

Electronic Supplementary Information

Construction of Functionalized Hierarchical Pore Metal-Organic Framework via a Palladium-Reduction Induced Strategy

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Experimental section

Chemicals.

Monosodium 2-sulfoterephthalic acid (>98%) was obtained from TCI. HfCl_4 (98+%), acetic acid (99.7+%) and dodecane (99%) were provided by Alfa Aesar. Palladium nitrate ($\text{Pd}(\text{NO}_3)_2$) and vanillin were obtained from Damas-beta. 1-hexene (99%), decane (99%), tetraphenylethylene (97%) and 1,3,5-Trimethylbenzene ($\geq 99\%$) were provided by Shanghai Macklin Biochemical Co., Ltd. Cyclooctene (95%) and crystal violet ($\geq 90\%$) were obtained from Aladdin Industrial Co., China. Methanol, ethanol, ethyl acetate, sodium borohydride, n-hexane, N,N-dimethylformamide and hydrochloric acid were purchased from Sinopharm Chemical Reagent Co., Ltd. All of the chemicals were analytical grade and used without further purification.

Characterization.

The surface morphology of mesoPd@NUS-6 observation was performed on a field emission scanning electron microscope (FESEM, S-4800, HITACHI) and a transmission electron microscope (TEM, JEOL-2100F). The high angle annular dark field (HAADF) and energy-dispersive X-ray spectroscopy (EDS) elemental mapping images were performed on an EDAX Genesis. The power X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer with Cu K α radiation (D8 Advance, Bruker, $\lambda=1.5418 \text{ \AA}$). The gas adsorption isotherms were collected on the surface area analyzer Tristar II 3020. The N_2 sorption isotherms were measured at 77 K using a liquid N_2 bath. ICP measurements were examined on inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Prodigy7). Fourier transform infrared spectroscopy (FT-IR) spectra were obtained using a Bruker VerTex 80v spectrometer. Ultraviolet–visible spectroscopy diffuse reflectance spectra (UV–vis DRS) were attained using a Shimadzu UV–vis spectrophotometer (UV-2550). X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI Quantera II, (ULVAC-PHI, Japan) for chemical composition analysis, all binding energies were calibrated to the C1s peak at 284.8 eV. ^1H MAS and 2D ^1H TQ-SQ and DQ-SQ MAS NMR spectra were carried out in a 1.9 mm MAS probe on a Bruker AVANCE-III 500

spectrometer with a sample spinning rate of 40 kHz, a ^1H $\pi/2$ pulse length of 1.75 μs and a recycle delay of 5 s.

Synthesis of NUS-6(Hf).

NUS-6(Hf) precursor was synthesized and purified according to the previously reported procedures.^{1,2} In this typical procedure, 2.6 g (~ 9.6 mmol) monosodium 2-sulfoterephthalic acid and 3.2 g (~ 10 mmol) HfCl_4 were dissolved in 100 mL mixed solution of water/acetic acid (30/20, v/v) and then heated at 90 $^\circ\text{C}$ for 24 h to yield a powder product. After cooling to room temperature, the resulting white solids were isolated by centrifugation and washed with water three times. And then the product was immersed in anhydrous methanol for 3 days at room temperature, during which, the activation solvent was decanted and fresh methanol was added three times. Finally, the obtained powders were dried overnight at 80 $^\circ\text{C}$ under high vacuum to afford a white powder as the final product.

Synthesis of $\text{Pd}^{2+}@$ NUS-6 composites.

$\text{Pd}^{2+}@$ NUS-6 composites was synthesized according to the previously reported procedures.³ Using the synthesis of 1.0 wt% $\text{Pd}^{2+}@$ NUS-6 as an example, the dehydrated NUS-6(Hf) (200 mg) was suspended in dry *n*-hexane (20 mL) as hydrophobic solvent and the mixture was sonicated for about 30 min until it became homogenous. After stirring for 2h, an aqueous solution of $\text{Pd}(\text{NO}_3)_2$ (29 mg/mL, 150 μL) as hydrophilic solvent was first prepared and then added dropwise over a period of 15 min with constant vigorous stirring. The resulting solution was continuously stirred for another 3 h. After stopping stirring, the solid was isolated from the supernatant by decanting and drying overnight at 80 $^\circ\text{C}$ under high vacuum.

