

Supplementary Information

Cooperative Catalysis at Metal-MOF Interface: Hydrodeoxygenation of Vanillin over Pd Nanoparticles Covered with UiO-66(Hf) MOF

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1. General information

1.1. Reagents

Vanillyl alcohol (>99.0 %) and 2-methoxy-4-methylphenol (> 98.0 %) were purchased from TCI chemicals. Sodium tetrachloropalladate (II) (Na₂PdCl₄, 98%) and hafniumchloride (HfCl₄, 98%) were acquired from Sigma-Aldrich. L-Ascorbic acid LR (C₆H₈O₆, 99%) and 1, 4-benzenedicarboxylate (H₂BDC, 98%) were obtained from SDFCL, Mumbai, India. Potassium bromide (KBr, 98.5%), Acetone (≥99%), and ethyl acetate (99%) were purchased from Merck Life Science Pvt.Ltd. Mumbai, India. Polyvinylpyrrolidone K30 (PVP, Mw=55000, 90%) was purchased from Spectrochem Pvt. Ltd, Mumbai, India. Vanillin (>99 %) and N, N-dimethylformamide (DMF, 99 wt %) were supplied by Avra Synthesis Pvt. Ltd. Hyderabad, India. All chemicals were used without further purification.

1.2. Characterization

Powder X-ray diffraction (PXRD) patterns were recorded on Bruker with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) operating at 20 kV and 10 mA. The specific surface area, pore volume and pore size of catalysts were measured using a BEL Sorp II BET (Brunauer-Emmett-Teller) instrument. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) imaging was carried out using JEOL 2100F, FEG source, 200 kV source voltage Oxford EDS detector. The Pd and Hf(IV) content in different samples were determined by ICP-OES varian 720-ES instrument.

2. Synthesis methods

2.1. Synthesis of Pd nanoparticles

Pd metal nanoparticles were synthesized according to reported procedure.¹ In a typical synthesis, 228 mg (0.77 mmol) of Na₂PdCl₄ precursor was dissolved in 12 mL of distilled water in a 20 mL vial. Later, in a separate 100 mL round bottom flask 420 mg (3.85 mmol) of PVP, 240 mg (1.36 mmol) of L-ascorbic acid, 300mg (2.52mmol) of KBr and 564 mg (7.56 mmol) of KCl were dissolved in 32 mL of distilled H₂O and placed it under stirring (500 rpm) at 80°C in oil bath for 10 min. To this clear solution, yellow colored Pd(II) precursor solution was added drop wise under stirring and kept it for 3 h at 80 °C. On completion of reaction time, Pd colloidal solution temperature was brought to room temperature. The Pd NPs separated from reaction solution by washing three times with acetone (150 mL) and distilled water (15 mL) using centrifuge. Finally, dried under vacuum at room temperature.

2.2. Synthesis of UiO-66(Hf) MOF

In a typical solvothermal synthesis,² HfCl₄·6H₂O (300 mg, 0.94 mmol) and terephthalic acid (174 mg, 1.04 mmol) were dissolved in 10 mL DMF solvent containing 0.1M H₂O (18 μ L) in a 30 mL screw capped bottle and sealed. The sealed bottle was placed in a pre-heated oven at 100°C for 24 h. On completion of the reaction time, the reaction mixture was brought to room temperature and the supernatant was separated from solid product using centrifuge. The solid product further washed with fresh DMF (50 mL) once, twice with ethanol (2 x 50 mL) using centrifuge. After completion of washing with DMF and ethanol solvents, the powder was dried under vacuum at room temperature.

2.3. Synthesis of Pd@UiO-66(Hf) core-shell material

In a typical synthesis, HfCl₄·6H₂O (300 mg, 0.94 mmol) and terephthalic acid (174 mg, 1.04 mmol) were dissolved in 10 mL of DMF solvent containing 0.1M H₂O (18 μ L) in a 30 mL screw capped bottle. Around 20 mg of Pd NPs were transferred into the above clear solution, and dispersed using sonication for 15 min. The sealed bottle was placed in a pre-heated oven at 100 °C for 24 h. On completion of the reaction time, the reaction mixture was brought to room

temperature and the supernatant was separated from solid product using centrifuge. The solid product further washed with fresh DMF (50 mL) once, twice with ethanol (2 x 50 mL) using centrifuge. After completion of washing with DMF and ethanol solvents, the powder was dried under vacuum at room temperature.

2.4. Synthesis of supported Pd NPs onto the UiO-66(Hf)

In a typical procedure, in a 10 mL of DMF ~20 mg of Pd NPs were dispersed using sonication for 15 minutes in a 50 mL RB flask. Afterward, around ~380 mg of activated UiO-66(Hf) sample was transferred into Pd dispersed solution. The mixture solution was kept for stirring at room temperature for 2 h. After reaction time, supernatant was removed from dark brown precipitate using centrifuge and the dark brown precipitate was washed twice with 50 mL of EtOH. Finally, the solid product was dried under vacuum at room temperature.

