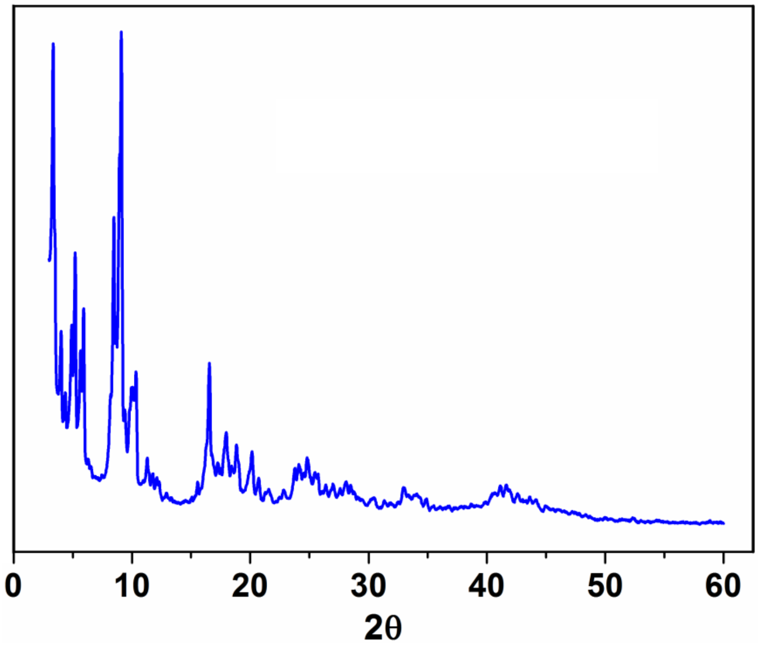


Figure S10. Powder XRD pattern of recovered catalyst (2% Pd@MIL-101) after three cycles of vanillin reduction at 75 ^{o}C.

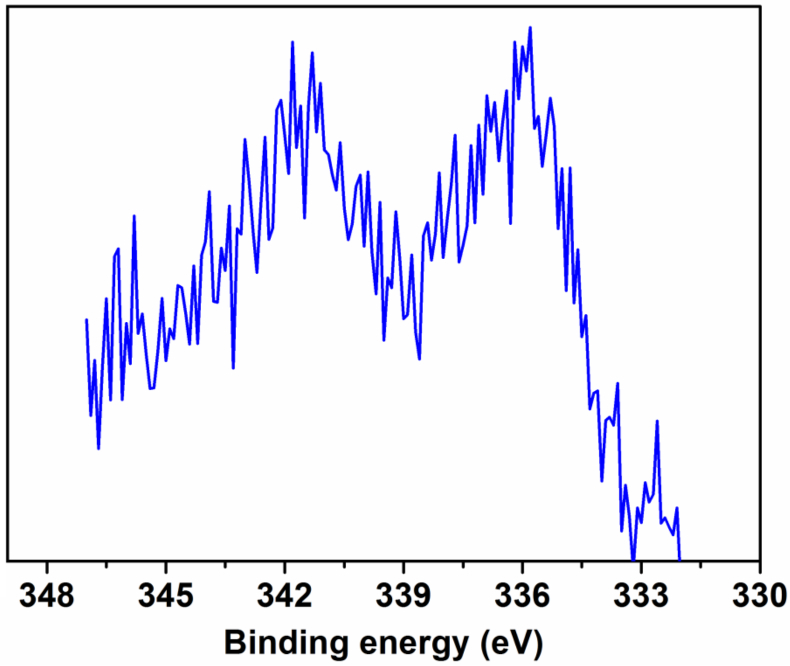


Figure S11. XPS of recovered catalyst (2% Pd@MIL-101) after three cycles of vanillin reduction at 75 °C for 24 h of durations at Pd 3d levels.

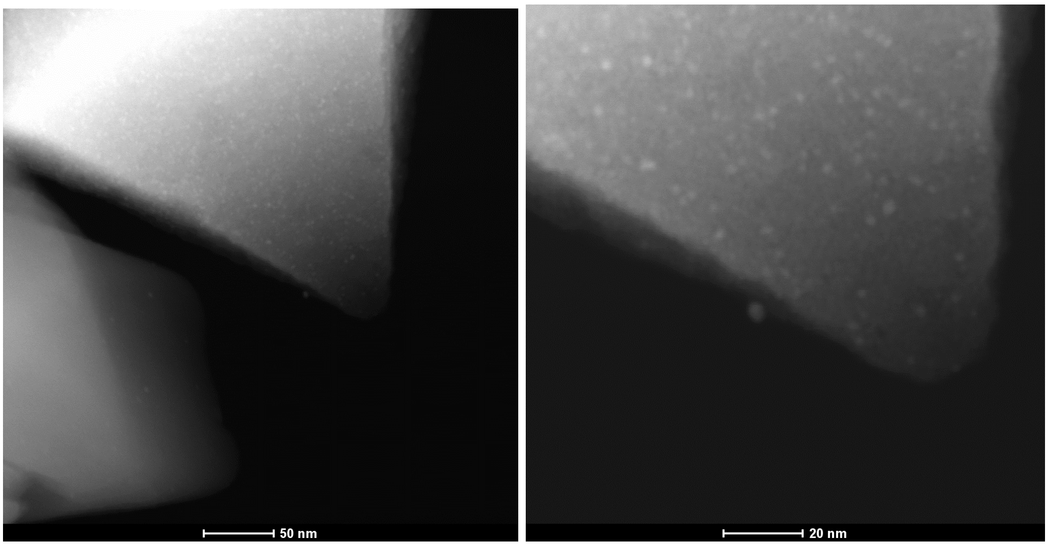


Figure S12. HAADF-STEM images of recovered 2% Pd@MIL-101 after vanillin reduction.