Synthesis of mesoPd@NUS-6 composites.

Using the synthesis of 1.0 wt% mesoPd@NUS-6 as an example, the dehydrated 1.0wt% $\text{Pd}^{2+}@$ NUS-6 (100 mg) was suspended in ethanol (10 mL) and the mixture was sonicated for about 10 min until it became homogenous. The mixed solution was placed in an ice bath and vigorously stirred for 10 min. Then, a freshly prepared aqueous solution of NaBH_4 (3 mg/mL) was added under vigorous stirring. The resulting solution was continuously stirred for another 15 min. The resulting solids

were isolated by centrifugation, washed with ethanol three times. Finally, the obtained powders were dried overnight at 80 °C under high vacuum to afford 1.0wt% mesoPd@NUS-6. Note that the accurate Pd loading amounts are measured to be 0.87 wt%, 2.86 wt% and 5.14 wt%, respectively for mesoPd@NUS-6 (1 wt%, 3 wt% and 5 wt%).

Synthesis of microPd@NUS-6.

The microPd@NUS-6 was synthesized and purified using a sol-gel method according to the previously reported procedures.⁴ In this typical procedure, an aqueous solution of Pd(NO₃)₂ was first prepared, and PVP was added as a protecting agent (PVP monomer/metal = 10 : 1 molar ratio). The mixed solution was placed in an ice bath and vigorously stirred for 1 h. Then, a freshly prepared aqueous solution of NaBH₄ (NaBH₄/metal = 5 : 1 (molar ratio)) was added under vigorous stirring to obtain a dark colloidal dispersion. The pH value of the solution was adjusted to 7–8 with diluted hydrochloric acid. After the Pd-PVP colloids were formed, the activated NUS-6(Hf) was immediately added. The suspension was stirred at 0 °C for 30min followed by washing thoroughly with deionized water. The sample was finally dried at 80 °C under vacuum for 12 h.

Catalytic tests.

The catalytic hydrodeoxygenation of vanillin: The reactions were performed in a 25 mL stainless autoclave. In a typical procedure, vanillin (60 mg, 0.4 mmol) was well dispersed into deionized water (5 mL) followed by adding catalysts. After sonication for 5 min, the autoclave was repeatedly purged with H₂ for 5 times and the pressure was set at 0.15 MPa. Then the reaction solution was magnetically stirred at room temperature for designated time. After the reaction was finished, the products were extracted by ethyl acetate, and the catalyst could be recovered by filtration and washed several times with ethanol, which was finally dried at 80 °C for overnight. The conversion of substrate and the selectivity of target products were authenticated by gas chromatography (GC, Agilent 7890B) equipped with a HP-5 capillary column (30 m × 0.32 mm × 0.25 μm) using decane as an internal standard. For recyclability tests, the catalyst was isolated and washed with ethanol after each reaction and

subsequently reused in the next run with the same reaction conditions.

The catalytic hydrogenation of olefin: The reactions were performed in a 25 mL stainless autoclave. In a typical procedure, 1-hexene (100 uL) / cyclooctene (100 uL) / tetraphenylethylene (20 mg) was well dispersed into ethyl acetate (3 mL) followed by adding catalysts. After sonication for 5 min, the autoclave was repeatedly purged with H₂ for 5 times and the pressure was set at 0.2 MPa. Then the reaction solution was magnetically stirred at 60 °C/ 25 °C / 60 °C for designated time. After the reaction was finished, the products and substrates of 1-hexene and cyclooctene were analyzed by gas chromatography using dodecane as an internal standard. The products and substrates of tetraphenylethylene were analyzed using NMR spectrometer (Bruker AV400 (400MHZ)).

Adsorption of dyes.