3. Characterization of Pd-UiO-66(Hf) hybrid materials

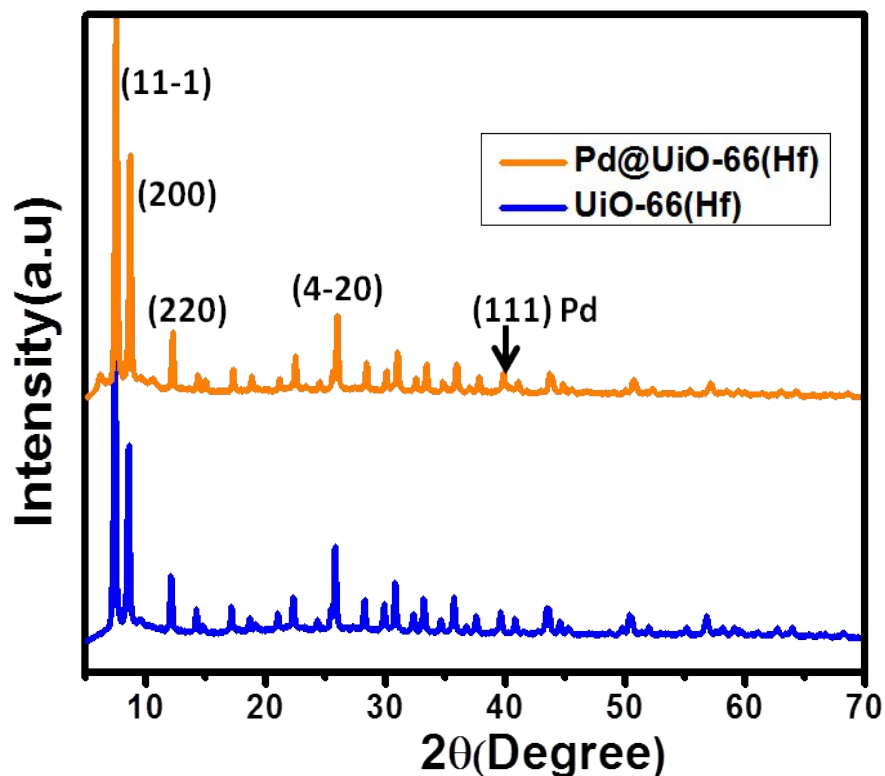


Figure S1: PXRD pattern of as synthesized UiO-66(Hf) and Pd@UiO-66(Hf) materials.

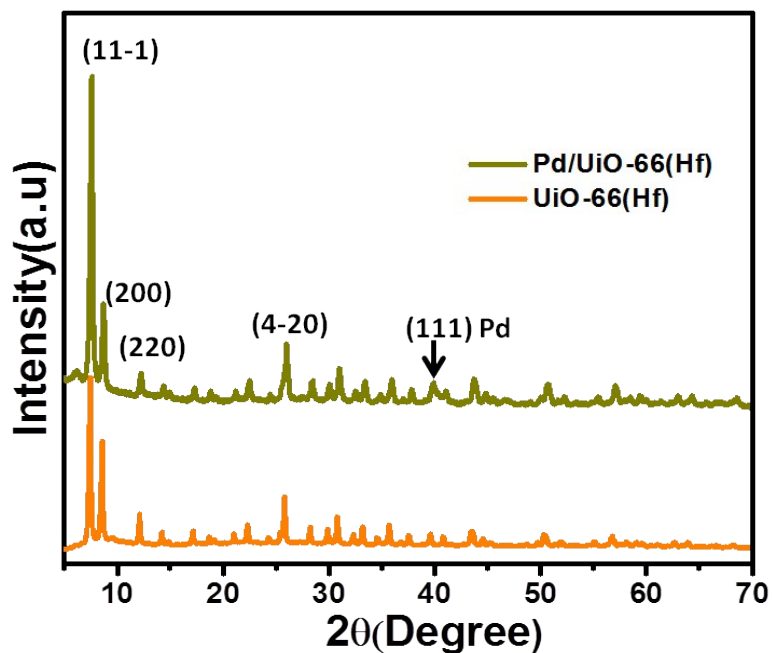


Figure S2: PXRD pattern of as-synthesized UiO-66(Hf) and Pd/UIO-66(Hf) materials.

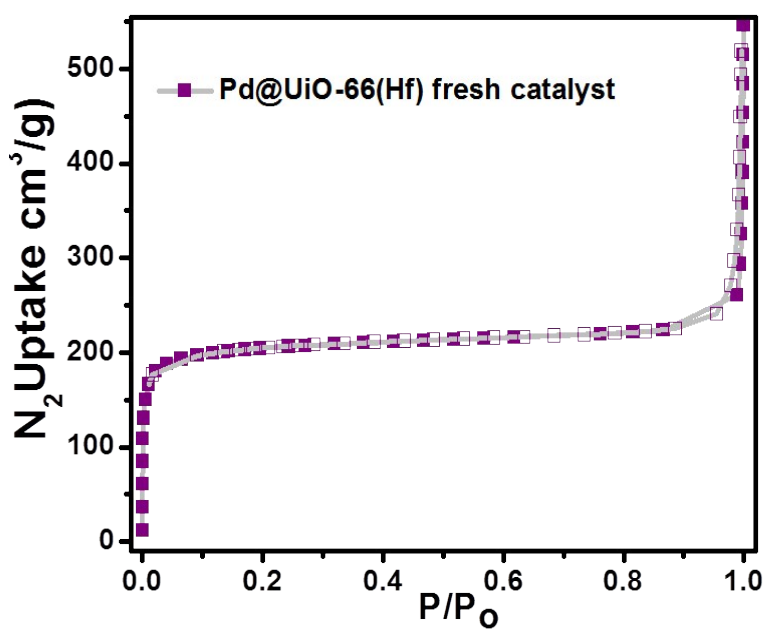


Figure S3: N_2 isotherms (77K) of Pd@UiO-66(Hf) material. Calculated BET surface area and pore volume were $755 \pm 50 \text{ m}^2/\text{g}$ and $0.33 \text{ cm}^3/\text{g}$, respectively.

