

Pd, Rh and Ru Nanohybrid-catalyzed Tetramethyldisiloxane Hydrolysis for H₂ Generation, Nitrophenol Reduction and Suzuki-Miyaura Cross-Coupling

Junjie Zhou,^a Wenxin Hou,^a Xiang Liu^{a,c} and Didier Astruc^{b*}*

^aCollege of Materials and Chemical Engineering, Key Laboratory of Inorganic Nonmetallic Crystalline and Energy Conversion Materials, China Three Gorges University, 443002 Yichang, Hubei, China. Email: xiang.liu@ctgu.edu.cn

^bISM, UMR CNRS 5255, Université de Bordeaux, 351 Cours de la Libération, 33405 Talence Cedex, France. E-mail: didier.astruc@ism.u-bordeaux.fr

^cHubei Three Gorges Laboratory, 443007 Yichang, Hubei, China.

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1. Chemicals and Reagents

All chemical medicines and reagents were used without any purification. The deionized water was made in the laboratory. 1,4-Dioxane and 1,1,3,3,-Tetramethyldisiloxane(TMDSO) were purchased from Aladdin Co., Ltd.; reactive red 2 (RR2) was purchased from Rhawn Co., Ltd.; RuCl_3 was purchased from Wuhan ge'ao Chemical Technology Co., Ltd; $\text{Rh}(\text{NO}_3)_3$ was purchased from Macklin Co., Ltd.; K_2PdCl_4 was purchased from Bide Pharmatech Ltd; Deuterium Oxide was purchased from Shanghai Jiuding Chemical Technology Co., Ltd.

2. Characterization techniques

XRD analysis was carried out on a Rigaku Ultima IV. The morphologies of the catalysts were observed by scanning electron microscopy (SEM, HITACHI, SU8020) and transmission electron microscopy (TEM) was recorded on a Tecnai F-20 electron microscope (JEOL 2100F, Netherlands) at an accelerating voltage of 200 kV. XPS surface analysis was performed in an ultra-high vacuum (UHV) chamber by using a Thermo Scientific Escalab 250XI (Thermo Fischer, USA). The textural properties of catalysts were tested by N_2 sorption isotherms on a Micrometrics Tristar II 3020. Electron paramagnetic resonance (EPR) spectroscopy was conducted on a Bruker EMXnano. UV-vis. analysis was performed by using a Shimadzu UV-1900. Energy Dispersive Spectrometer (EDS) Mapping were performed with a TECNAI F-20 microscope (JEOL 2100F) operated at 200 kV. Fourier Transform Infrared Spectrometer (FTIR) of the catalysts was recorded on a PE·Fourier Transform, USA. Atomic Force Microscope (AFM) of the catalysts was studied on a BRUKER Dimension. Raman spectra the of catalysts were measured on a Thermo Scientific DXR.

3. Synthesis of GCN

First, 1 g of Reactive Red 2 was calcined at 600 °C in a tubular furnace with the heating rate of 2.5 °C /min for 4 h. After the reaction was completed, the medium was cooled down to room temperature with a cooling rate of 2.5 °C/min. Then, the residue was collected and washed three times with deionized water and then dried at 60 °C under vacuum oven for 24 h. The final products were denoted as GCN. The yield of GCN catalyst is 10 %.

4. Synthesis of Pd/GCN

First, 100 mg of GCN, 5 mL of deionized water and 0.5 mL of K₂PdCl₄ solution (0.05 M) were added to a 50 mL Schlenk flask, and followed an ultrasonic treatment (5 min). Next, the mixture was allowed to stir for 30 min under N₂ followed by degassing for 5 min. After that, further 15 min stirring was carried out. Subsequently, a colourless solution of NaBH₄ (0.25 mmol in 1 mL water) was added dropwise to above solution. Then the mixture solution was stirred for another 10 min. Finally, the Pd/GCN was collected by centrifugation, washed by water and ethanol and dried at 30 °C overnight. Other nano-catalysts were synthesized by the same method.

5. Hydrogen evolution from the hydrolysis of TMDSO

Generally, hydrogen evolution from the hydrolysis of TMDSO was carried out at 30 °C. 2.6 mg of Pd/GCN nanocatalyst (0.062 mol% Pd) was added into a 50 mL round bottom flask, then 1, 4-dioxane (1 mL) and water (1 mL) were injected into the flask. Once 180 uL of TMDSO was injected in this round bottom flask, and timing started. The Pd to TMDSO ratio was fixed at 0.062 mol %. The flask was fitted with a gas outlet, and a side arm was sealed with a tight-fitting septum cap. The flask was connected *via* the gas outlet to a water-filled gas burette. Gas evolution immediately began, and the amount of gas evolved was determined periodically by measuring the displacement of water in the burette. A quantitative conversion of TMDSO produced 2.0 equivalents of H₂, and occupied ca. 22.4 mL at atmospheric pressure. Prior to the reactions, the volumes were measured at atmospheric pressure and corrected for water vapor pressure at room temperature. Turnover frequency (TOF) is measured to estimate the efficiency of catalyst through the follow equation:

$$TOF = \frac{n_{H_2}}{n_{Pd} \cdot t}$$

n(H₂) is molar of hydrogen, n(Pd) is molar of Pd and t is corresponding reaction time, calculated at 10% conversion of TMDSO hydrolysis

The active energy (E_a) is calculated through the Arrhenius equation:

$$\ln k = \ln A - E_a/RT$$

A is the pre-exponential factor (min⁻¹), k is reaction rate constant, R is 8.314J/(mol·K) and T is reaction temperature (K)