A stock solution of crystal violet (CV) (0.025 mg/mL) was prepared by dissolving solid CV in deionized water. To initiate the experiments, adsorbent (5 mg) was put into the aqueous dye solutions (3 mL). After sonication for 5 min, the mixture was continuously stirred for 12 h at room temperature. After the adsorption, the adsorbent was separated from the solutions by centrifugation. Then the concentrations of residual CV in the supernatant solutions were analyzed by UV-vis spectrophotometer.

Supplementary Figures

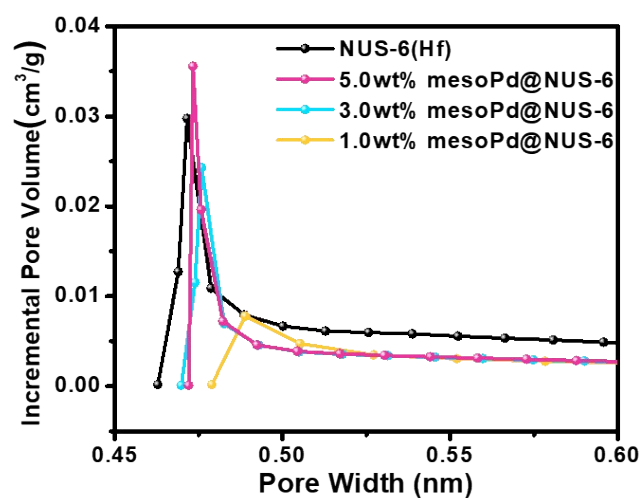


Figure S1. The corresponding pore size distribution profiles of NUS-6(Hf) and mesoPd@NUS-6 with varied loadings (micropore range).

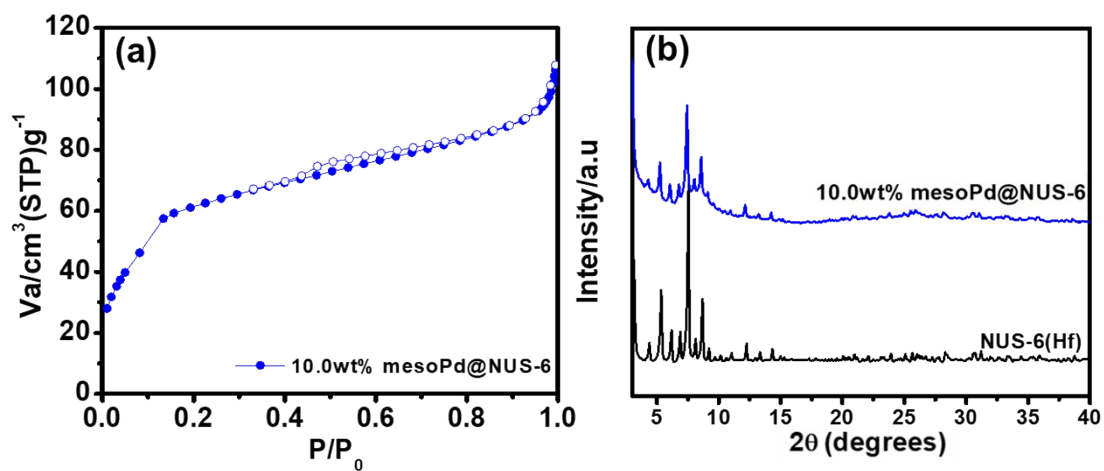


Figure S2. (a) N₂ adsorption-desorption isotherms of the 10.0 wt% mesoPd@NUS-6, and (b) the corresponding powder XRD patterns.