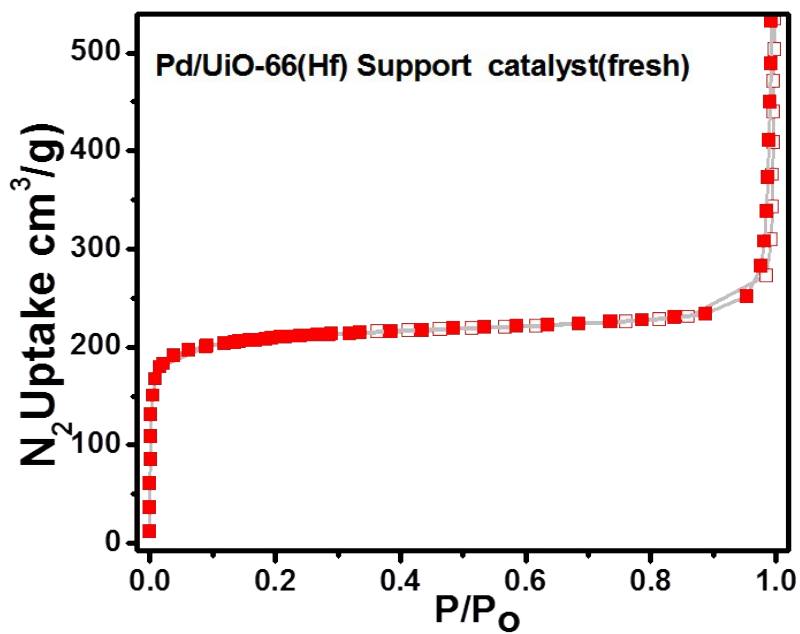


Figure S4: N₂ isotherms (77 K) of Pd/UiO-66(Hf) material. Calculated BET surface area and pore volume were 772± 50 m²/g and 0.33 cm³/g, respectively.

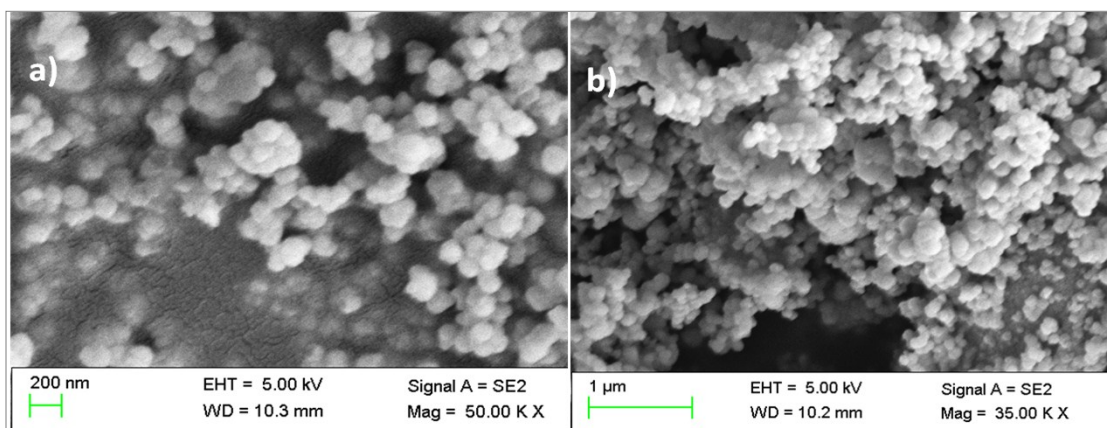


Figure S5: Scanning electron microscopy of a) Pd@UiO-66(Hf) hybrid and b) Pd/UiO-66(Hf) supported materials.

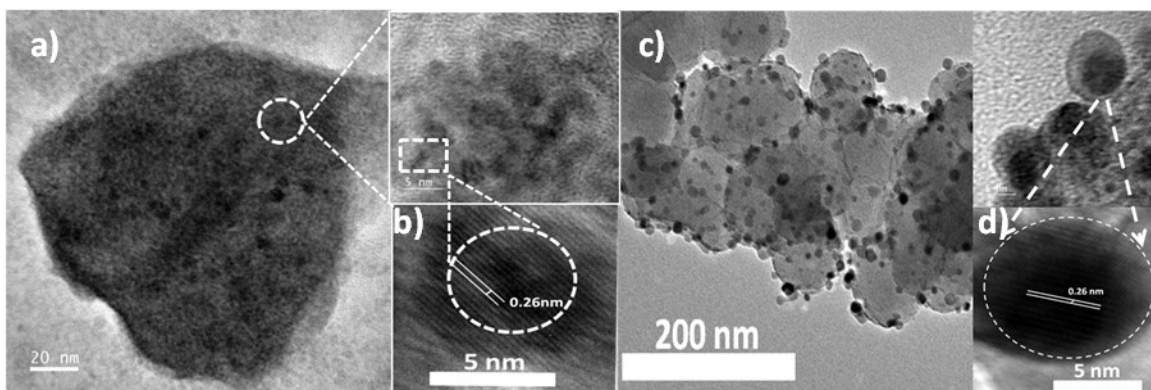


Figure S6: Bright Field Images (a and c) and HR-TEM images (b and d) of Pd@UiO-66(Hf) hybrid and Pd/UiO-66(Hf) supported materials, respectively.

