

Supporting Materials

Palladium nanoparticles supported on a triptycene-based microporous polymer: Highly active catalysts for CO oxidation

Qian Liang,^a Jian Liu,^a Yuechang Wei,^a Zhen Zhao*^a and Mark MacLachlan*^b

a: State Key Laboratory of Heavy Oil Processing, China University of Petroleum,
Beijing 102249, China.

b: Department of Chemistry, University of British Columbia, Vancouver, BC, V6T
1Z1, Canada.

Materials and Characterization

2,7,14-Tribromotriptycene was prepared by a literature procedure.¹⁻² Other reagents were obtained from standard suppliers. Powder X-ray diffraction was measured with a Shimadzu XRD 6000 using Ni-filtered Cu K α ($\lambda = 0.15406$ nm) radiation operating at 40 kV and 10 mA. The surface morphology of the catalyst was observed by field emission scanning electron microscopy (FESEM) on a Quanta 200F instruments using accelerating voltages of 5 kV. Samples for SEM were dusted on an adhesive conductive carbon belt attached to a copper disk and were coated with 10 nm Au prior to measurement. The TEM and HRTEM images were carried out at an accelerating voltage of 200 kV using a JEOL JEM 2100 electron microscope equipped with a field emission source. Fourier transform infrared spectroscopy (FT-IR) spectra were obtained on a FTS-3000 spectrophotometer manufactured by American Digilab company. The measured wafer was prepared as a KBr pellet with the weight ratio of sample to KBr, 1/100. Specific surface area was measured by adsorption-desorption of N₂ gas at 77 K with Micromeritics ASAP 2000 instrument. Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas from the adsorption data. Before the measurements, the samples were outgassed at 120 °C for 10 h. The surface area of the polymer noticeably decreased after Pd loading. X-ray photoelectron spectra (XPS) were recorded on a Perkin-Elmer PHI-1600 ESCA spectrometer using Mg K α ($h\nu = 1253.6$ eV, 1 eV = 1.603×10^{-19} J) X-ray source. The actual content of palladium supported on NTP was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) (PE, OPTIMA 5300DV). The ¹³C CP/MAS NMR spectra were recorded with the contact time of 2 ms (ramp 100) and pulse delay of 3 s. TGA data was obtained using a Perker Elmer TGA6 instrument.

Synthesis of NTP

1,5-Cyclooctadiene (cod, 900 μ L, 7.35 mmol) was added to a solution of 2,7,14-tribromotriptycene (1 g, 2 mmol), bis(1,5-cyclooctadiene)nickel(0) (2 g, 7.35mmol) and 2,2'-bipyridyl (1.15 g, 7.35 mmol) in dehydrated DMF (15 mL), and the mixture was heated at reflux (85 °C) under N₂ for 96 h. After cooling the mixture to room temperature, concentrated hydrochloric acid (36.5-38.0%) was added. The precipitate was isolated by filtration and washed with CHCl₃, THF and DCM, respectively, and dried overnight to give the product (0.44 g, 85%) as an off-white solid. Elemental analysis for C₂₀H₁₁: Calcd. C, 95.59; H, 4.41. Found: C, 94.21; H, 4.02.

Synthesis of Pd/NTP

An aqueous solution of H_2PdCl_4 (10 mg mL^{-1}) was added dropwise to the NTP support under vigorous agitation for 10 min. The suspension was subjected to sonication (100 W, 40 kHz) at $25 \text{ }^\circ\text{C}$ for 3 h to mix the palladium precursor and porous support NTP evenly. The mixture solution was driven by a peristaltic pump (Baoding Lange Co., Ltd.) at a rotation speed of 200 rpm ($\sim 360 \text{ mL min}^{-1}$) to form a tubal cycling flow. A reductant solution (NaBH_4) (1 mg mL^{-1} , 1 mL min^{-1}) was injected into the membrane reactor with two ceramic membrane tubes ($\phi = 3 \text{ mm} \times 160 \text{ mm}$, Hyflux Group of Companies, Singapore) by a constant flow pump (HLB-2020, Satellite Manufactory of Beijing). At the same time, hydrogen gas was also flowed through the membrane reactor with the other two membrane tubes. The metal precursor solution flowed inside the glass tube reactor and outside the ceramic tubes. The NaBH_4 solution was infiltrated through the abundant holes ($d = 40 \text{ nm}$) on the wall of the ceramic tubes into the glass tube reactor, where the reduction of metal ions occurred immediately when the two solutions met. The hydrogen bubbling-assisted stirring operation (40 mL min^{-1}) was developed to vigorously stir the solution and to make the reaction homogenous. The synthesis process was stopped after complete consumption of the NaBH_4 solution. The reaction system was further vigorously bubbled with hydrogen gas for 1 h and then kept static for 1 h. Then, the product was filtered and washed with distilled water until the Cl^- was completely removed according to a test with AgNO_3 , and the final products were dried in an oven at $60 \text{ }^\circ\text{C}$ overnight and the desired Pd/NTP catalysts were obtained.



