# Electronic Supporting Information

## Efficient Hydrogenolysis of Aryl Ethers over Ce-MOF supported Pd NPs under Mild Conditions: Mechanistic Insight using Density Functional Theoretical Calculations

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## Contents

## *Materials and Methods*

### *Materials and reagents*

$Ce(NO_3)_3 \cdot 6H_2O$ was purchased from Loba Chemie Pvt Ltd. 1,3,5-benzenetricarboxylic acid, sodium borohydride, $PdCl_2$ and other required chemicals were purchased from Sigma Aldrich chemicals. All the chemicals used in this experiment were analytical grade and used without further purification.

### *Synthesis of Ce-BTC and Pd(x%)/Ce-BTC (x = 0.5, 1.5, and 2.5)*

In a typical procedure for Ce-BTC synthesis, Ce $(NO_3)_3.6H_2O$ (434 mg) was dissolved in 20 mL of $H_2O$ : EtOH (v:v = 2:1). In another flask, trimesic acid ($H_3BTC$) (210 mg) was dissolved in 20 mL of EtOH. The $H_3BTC$ solution was slowly added to the Cerium metal-containing solution under stirring condition followed by reflux at 363 K for 2 h. Then, the obtained precipitate was collected over centrifugation and dried at 343 K for 12 h. The remaining support materials $CeO_2$ and SBA-15 were synthesized using the previously reported method.[1,2]

For the synthesis of Pd/Ce-BTC samples, designated as Pd(x%)/Ce-BTC (where x = 0.5, 1.5, and 2.5), 500 mg of Ce-BTC was dispersed in a mixture of 40 mL $H_2O$ and 50 mL EtOH. The required amount of $PdCl_2$ was added to the Ce-BTC solution and sonicated for 15 minutes. Then, an aqueous solution of $NaBH_4$ (20 mg in 10 mL) was added drop-wise to the above solution and kept for overnight under constant stirring. A similar procedure was adopted for the synthesis of Pd/$CeO_2$ & Pd/SBA-15.

## *Characterisation*

Powder X-ray diffraction (XRD) patterns were recorded on the Rigaku Miniflex III diffractometer (30 kV and 10 mA). The surface area of the catalyst was determined by Nitrogen sorption measurements performed at 77 K by Quantachrome Instruments, Autosorb-iQ volumetric adsorption analyzer. The sample was degassed at 473 K for 3 h in the degassing port of the adsorption apparatus. The surface area of the catalyst was calculated from the adsorption data points obtained for $P/P_0$ between 0.05-0.3 using the Branauer-Emmette-Teller (BET) equation. The Field emission scanning electron microscopy (FE-SEM) (JEOL JSM-6610LV) was used for the morphological investigation. High-resolution transmission electron microscopy (HRTEM) images were recorded on a JEOL-2010 transmission electron microscope operating at 200 kV at CeNS, Bengaluru.. The amount of

Pd loading was determined from microwave plasma-atomic emission spectroscopy (MP-AES). The analysis was carried out in a single spray chamber by injecting the samples into a stream of nitrogen plasma. For each sample the analysis is repeated three times and the average of the obtained results was used to calculate the elemental compositions. Thermogravimetric analysis (TGA) was performed in the range of 30-1000 °C on a TGA/DSC 1 STARe SYSTEM from Mettler Toledo, Switzerland, with temperature increments of 10°C/min in $N_2$ atmosphere. Surface composition of the catalyst was investigated at IIT Mandi, India, by X-ray photoelectron spectroscopy (XPS) analysis by an XPS system PHI 5000 VersaProbeII (ULVAC– PHI, INC, Japan) with a microfocus (100 µm, 25 W, 15 kV) monochromatic Al-Kα source (hν = 1486.6 eV), a hemispherical analyzer and a multichannel detector.