3.1. Potentiometric titration to calculate the strength of acidity of UiO-66(Hf) in Pd@UiO-66 (Hf)

Acidity of neat UiO-66(Hf) and Pd@UiO-66(Hf) materials have been determined by ion exchange method followed by acid-base titration. In a typical procedure, 50 mg of catalyst was soaked in 60 mL of 0.01 M NaNO₃ solution and kept it for stirring for 18 h to undergo ion exchange at room temperature. Each titrant was titrated against 0.1 M aq. NaOH by adding the solution drop wise (0.05 mL) until pH become 10 and above.

Table S1: Calculated pKa values for UiO-66(Hf) and Pd@UiO-66(Hf) materials.

MOF	pKa1 $\mu_3\text{-OH}$	pKa2 -OH_2	pKa3 -OH
UiO-66 (Hf)	3.38	5.77	7.31
Pd@UiO-66 (Hf)	3.40	5.75	7.30

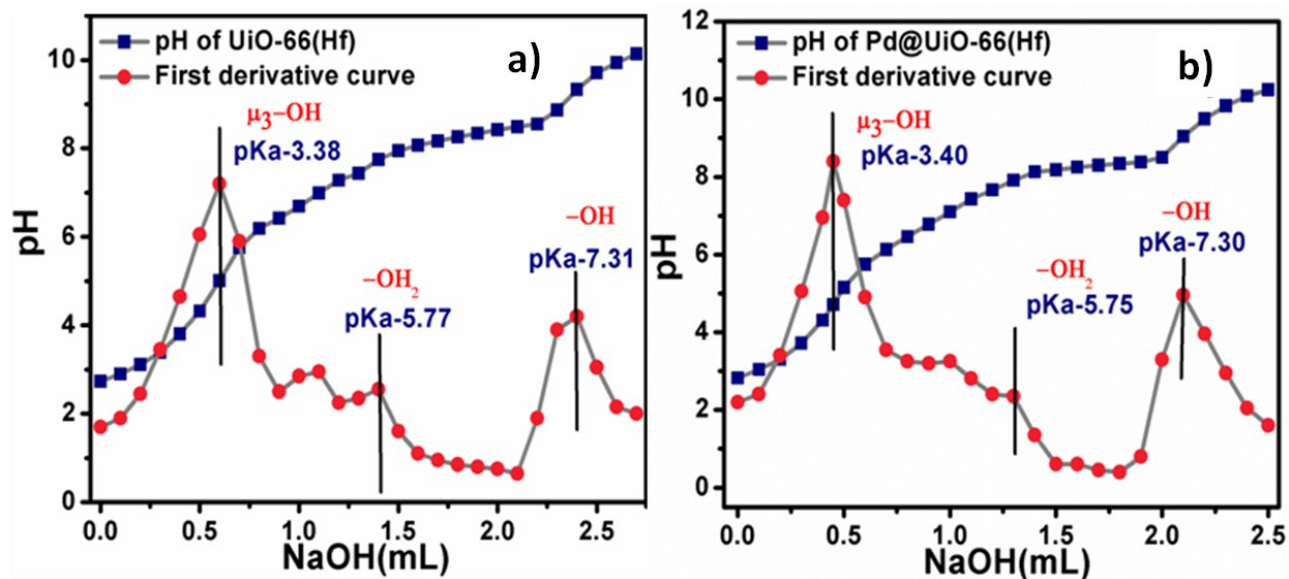


Figure S7: Potentiometric acid-base titration curves for a) UiO-66(Hf) and b) Pd@UiO-66(Hf).

4. Catalysis

4.1. Hydrodeoxygenation of Vanillin

In a typical hydrodeoxygenation reaction, 76.0 mg (0.5 mmol) of vanillin was dissolved in 5 mL of distilled water in a fischer bottle and to the solution 1.2 mol% of Pd with respect to vanillin of catalyst was added. The fischer bottle was closed and reactor purged with 3 bar H_2 gas. Finally, reactor was placed into pre-heated oil bath at 90 °C and reaction was carried out for 2 h. After completion of reaction, reaction mixture temperature was brought to room temperature and to the reaction mixture 2 mL of ethylacetate was added in order to bring all reaction products and reactants into organic solvent. Finally, organic solvent with product mixture was separated from the aqueous solvent using centrifuge. The reaction mixture was analyzed by gas chromatography (GC, Agilent-7820A, and column: HP-5, 30 m \times 0.32 mm \times 0.25 μm). The isolated catalyst was washed with ethanol several times in order to use it for next cycle.