Figure S1. Digital photos of GBMR device. The right photo is the ceramic membrane reactor composed of four ceramic membrane tubes, which is the core of the device of GBMR method.

Catalytic reaction

The CO catalysis measurements were performed in a fixed-bed tubular quartz system ($\phi = 8$ mm) under ambient pressure. The reaction temperature was controlled through a PID regulation system based on the measurements of a K-type thermocouple and varied from 20 °C to 400 °C. Reactant gases (50 mL min⁻¹) containing 1 vol% CO, 21 vol% O₂ and 78 vol% Ar were passed through the catalyst bed (0.05 g). Temperature was increased linearly at 5 °C min⁻¹, and remained at every measured temperature point for 30 min to analyze the gas composition. The inlet and outlet gas compositions were analyzed with an online gas chromatograph (GC, Sp-3420, Beijing) by using FID detectors. The catalytic activity was evaluated on the basis of CO conversion, which was calculated with the CO concentration in the reactant gas and in the effluent gas at each temperature point. We calculated CO conversion for each data point as follows: CO conversion (%) = $\{1 - ([CO]/([CO]+[CO_2]))\} * 100$

Supporting Characterization Data

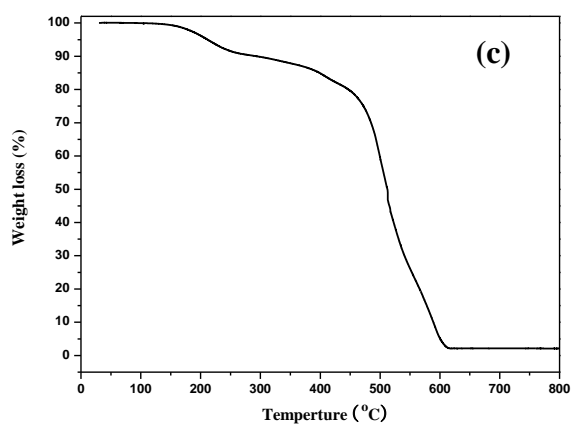
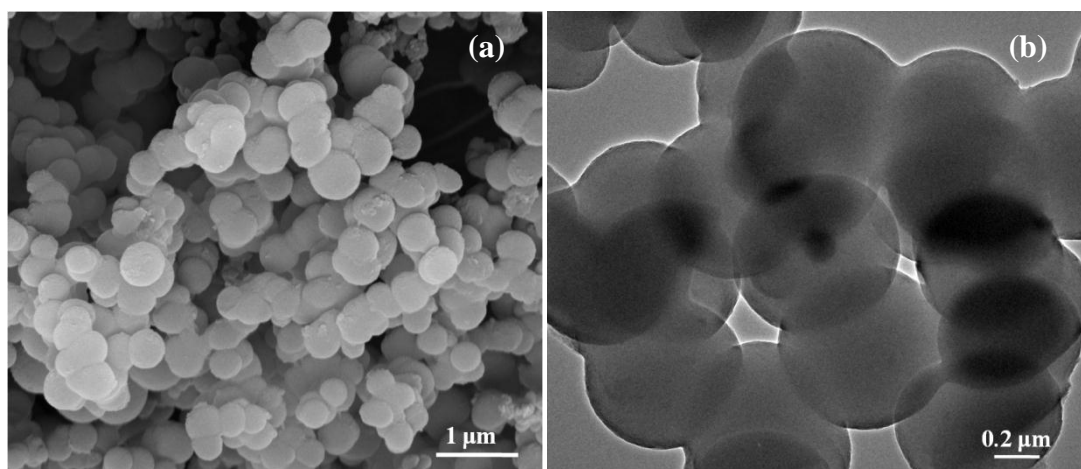


Figure S2. (a) SEM image of NTP; (b) TEM image of NTP; (c) TGA of NTP under nitrogen atmosphere.