6. Characterization of catalysts (Fig. S1-S17)

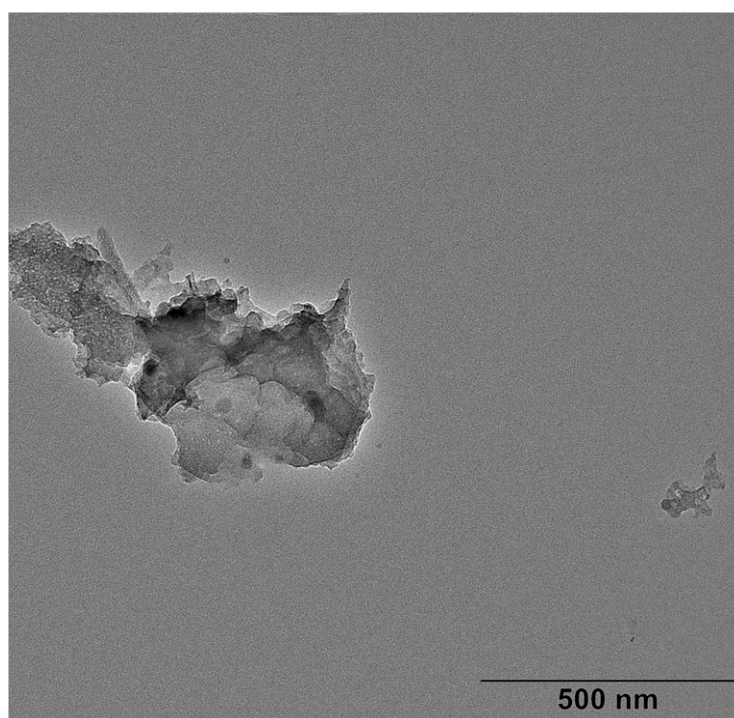


Figure S1. TEM of GCN.

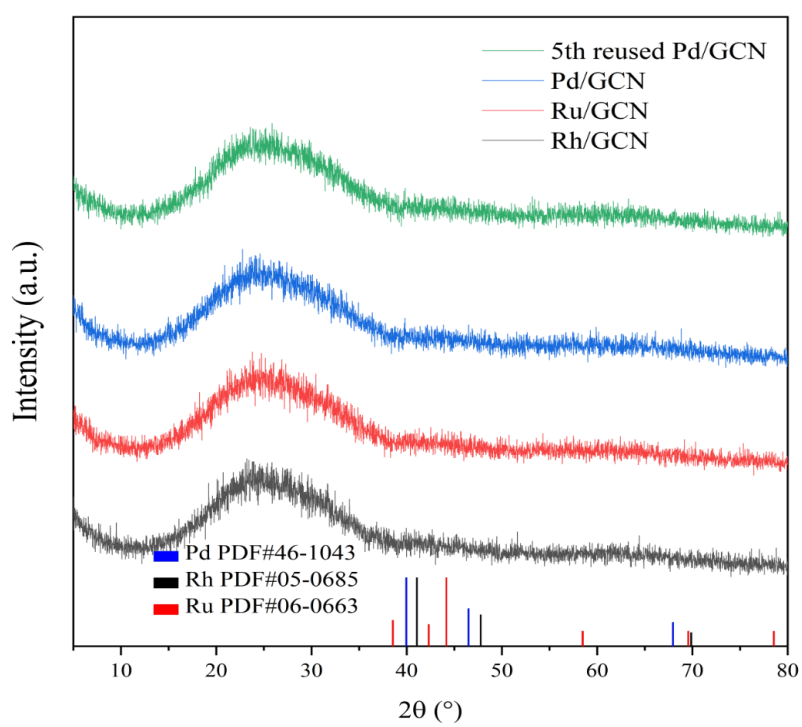


Figure S2. XRD of Pd/GCN, Rh/GCN and Ru/GCN.

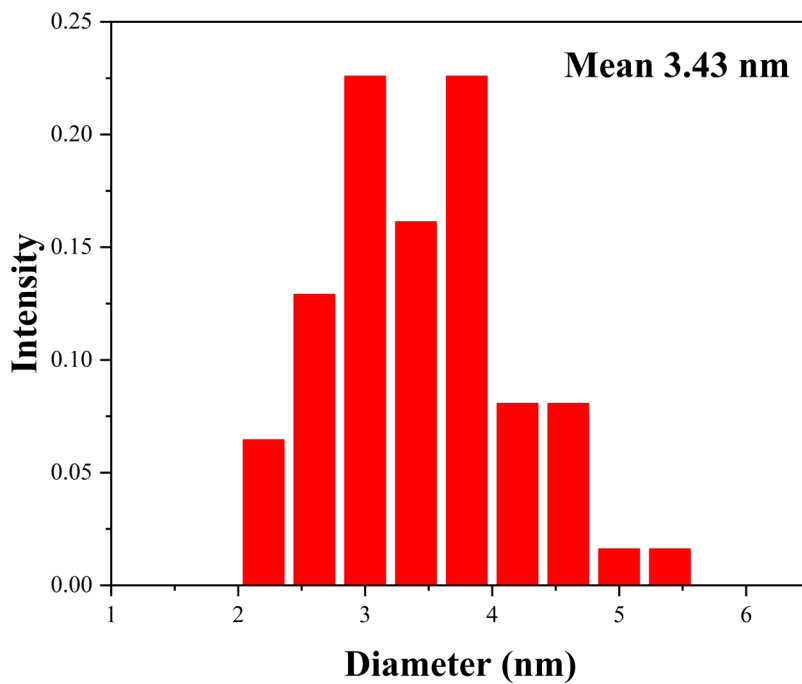


Figure S3. Distribution diagram of Pd/GCN.