4.2 Turn over frequency(TOF) calculation

Dispersion of Pd calculation:

$$\text{Dispersion} = 6 * M_{\text{Pd}}/\rho_{\text{Pd}} * d_{\text{cm}} * a_{\text{Pd}} * N_{\text{a}} \dots \text{(1)}$$

Here, M_{Pd} = M.Wt of Pd (106.42 g/mol)

ρ_{Pd} = Density of Pd (12.02 g/cm³)

d_{cm} = Average crystallite diameter (7.68×10^{-7} cm)

a_{Pd} = Atomic surface area of Pd (6.8×10^{-16} cm²/atom)

N_a = Avogadro's number

Turn over frequency (TOF) calculation:

$$\text{TOF (h}^{-1}\text{)} = r / n_{\text{tot}} * \text{Dispersion ... (2)}$$

Here, r = Moles converted per hour (rate of hydrogenation)

n_{tot} = Total no. of Pd mole

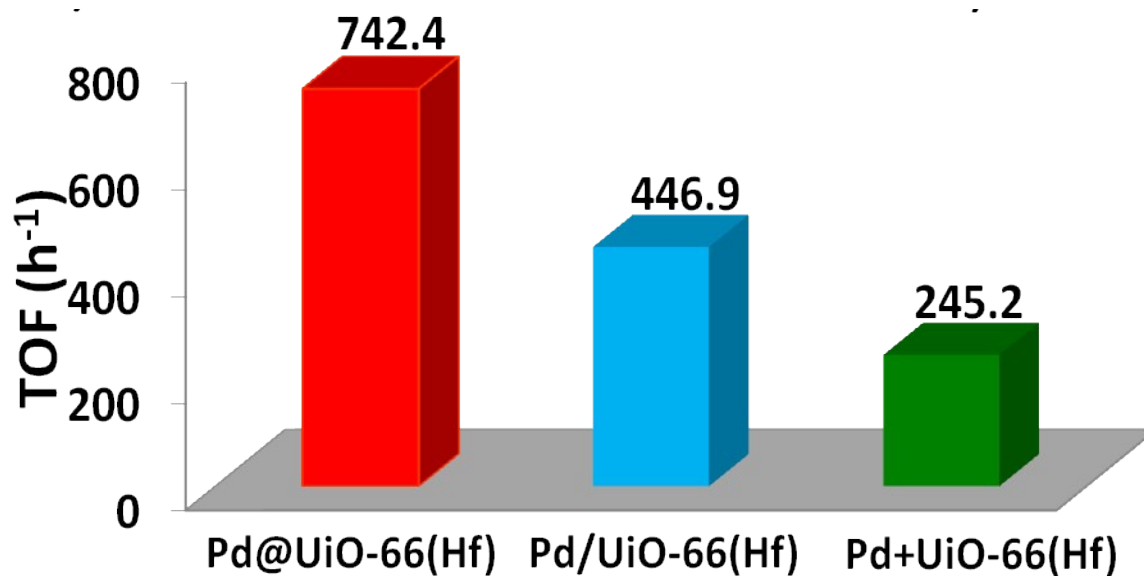
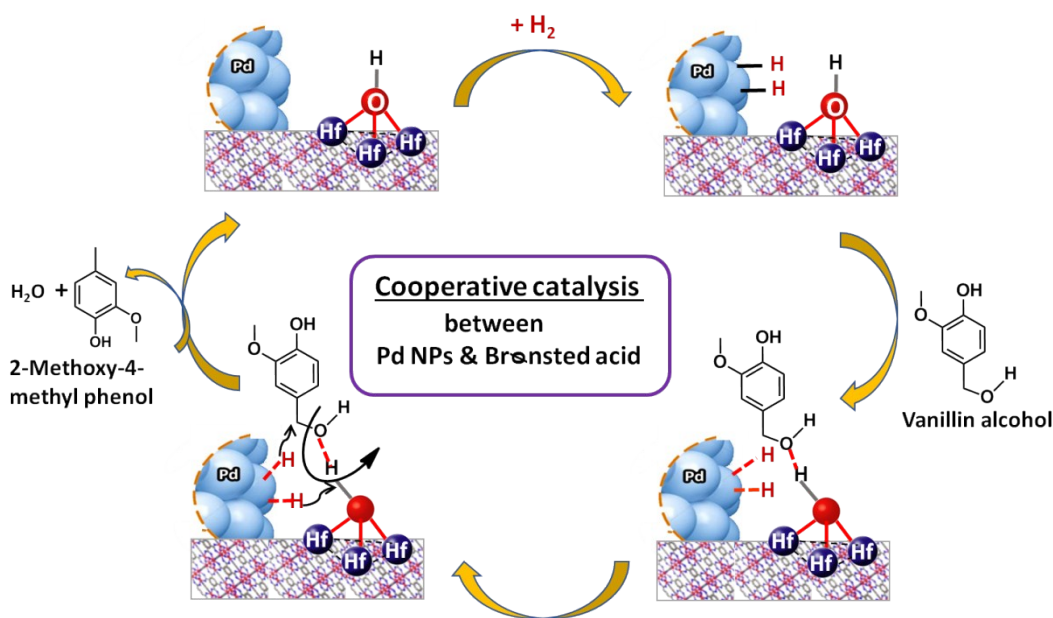


Figure S8: Comparison of TOFs between catalysts. Reaction conditions: 76.02 mg (0.5 mmol) of vanilline, 5 mL of water and 12.5 mg (1.2 mol% of Pd with respect to vanillin) of catalyst.

4.3. Proposed mechanism for dehydrogenation of vanillin alcohol over Pd-UiO-66(Hf) hybrid material.



Scheme S1: Proposed mechanism for vanillin alcohol into 2-methoxy-4-methylphenol over Pd-UiO-66(Hf) material.