### *Catalytic process of C-O hydrogenolysis reaction of benzyl phenyl ether (BPE)*

In a typical reaction, BPE (0.5 mmol), catalyst (12 mg), and methanol (10 mL) were charged into a 100 mL steel autoclave containing reactor. Then it was pressurized with $H_2$ to 2 bar. The reaction was stirred for 1 h at 353 K. After the reaction, the reaction mixture was centrifuged and filtered. The progress of the reaction was monitored and quantified using a gas chromatograph (GC, Yonglin 6100; BP-5; 30 m × 0.25 mm × 0.25 mm) The product was confirmed using GC-MS (Shimadzu GCMS-QP 2010 Ultra Rtx-5 Sil Ms; 30 m × 0.25 mm × 0.25 mm). After the reaction, the catalyst was retrieved by centrifugation, washed several times with ethanol, dried in an oven, and then used in the next cycle. An internal standard, i.e., mesitylene, was used to determine the liquid product concentration and carbon balance. The carbon balance for all reported experiments in the liquid phase was in the range of 97-102. The calculations of conversion and selectivity were based on a carbon mole basis. TOF = (moles of reactants cleaved)/(moles of surface active sites x reaction time in an hour).

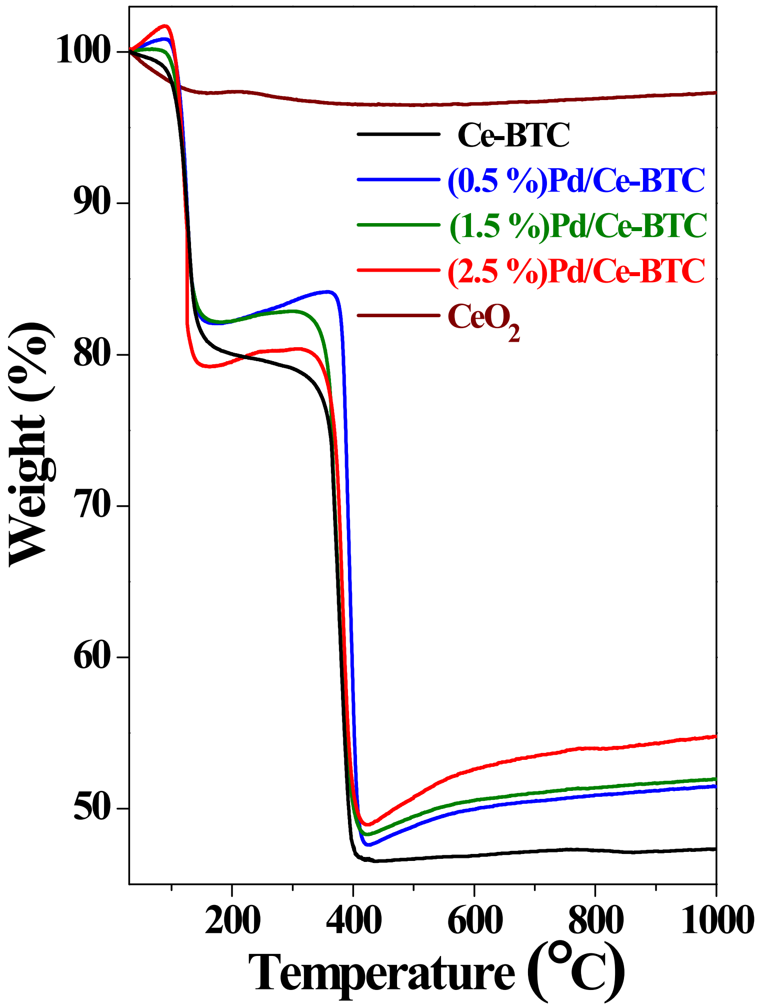

**Fig. S1**. TGA profiles of Ce-BTC, Pd(0.5%)/Ce-BTC, Pd(1.5%)/Ce-BTC, Pd(2.5%)/Ce-BTC, and $CeO_2$.

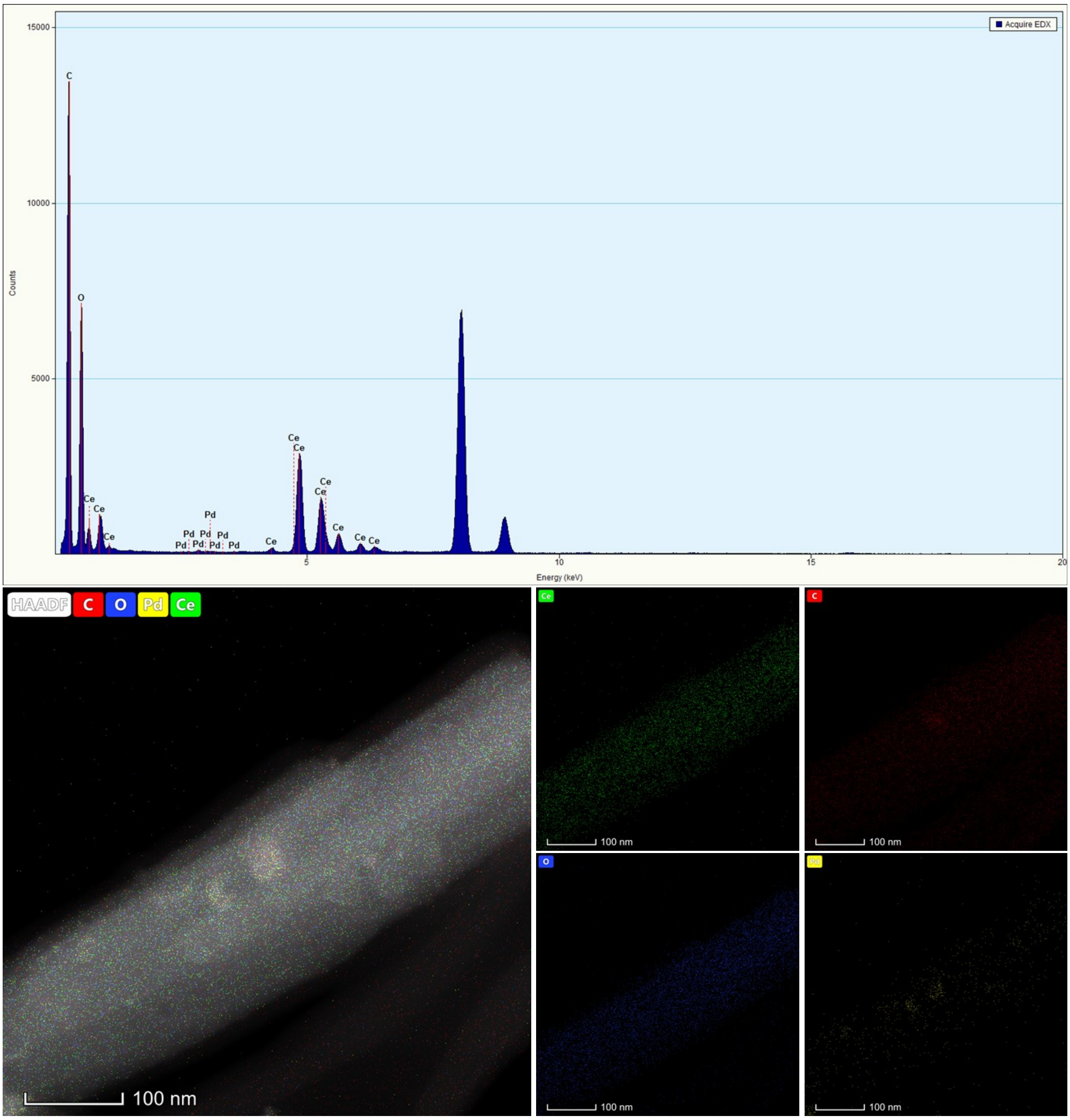

**Fig. S2.** EDX spectra and elemental mapping of Pd(1.5%)/Ce-BTC MOF.

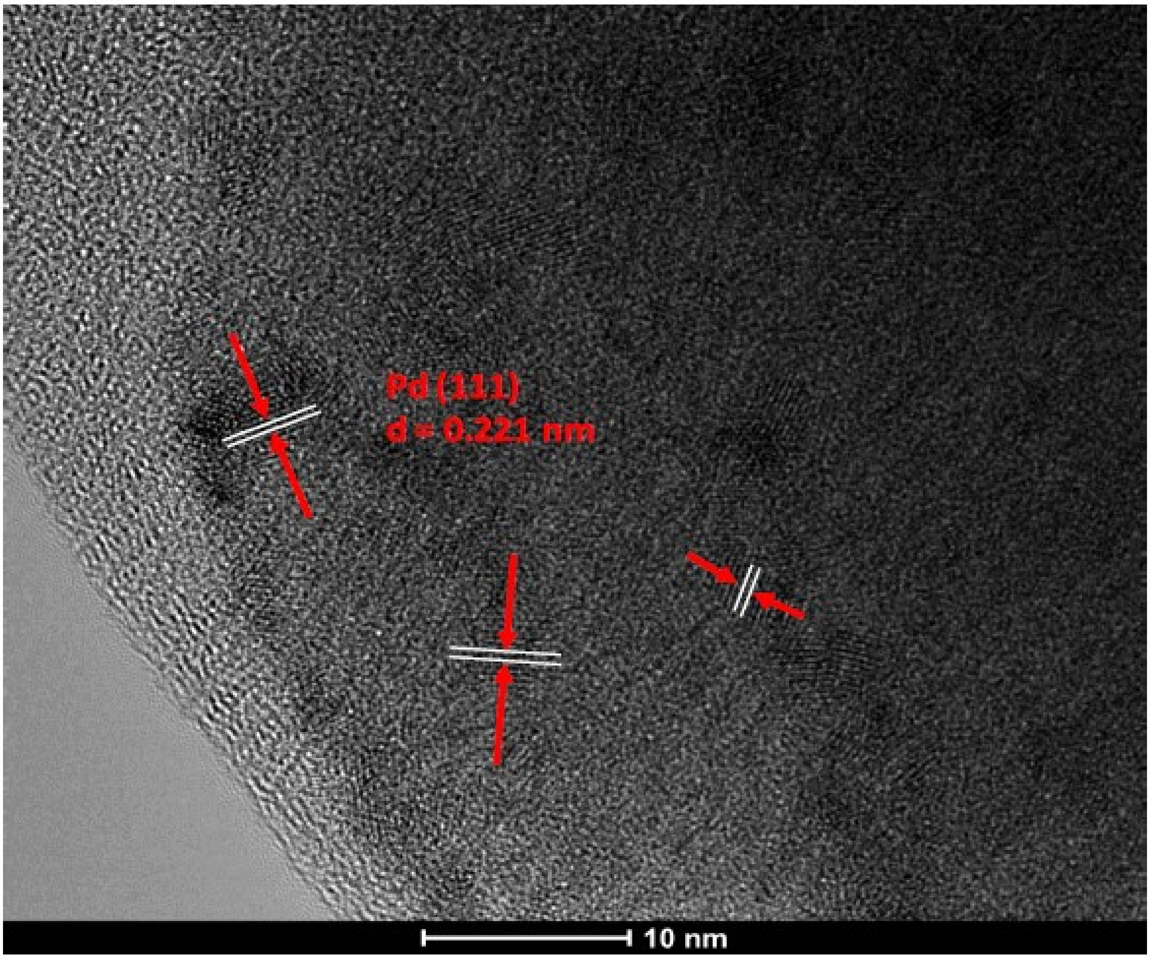