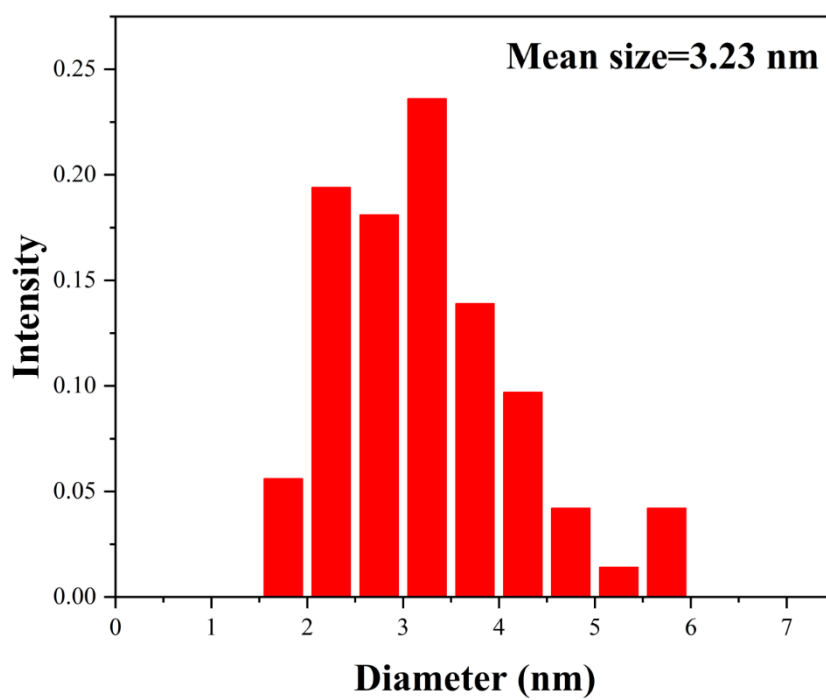


Figure S4. Distribution diagram of Rh/GCN.

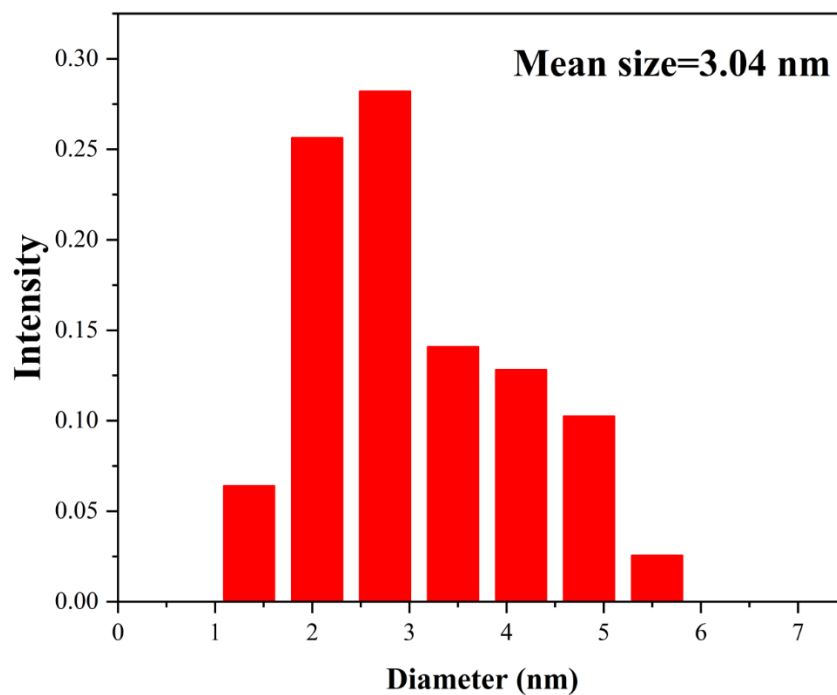


Figure S5. Distribution diagram of Ru/GCN.

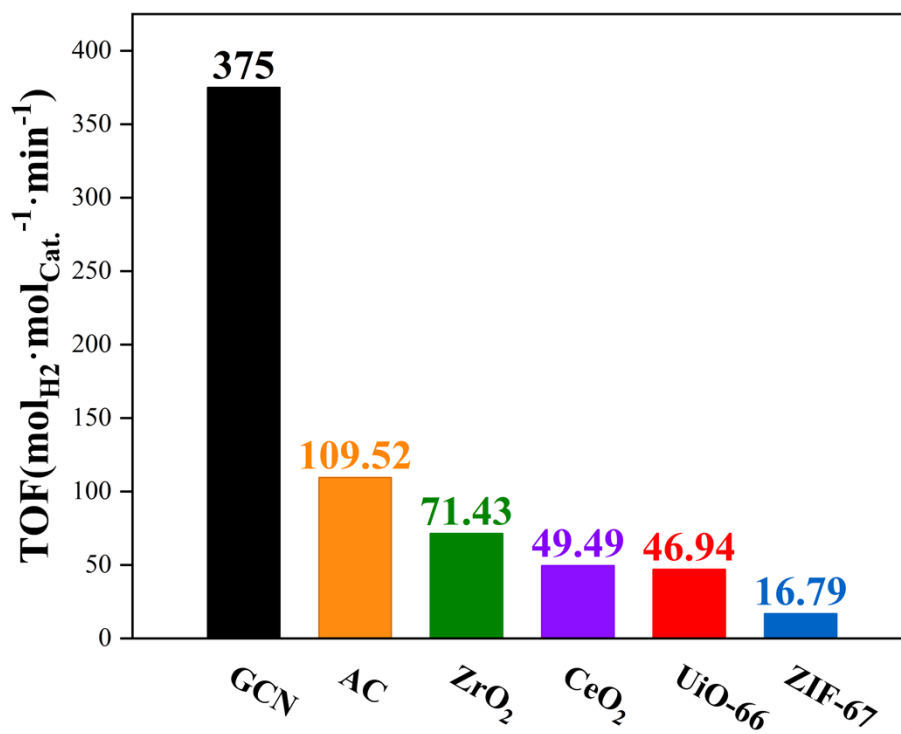


Figure S6. Corresponding TOF ratio of PdNPs on UiO-66, ZIF-67, ZrO₂, CeO₂ and active carbon