In the first step molecular H_2 adsorbed on the Pd NPs followed by dissociation of H_2 molecule. In the second step, the dissociated H/H^+ ions interact with alkyl-OH group of the vanillin alcohol, subsequently water molecule is eliminated.

5. NH_3 treated Pd@UiO-66 (Hf) material

In a typical procedure, ³ 100 mg of Pd@UiO-66(Hf) material was dispersed in 20 mL of ethanol and noted pH of the mixture solution to be 4.53. To this, 2 M NH_3 was added drop wise and pH value of mixture solution was adjusted to 8. Later, this mixture solution was kept under stirring for overnight and after this, Pd@UiO-66 (Hf) material was isolated from ethanol by several washings and dried under vacuum at room temperature. Finally, Pd@UiO-66 (Hf) material was dried at 60 °C for 4h in order to remove excess NH_3 and ethanol.

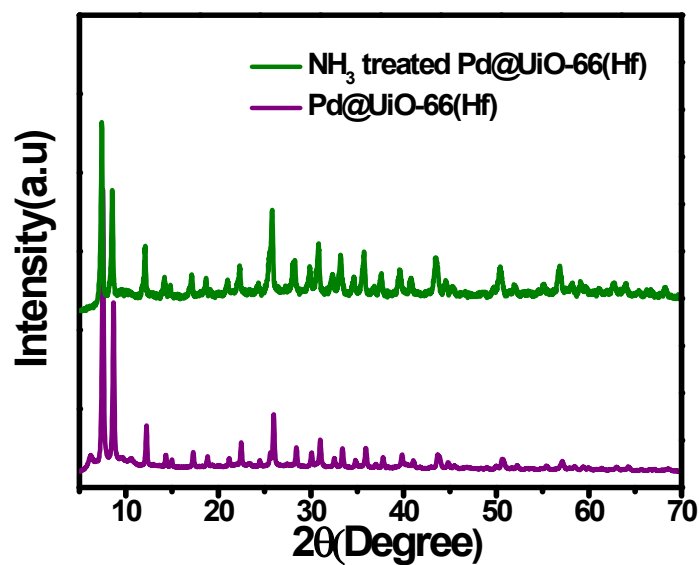


Figure S9: PXRD pattern of Pd@UiO-66 (Hf) material before and after treatment with aqueous NH₃. The material is stable after catalyst poisoning as evident from the data.

5.1. Hydrodeoxygenation of vanillin over Pd@UiO-66 (Hf) and NH₃ treated Pd@UiO-66 (Hf)

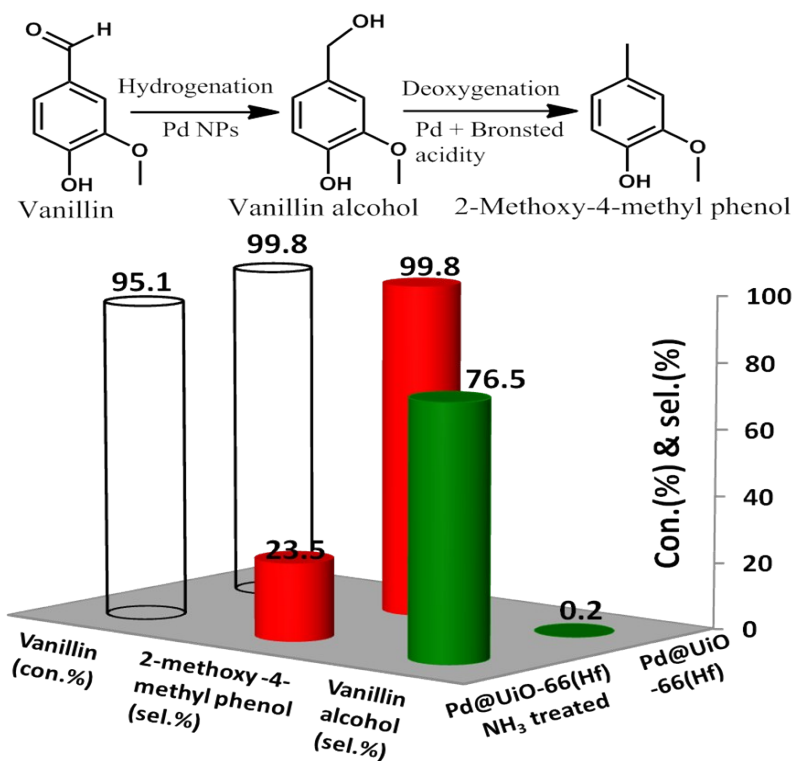


Figure S10: Hydrodeoxygenation of Vanillin over Pd@UiO-66(Hf) and NH₃ treated Pd@UiO-66(Hf). Reaction conditions: 76.02 mg (0.5 mmol) of vanillin, 5 mL of water, 1.2 mol% of Pd with respect to vanillin of catalyst.