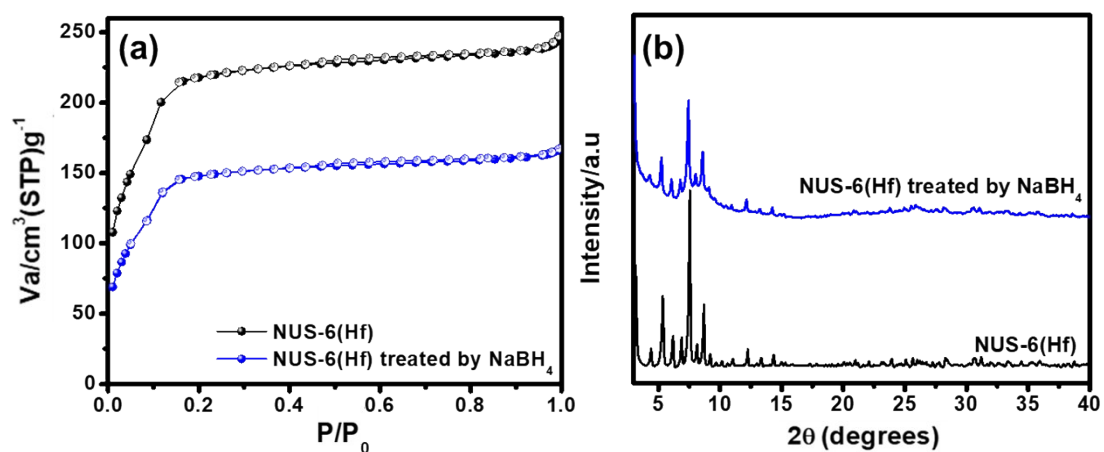


Figure S3. (a) N_2 adsorption-desorption isotherms of the pristine NUS-6(Hf) and NUS-6(Hf) treated by NaBH_4 , and (b) their corresponding powder XRD patterns.

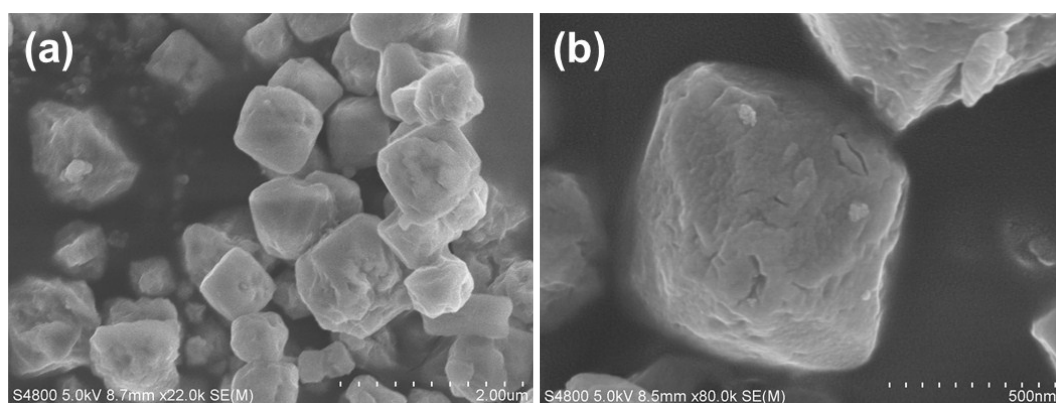


Figure S4. SEM images of the original NUS-6(Hf).