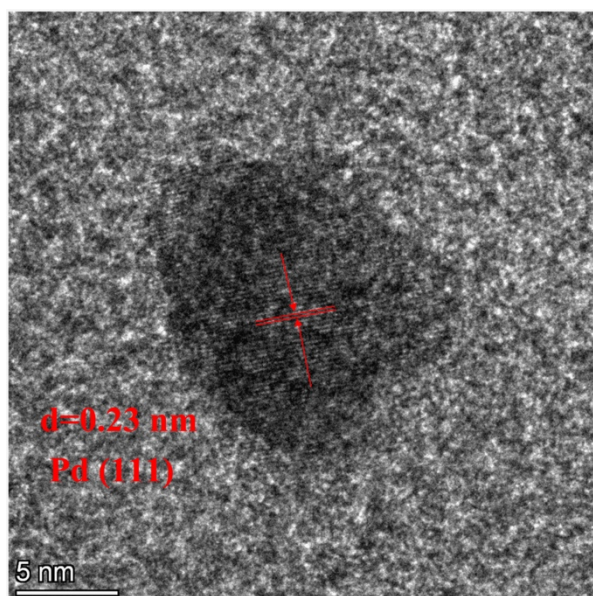


Figure S7. HRTEM of Pd/GCN.

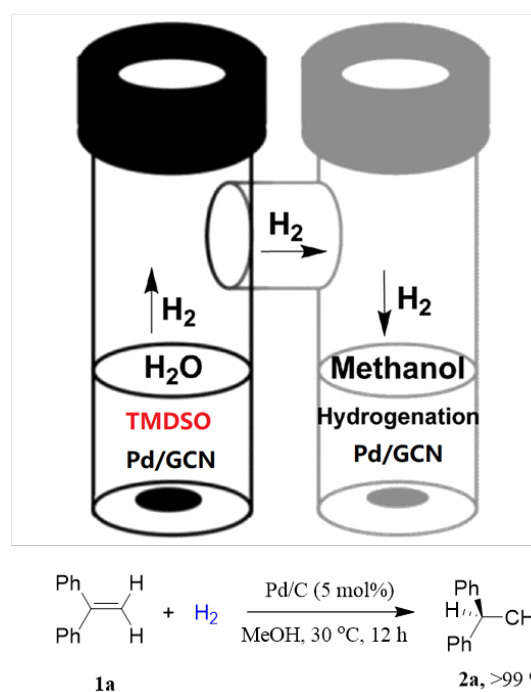


Figure S8. Sealed two-chamber system for the hydrogenation of 1,1-diphenylethene with H₂. Following H₂ evolution, the hydrogenation of styrene in the presence of generated H₂ occurred completely (99% yield) after 12 h at 30 °C. The tandem reaction was reacted in the sealed two-chamber system. The left tube was used for hydrogen generation, and the right one was used for hydrogenation with H₂ generated in the left tube. The generated hydrogen in the left tube transported to the hydrogenation reaction into the right tube through the connecting glass tube.

Hydrogenation of styrene: 1.25×10^{-3} mmol Pd/GCN was added into the left tube. Meanwhile, 10.6 mg (5 mmol % per styrene) Pd/GCN catalyst was added to the right tube. Air was removed *in vacuo*, and 1.5 mL methanol included 17.6 μ L (0.1 mmol) 1,1-diphenylethene was injected into the right tube. Then 4 mmol TMSO was injected into the left tube with 5 mL liquid that water mixed 1, 4-dioxane. After 5 min, reaction was conducted at 30 °C for 12 h. The combined organic phases were washed with brine (2×5 mL), dried over anhydrous MgSO_4 and concentrated under reduced pressure. The residue was subjected to flash column chromatography with hexanes/EtOAc (5:1) as eluent yielding phenylethane as light-yellow liquid.