**Fig. S3**. Lattice fringes corresponding to (111) planes of Pd NPs of Pd(1.5%)/Ce-BTC.

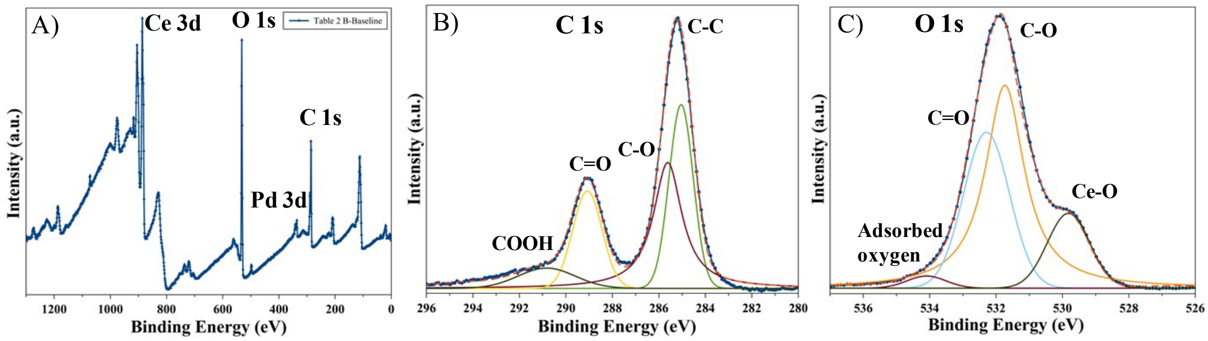

**Fig. S4**. (a) Surface survey, (b) C 1s, and (c) O 1s XPS spectrum of Pd(1.5%)/Ce-BTC.

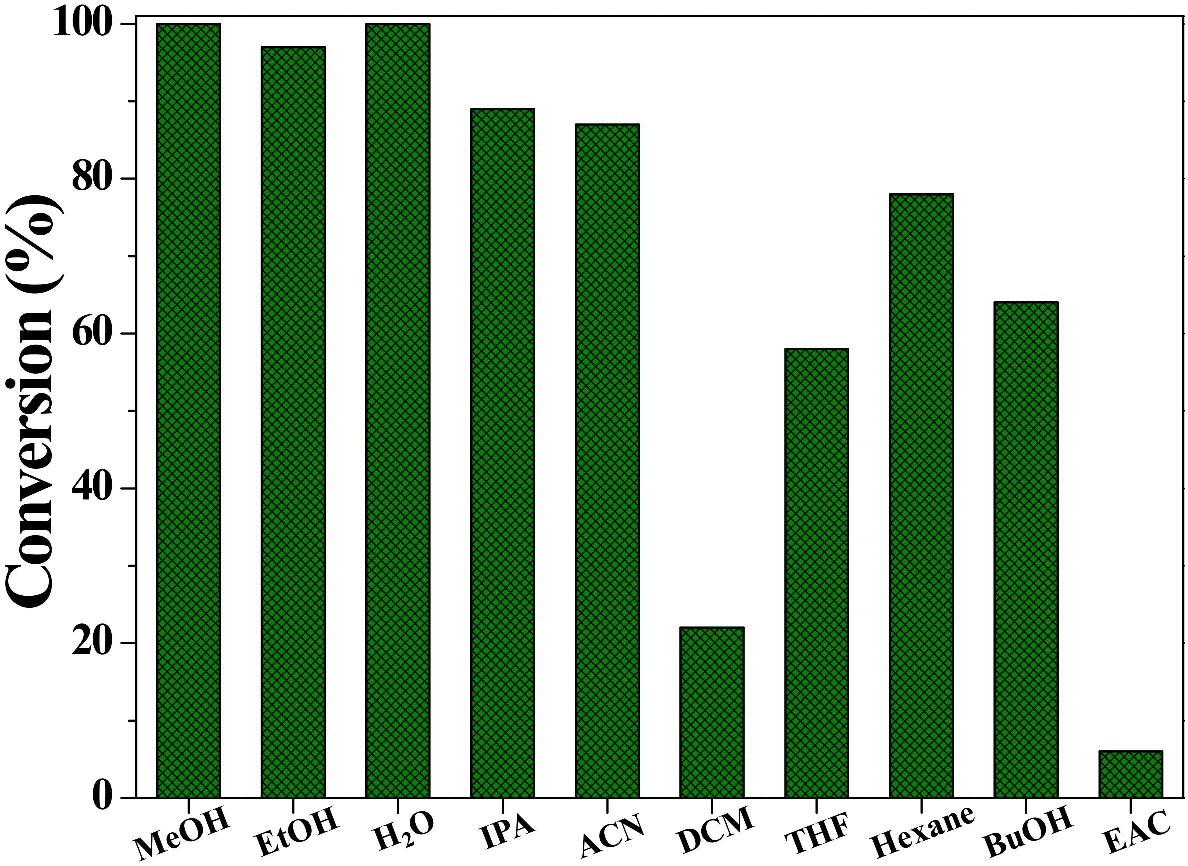

**Fig. S5.** Influence of solvent for the C-O hydrogenolysis of BPE. Reaction condition: BPE (0.5 mmol), catalyst (12 mg), $H_2$ pressure (2 bar), methanol (10 mL), temperature (353 K), time (1 h). For $H_2O$ the reaction was conducted at 383 K for 2 h.