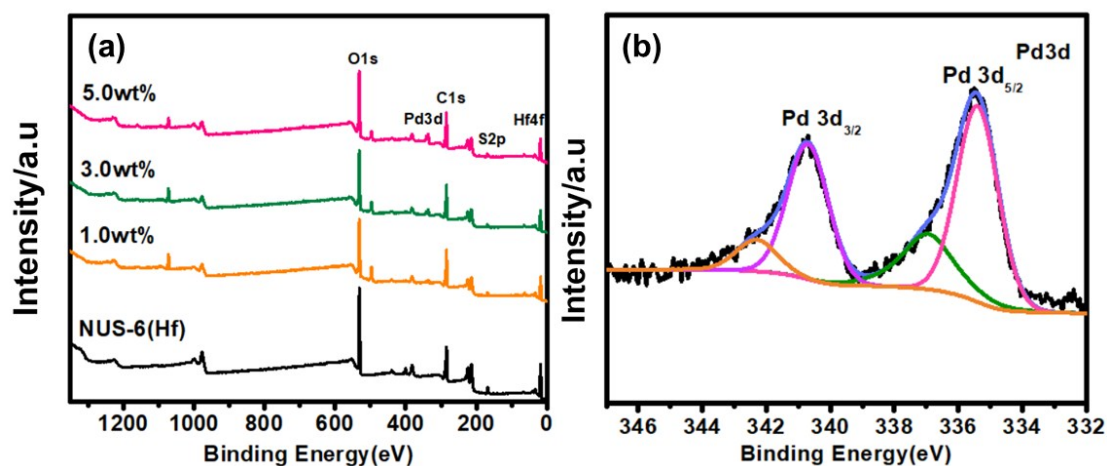


Figure S5. (a) Survey spectra of NUS-6(Hf) and mesoPd@NUS-6 with different weight percent (wt%) loading; and (b) high-resolution Pd3d of 5.0 wt% mesoPd@NUS-6.

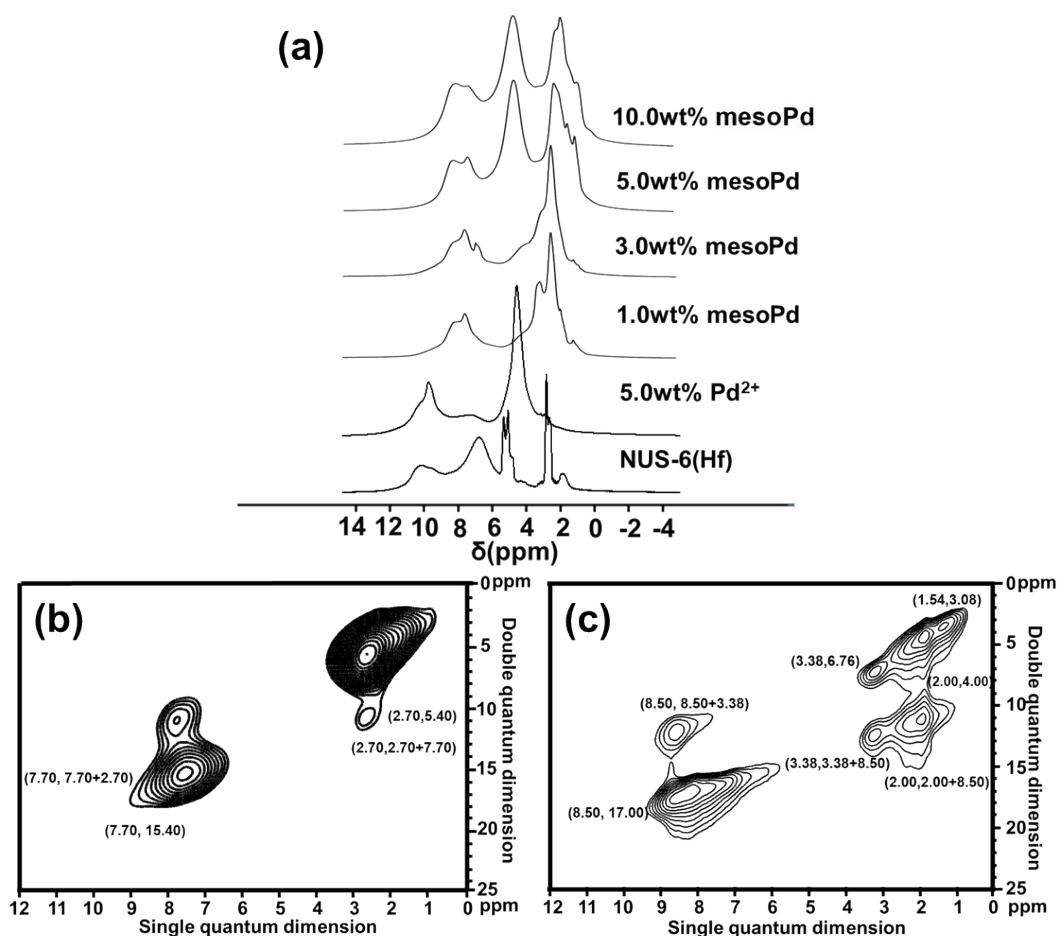


Figure S6. (a) ¹H MAS NMR spectra of NUS-6(Hf), 5.0 wt% Pd²⁺@NUS-6 and mesoPd@NUS-6 with different weight percent (wt%) loading; 2D ¹H DQ-SQ MAS

NMR spectra of (b) 5.0 wt% Pd²⁺@NUS-6 and (c) 10.0 wt% mesoPd@NUS-6.