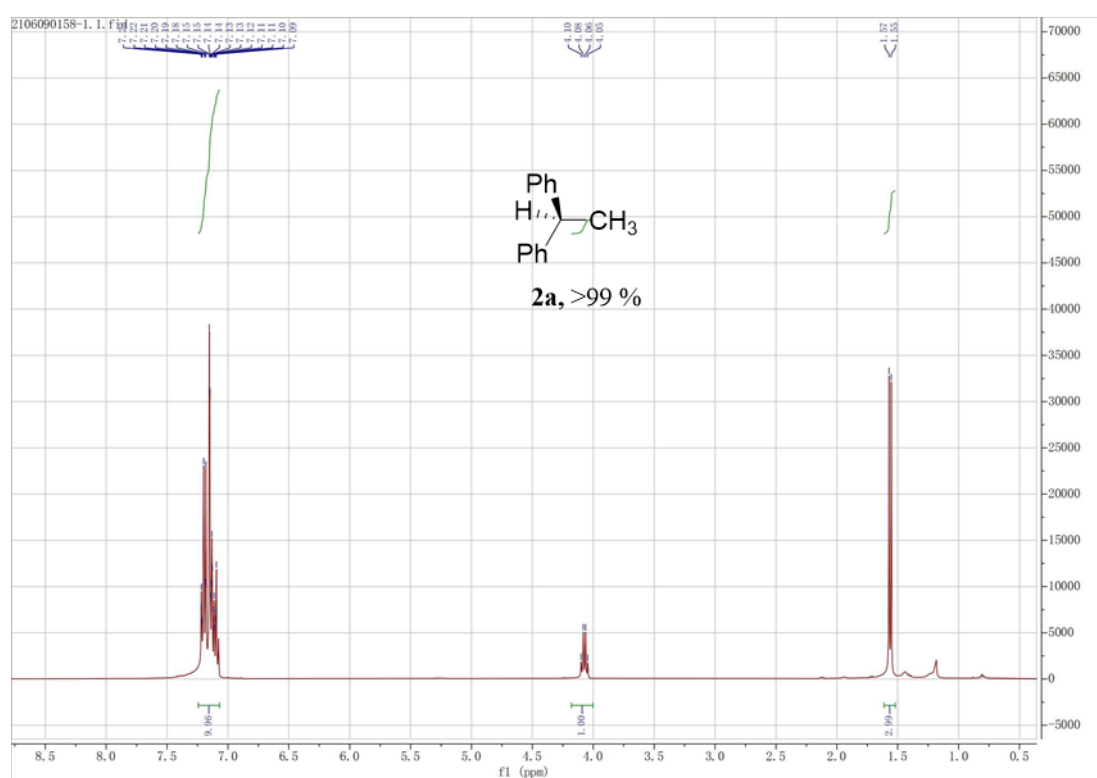


Figure S9. ^1H NMR of ethane-1,1-diyldibenzene. ^1H NMR (600 MHz, CDCl_3) δ 7.09-7.28 (m, 10H), 4.05-4.10 (dd, 1H), 1.55-1.57 (d, 3H).

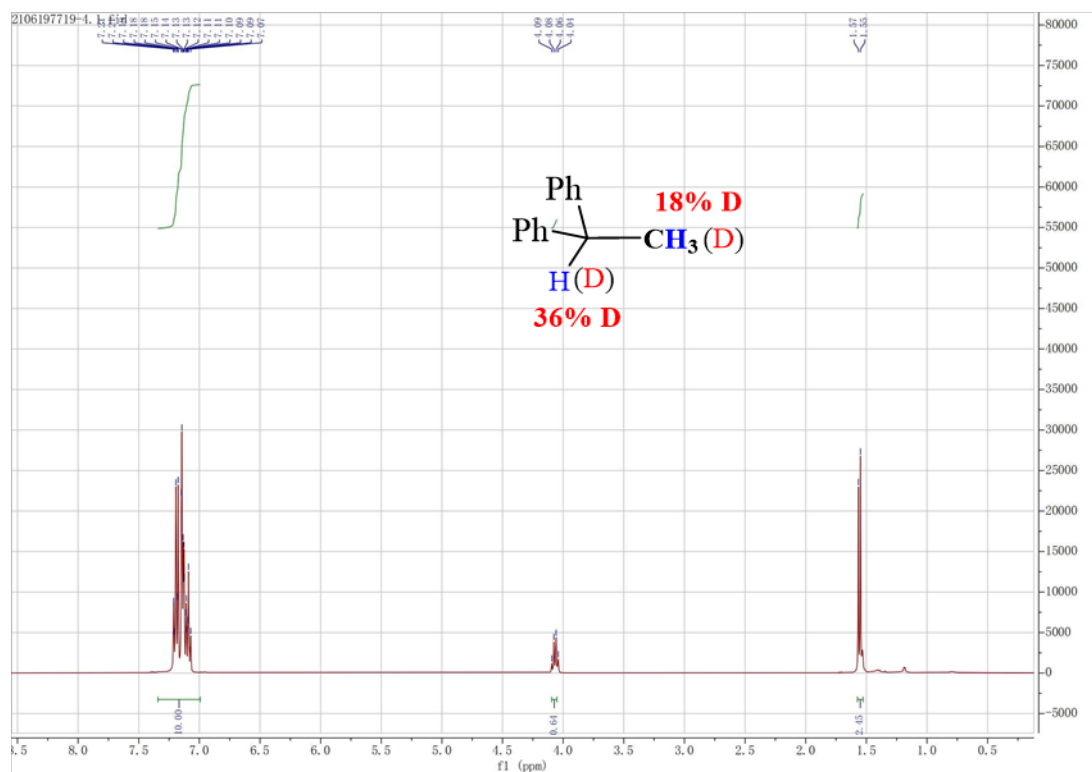


Figure S10. ¹H NMR of deuteration of ethane-1,1-diyldibenzene. ¹H NMR (600 MHz, CDCl₃) δ 7.07-7.21 (m, 10H), 4.04-4.09 (dd, 0.64H), 1.55-1.57 (d, 2.45H).