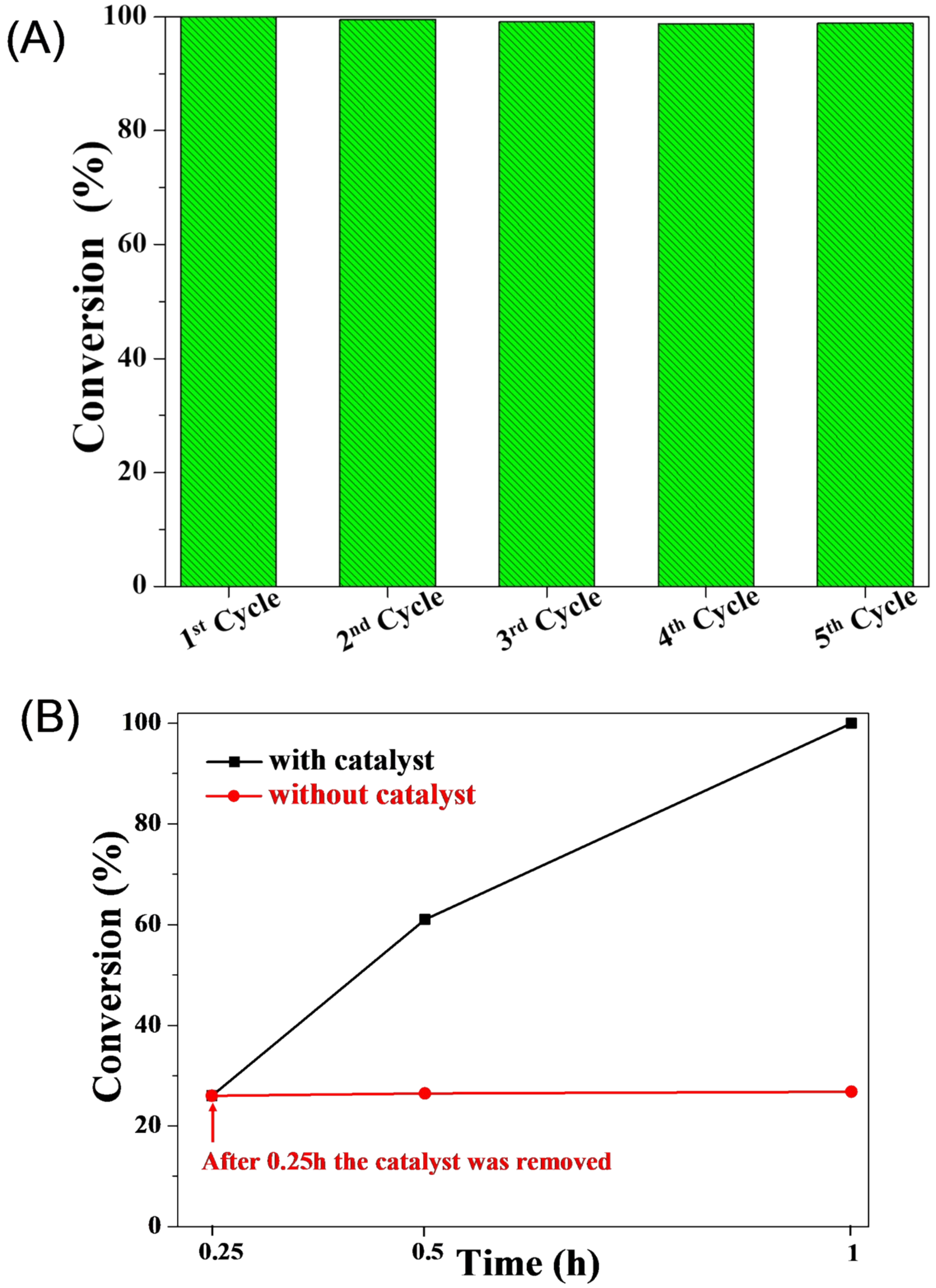

**Fig. S6**. Recycling (A) and hot-filtration test (B) conducted over Pd(1.5%)/Ce-BTC in the C-O hydrogenolysis of BPE.

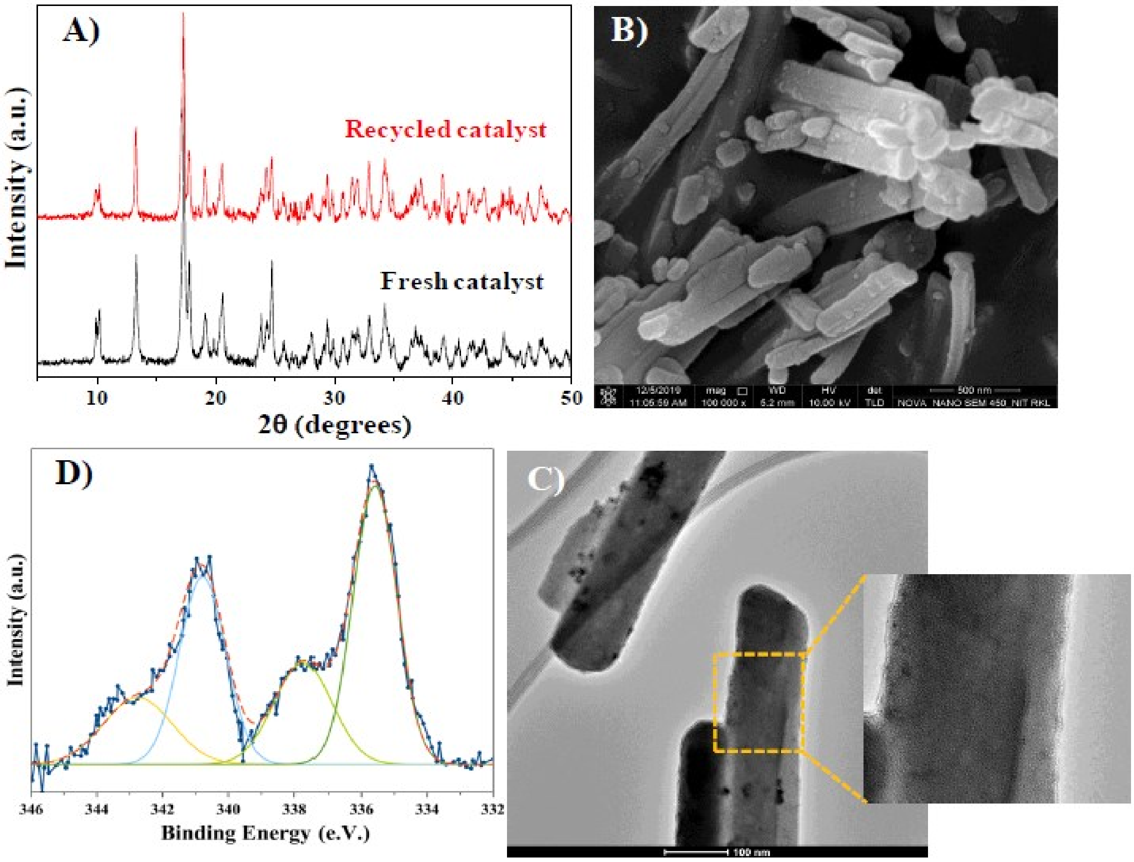

**Fig. S7**. XRD of the fresh and spent Pd(1.5%)/Ce-BTC (A); and FE-SEM image (B), TEM (C), and high resolution Pd XPS spectrum (D) of the spent Pd(1.5%)/Ce-BTC catalyst after the C-O hydrogenolysis of BPE.