6. Characterization of spent catalysts

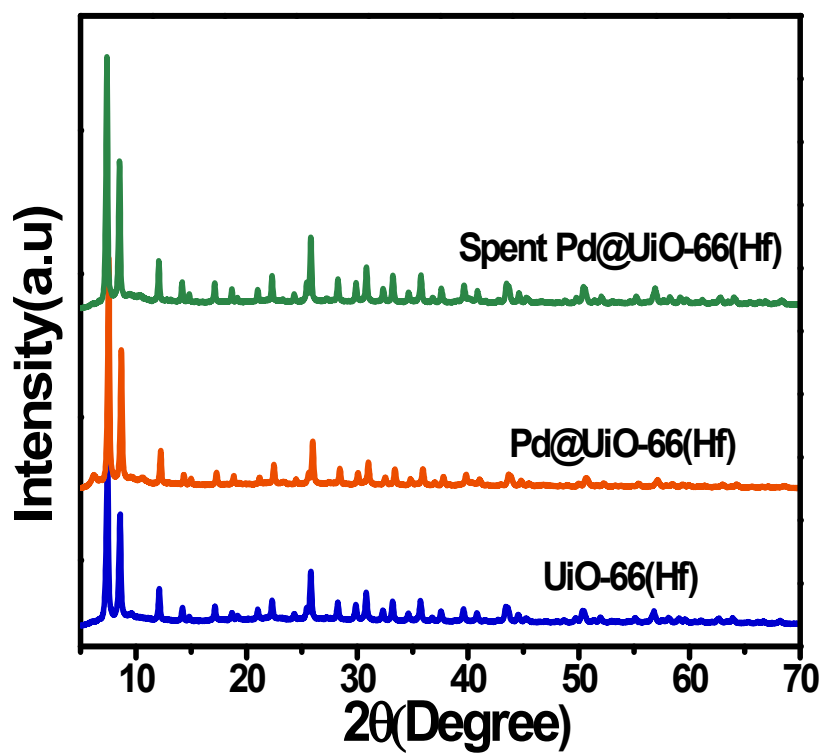


Figure S11: PXRD pattern of fresh and spent materials of Pd@UiO-66 (Hf).

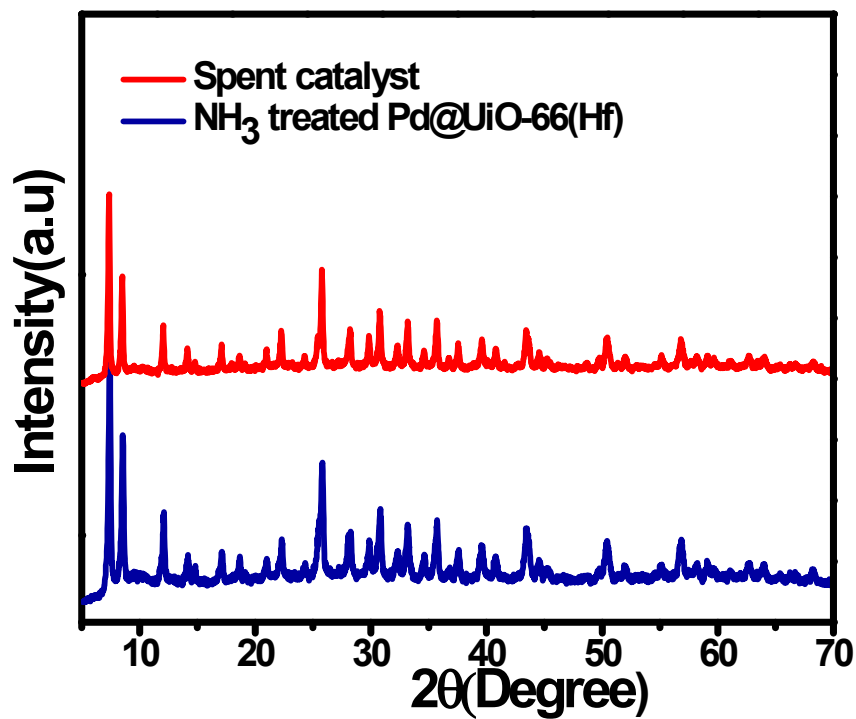


Figure S12: PXRD pattern of fresh and spent materials of NH_3 treated Pd@UiO-66 (Hf).