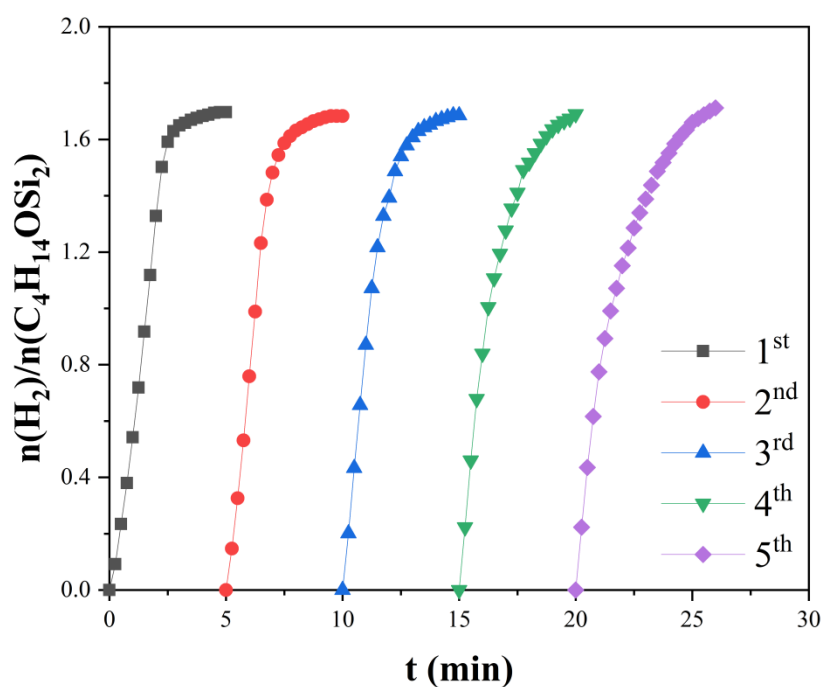


Figure S11. Stability test on Pd/GCN catalyst in the hydrolysis of TMDSO.

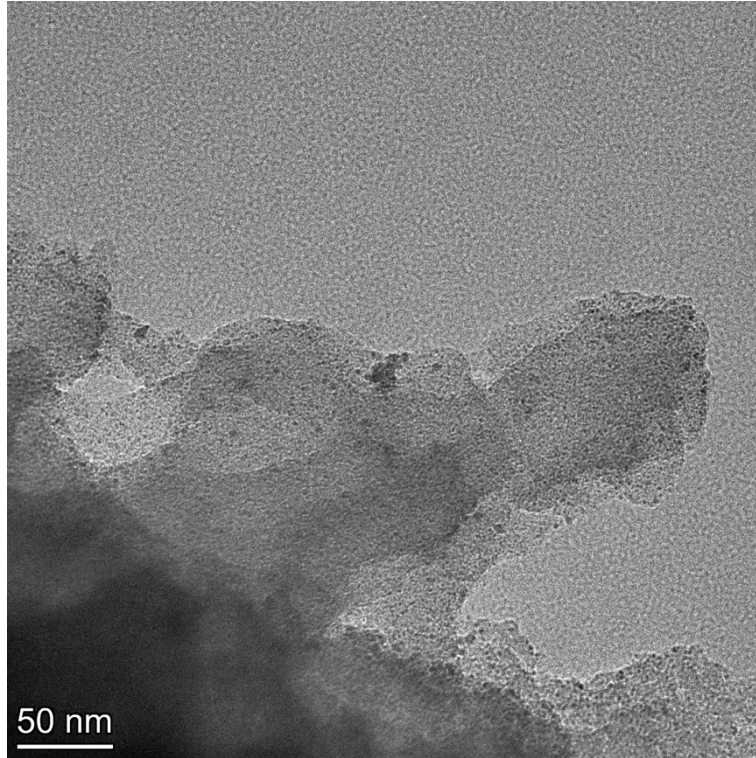


Figure S12. The TEM image of 5th reused Pd/GCN.

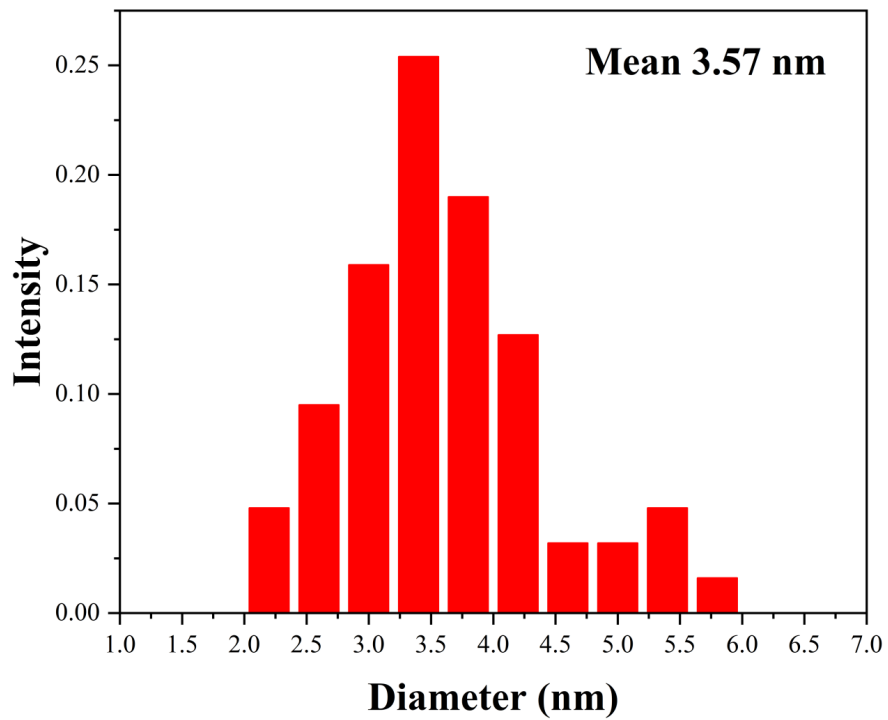


Figure S13. Distribution diagram of 5th reused Pd/GCN.