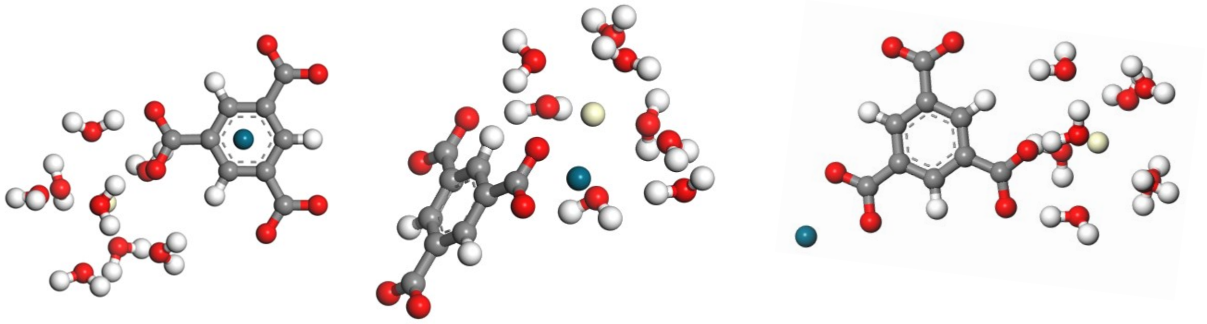

**Fig. S8.** Different possible binding sites of Pd with Ce-BTC MOF.

## References

1. X. Liu, J. Ding, X. Lin, R. Gao, Z. Li and W. L. Dai, *Appl. Catal. A-Gen.* 2015, **503**, 117–123.

2. A. Galarneau, H. Cambon, F. D. Renzo and F. Fajula, *Langmuir* 2001, **17***,* 8328-8335.