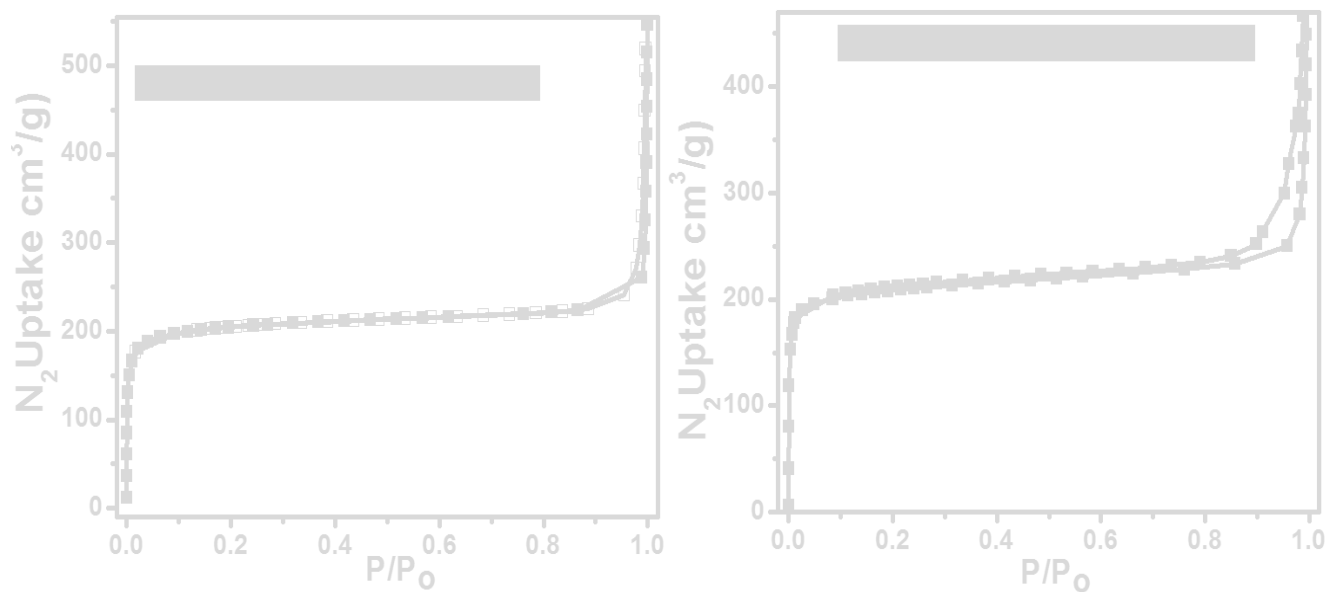


Figure S13: N_2 Isotherms of Pd@UiO-66 (Hf) material before and after catalysis.

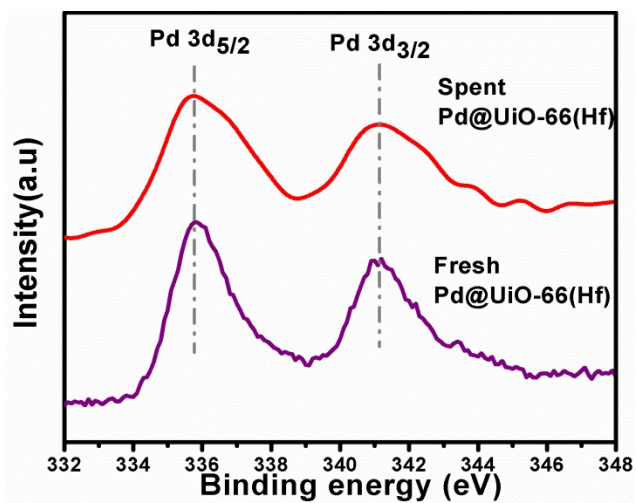


Figure S14: XPS data of fresh and spent Pd@UiO-66(Hf) hybrid materials.

Table S2: BET surface area analysis.

Catalyst	Surface area	Pore volume
Pd@UiO-66(Hf)	$755 \pm 50 \text{ m}^2/\text{g}$	$0.33 \text{ cm}^3/\text{g}$
Pd@UiO-66(Hf) (spent catalyst)	$769 \pm 50 \text{ m}^2/\text{g}$	$0.33 \text{ cm}^3/\text{g}$

Table S3. Comparison between various catalysts for Hydrodeoxygenation of Vanillin.

S. No.	Catalyst	Solvent	Reaction conditions			Conv. Of Vanillin	Selectivity (%)		Ref.	
			Temp.(° C)	Pressure (H ₂ bar)	Time (h)		vanillin alcohol	P-Cresol		
1	Pd/CN _{0.132}	H ₂ O (80 ml)	90	10	1	65	31	69	4	
2	Ru/CNT	H ₂ O/decalin(20 ml)	150	10	3	100	4	96	5	
3	Pd/CM230	Decalin/ H ₂ O (20/10 ml)	100	10	3	99	6	94	6	
4	Pd/C	H ₂ O	100	30	3	100	5	95	7	
5	CIMPA@Pd/Al ₂ O ₃	EtOH(32 mL)	50	13.7	1	>99	-	87 ± 11	8	
6	4.5 wt.% Pd/MSMF	H ₂ O (20 ml)	100	5	1	> 99.5	45.8	54.2	9	
7	5.0 wt.% Pd/SWNT-SiO ₂	H ₂ O /decalin, 20 ml	100	3.5	0.5	85	53	47	10	
8	Au/CNT	Decalin/H ₂ O(20/20)	150	10	8	98	0	100	11	
9	Co/N-C-600	IPA(10 mL)	170	10	4	100	0.5	99	12	
10	Ru1/mpg-C ₃ N ₄	H ₂ O (80 ml)	140	40	4	100	-	100	13	
11	5.0 wt% Pd/12.5 wt% PRGO/Ce-MOF	H ₂ O (40 ml)	100	10	4	100	-	100	14	
12	2.0 wt.% Pd@NH ₂ -UiO-66	H ₂ O (40 ml)	100	5	1	100	-	100	15	
13	2.0 wt.% Pd/SO ₃ H-MIL-101(Cr)	H ₂ O (20 ml)	100	5	5	100	3.9	96.1	16	
14	2.0 wt.% Pd/MIL-101(Cr)	H ₂ O (20 ml)	100	2	2	86.4	17.9	82.1	17	
15	Pd/NPC-ZIF-8	H ₂ O (3 ml)	90	2	2	100	-	100	18	
16	Pd/UiO-66(Hf)	H ₂ O (5 ml)	90	3	2	60.3	8.7	91.3	This work	15
17	Pd@UiO-66(Hf)	H ₂ O (5 ml)	90	3	2	99.8	0.2	99.8	This work	

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