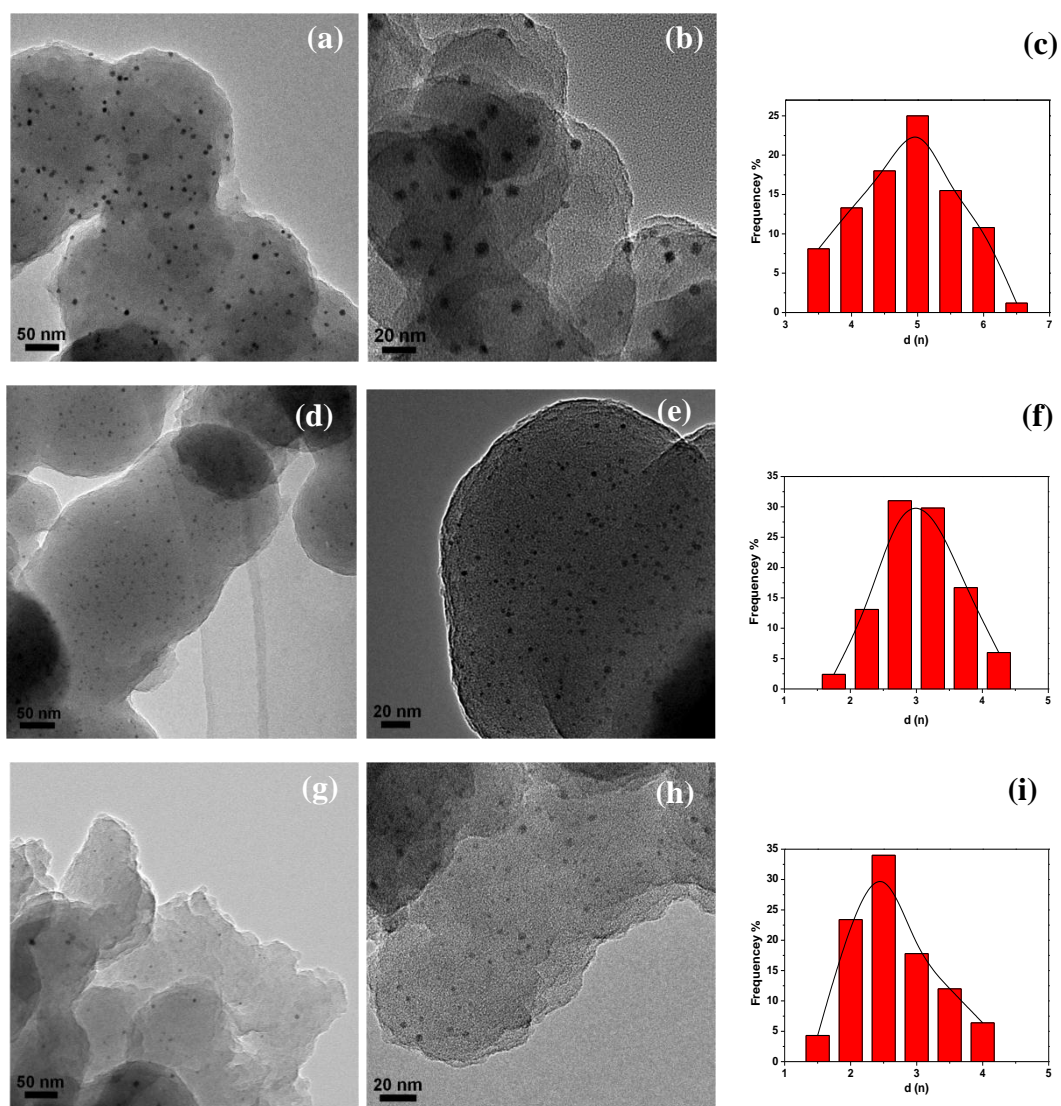


Figure S3. TEM images and size distribution of 4.5 wt% (a, b, c), 2.2 wt% (d, e, f) and 0.9 wt% (g, h, i) Pd/NTP