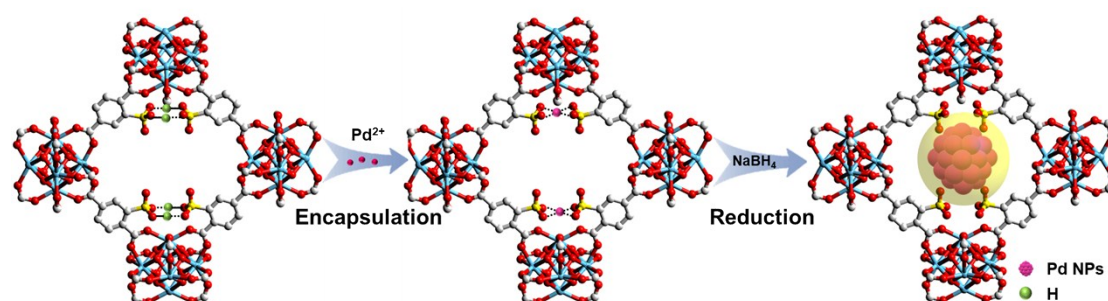


Figure S7. Illustration showing the generation mechanism of mesoporous within NUS-6(Hf) (the yellow ball stands for the pore cage).

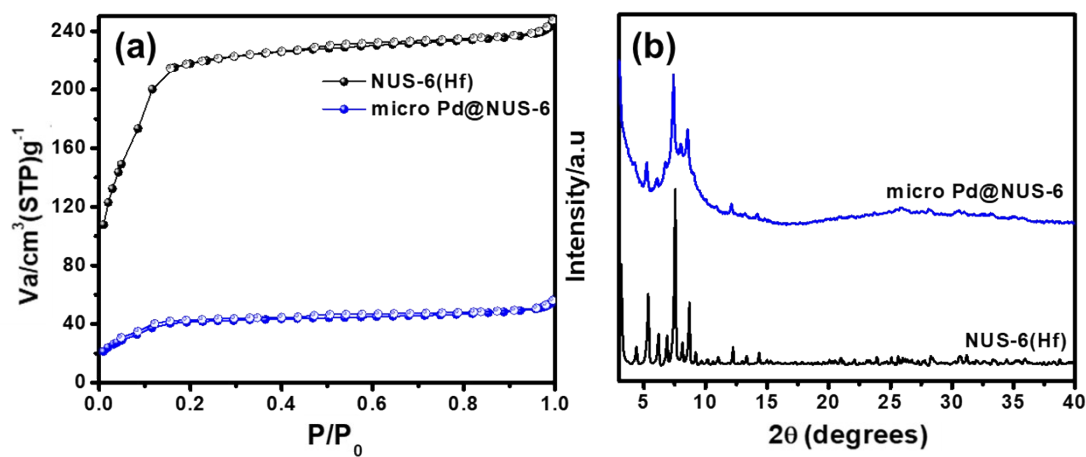


Figure S8. (a) N₂ adsorption-desorption isotherms of the pristine NUS-6(Hf) and microPd@NUS-6, and (b) their corresponding powder XRD patterns.