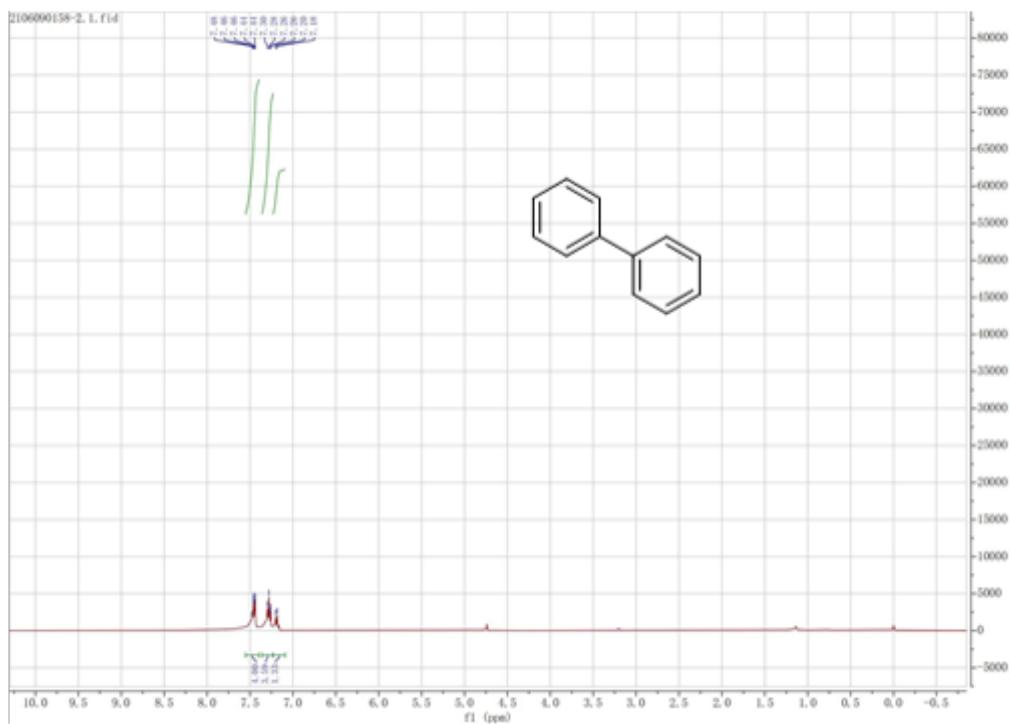


Figure S14. ¹H NMR of deuteration of 1,1'-biphenyl. ¹H NMR (600 MHz, CDCl₃) δ 7.44-7.48 (m, 4H), 7.26-7.30 (m, 4H), 7.18-7.20 (d, 2H).

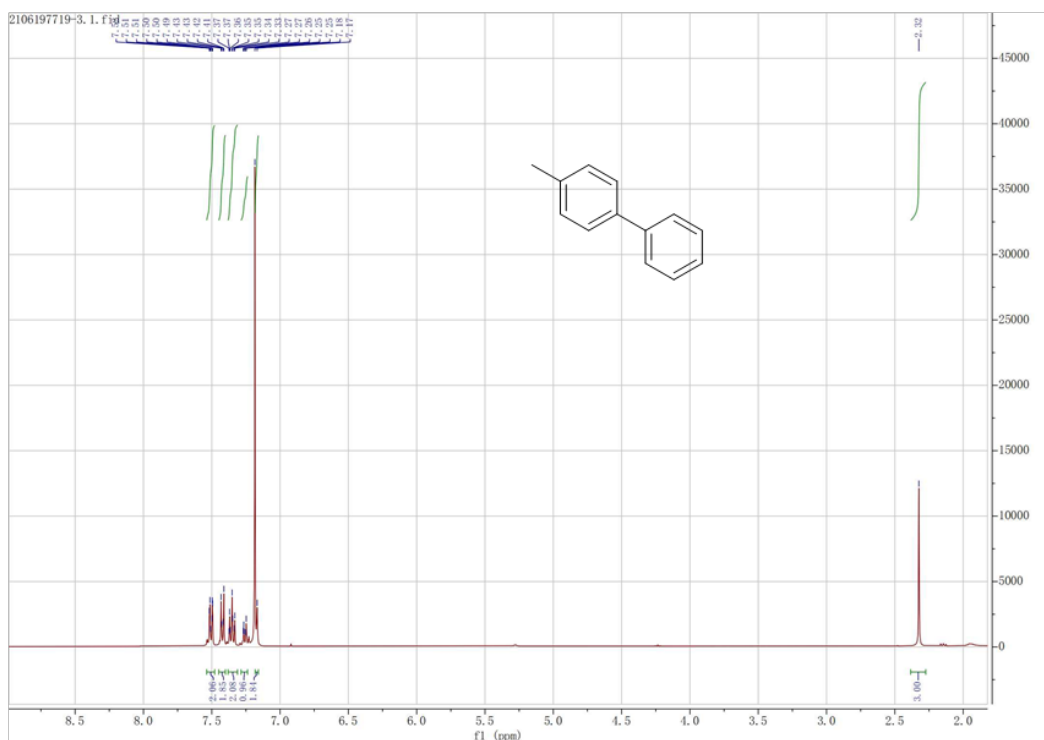


Figure S15. ¹H NMR of 4-methyl-1,1'-biphenyl. ¹H NMR (600 MHz, CDCl₃) δ 7.49-7.52 (m, 2H), 7.41-7.43 (m, 2H), 7.33-7.37 (m, 2H), 7.25-7.27 (m, 1H), 7.17-7.19 (m, 2H), 2.32 (s, 3H)