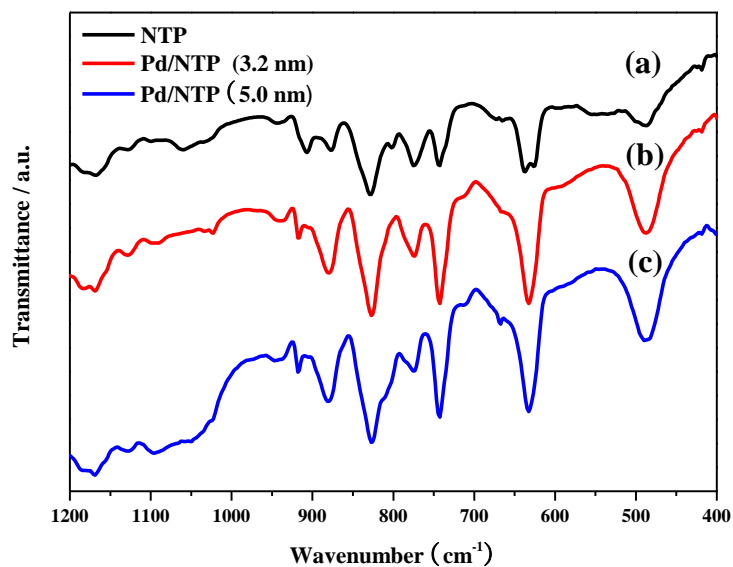


Figure S4. FT-IR spectra of (a) NTP, (b) 3.0 wt% Pd/NTP (3.2 nm) and (c) 4.5 wt % Pd/NTP (5.0 nm). The shift of the peak is nearly unchanged after Pd particles are loaded on the NTP support.

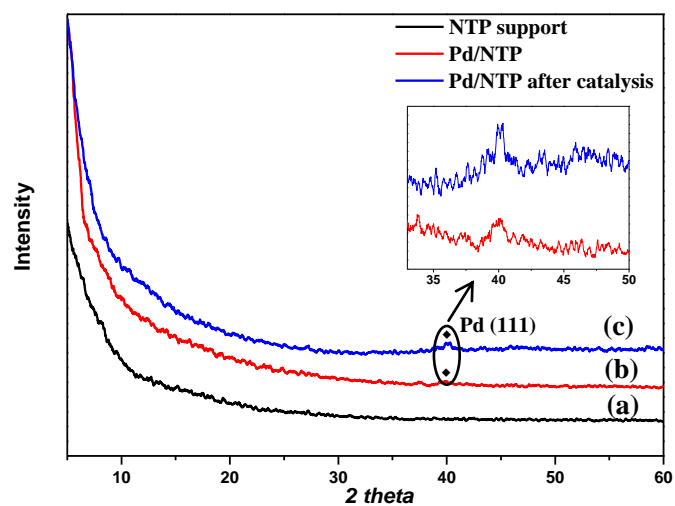
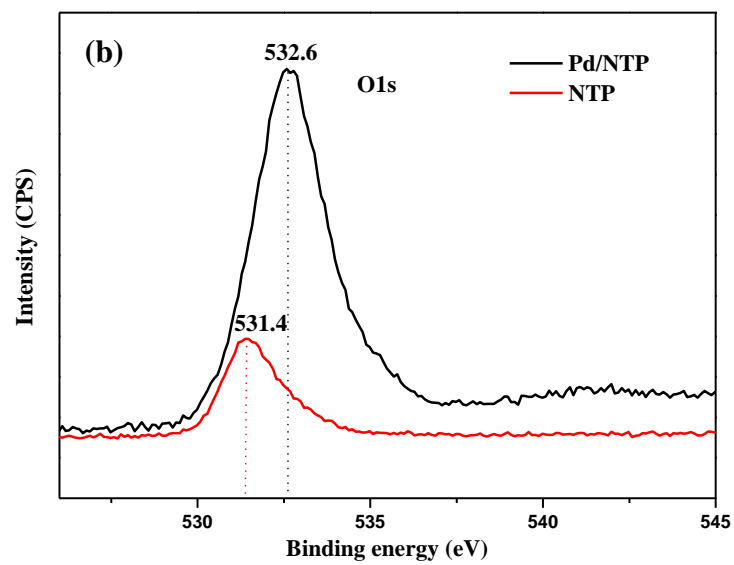
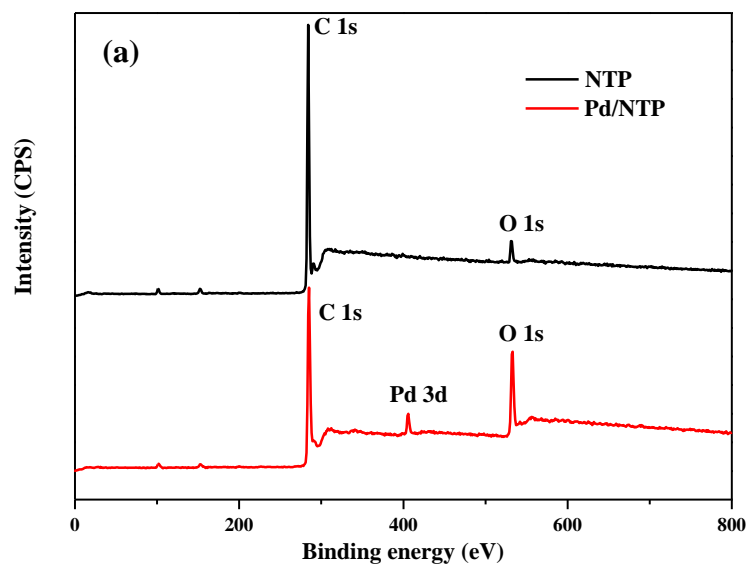