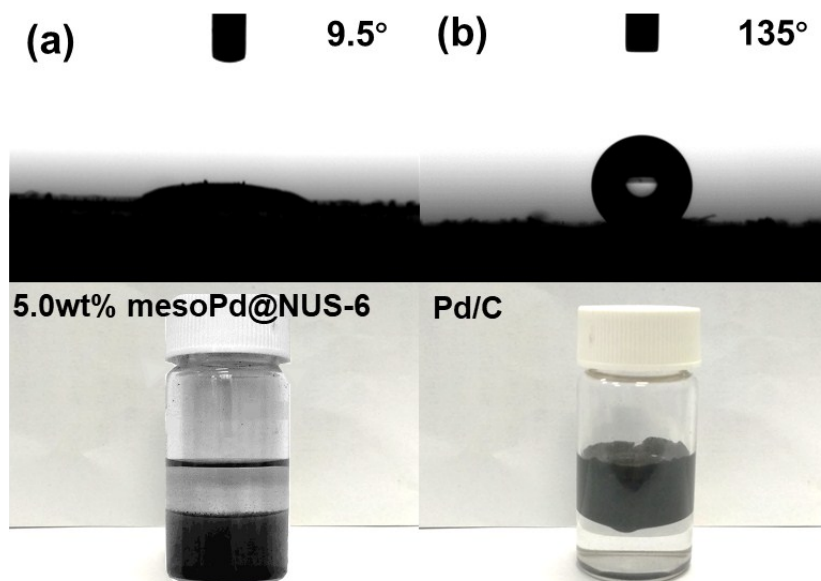


Figure S9. Contact angles of water droplets on 5.0 wt% mesoPd@NUS-6 (a) and Pd/C (b), and their corresponding wettability (water/ethyl acetate).

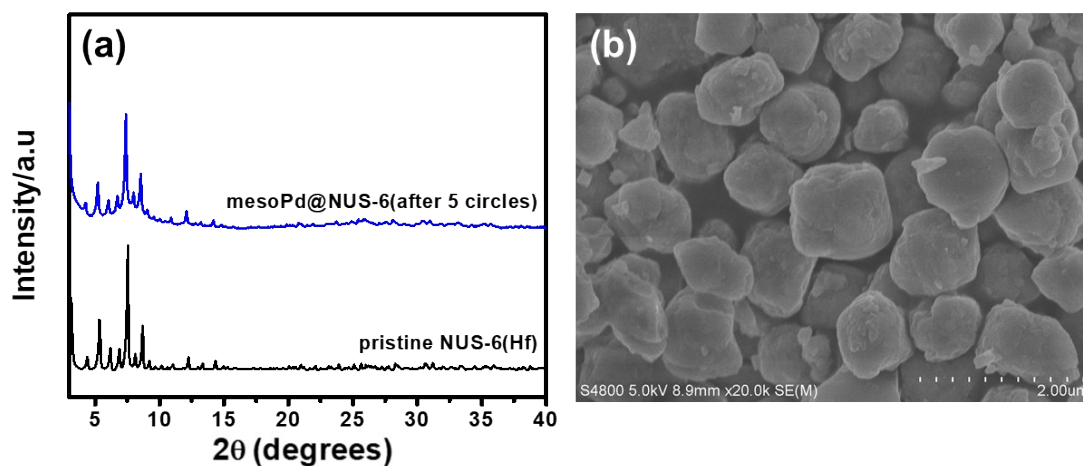


Figure S10. (a) Powder XRD patterns of pristine NUS-6(Hf) and 5.0 wt% mesoPd@NUS-6 after 5 cycles usage; (b) SEM image of 5.0 wt% mesoPd@NUS-6 after 5 cycles usage.

Table S1. Performance of different catalysts in the biodiesel hydrogenation of vanillin.

COc1cc(O)ccc1C=O (A) $\xrightarrow{\text{Hydrogenation}}$ COc1cc(O)ccc1CO (B) $\xrightarrow{\text{Hydrogenolysis}}$ COc1cc(O)ccc1C (C)

Entry	catalyst	temperature [°C]	t[h]	Conv. [%]	Selectivity [%]	
				A	B	C
1	1.0wt% mesoPd@NUS-6	25	24h	48	84	16
2	3.0wt% mesoPd@NUS-6	25	24h	100	44	56
3	5.0wt% mesoPd@NUS-6	25	24h	100	\	100
4	micro Pd@NUS-6	25	24h	97	81	19
5	Pd/C	25	24h	94	51	49
6	NUS-6(Hf)	25	24h	trace	\	\

Reaction conditions: 60 mg of Vanillin, 10 mg catalyst, 5 mL of water, 0.15 MPa H₂, room temperature, 24 h, stir at 500 rpm.

References

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