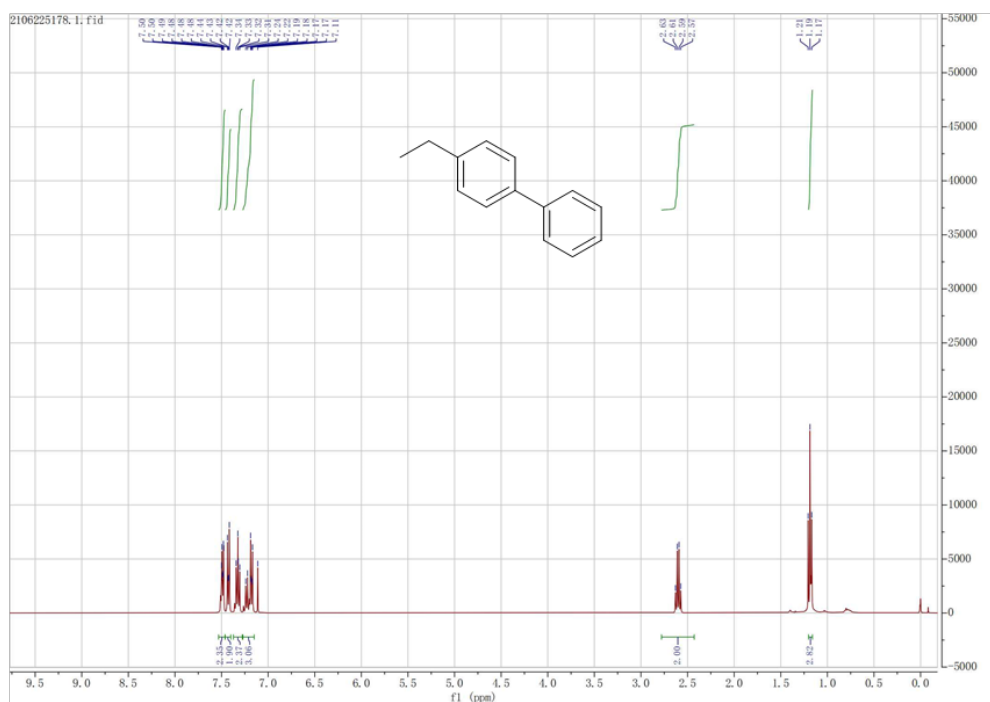


Figure S16. ^1H NMR of 4-ethyl-1,1'-biphenyl. ^1H NMR (600 MHz, CDCl_3) δ 7.48-7.50 (m, 2H), 7.42-7.44 (m, 2H), 7.31-7.34 (m, 2H), 7.17-7.24 (m, 3H), 2.57-2.63 (dd, 2H), 1.17-1.21 (d, 3H)

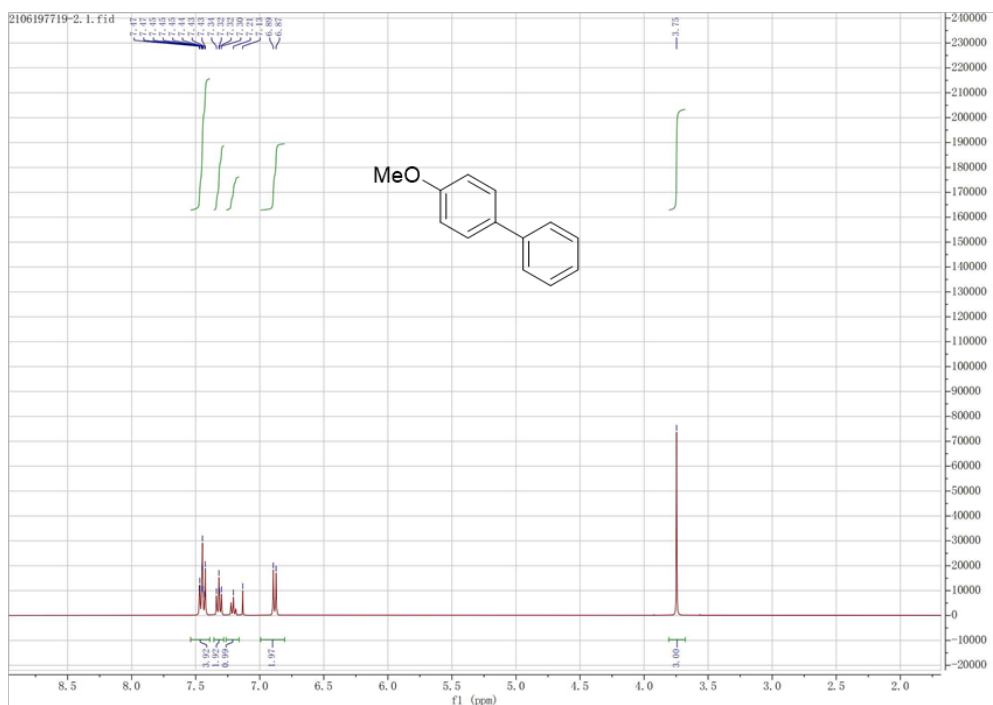


Figure S17. ^1H NMR of 4-methoxy-1,1'-biphenyl. ^1H NMR (600 MHz, CDCl_3) δ 7.43-7.47 (m, 4H), 7.30-7.34 (m, 2H), 7.18-7.20 (m, 3H), 6.87-6.89 (d, 2H), 3.75 (s, 3H).



Figure S18. ¹H NMR of 4-methoxy-1,1'-biphenyl. ¹H NMR (600 MHz, CDCl₃) δ 7.43-7.47 (m, 4H), 7.30-7.34 (m, 2H), 7.19-7.23 (m, 1H), 6.88-6.89 (d, 2H), 3.75 (s, 3H).