Figure S5. Powder XRD patterns of NTP samples: (a) NTP, (b) Pd/NTP before CO oxidation, (c) Pd/NTP after CO oxidation.



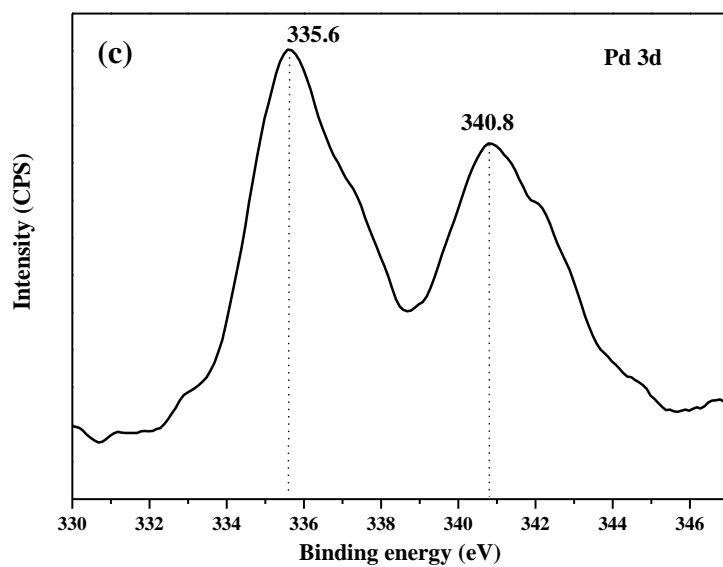


Figure S6. XPS spectra of the NTP and Pd/NTP, (a) survey of the sample, (b) O 1s and (c) Pd 3d.

Table S1. Surface area measurements for the blank NTP and Pd/NTP samples. Median pore width based on Horvath-Kawazoe equation.

Sample	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Langmuir surface area ($\text{m}^2 \text{g}^{-1}$)	Total pore volume ($\text{cm}^3 \text{g}^{-1}$)	Pore width (nm)
NTP	1502	2031	1.16	0.72
0.9 wt% Pd/NTP	1039	1434	0.85	0.70
2.2 wt% Pd/NTP	843	1129	0.54	0.71
3.0 wt% Pd/NTP	1029	1365	0.69	0.72
4.5 wt% Pd/NTP	701	953	0.42	0.70

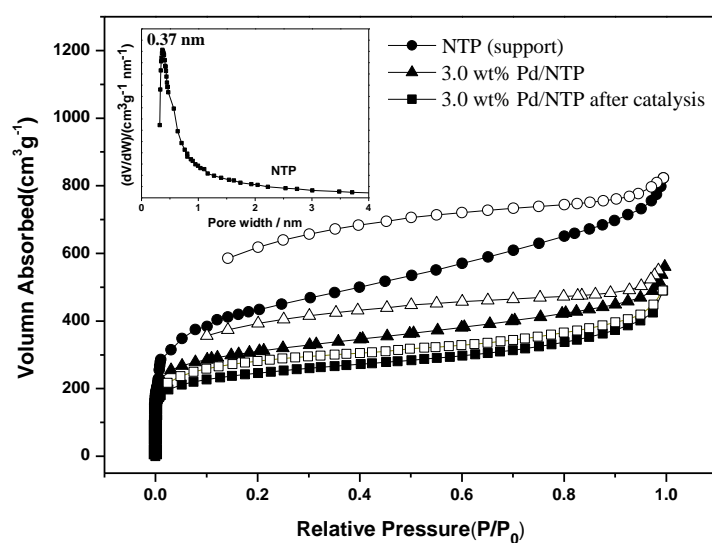


Figure S7. Nitrogen adsorption isotherms of NTP and 3.0 wt% Pd/NTP samples before and after CO oxidation measured at 77 K. HK pore size distribution of pure NTP. Empty symbols represent the desorption isotherms.

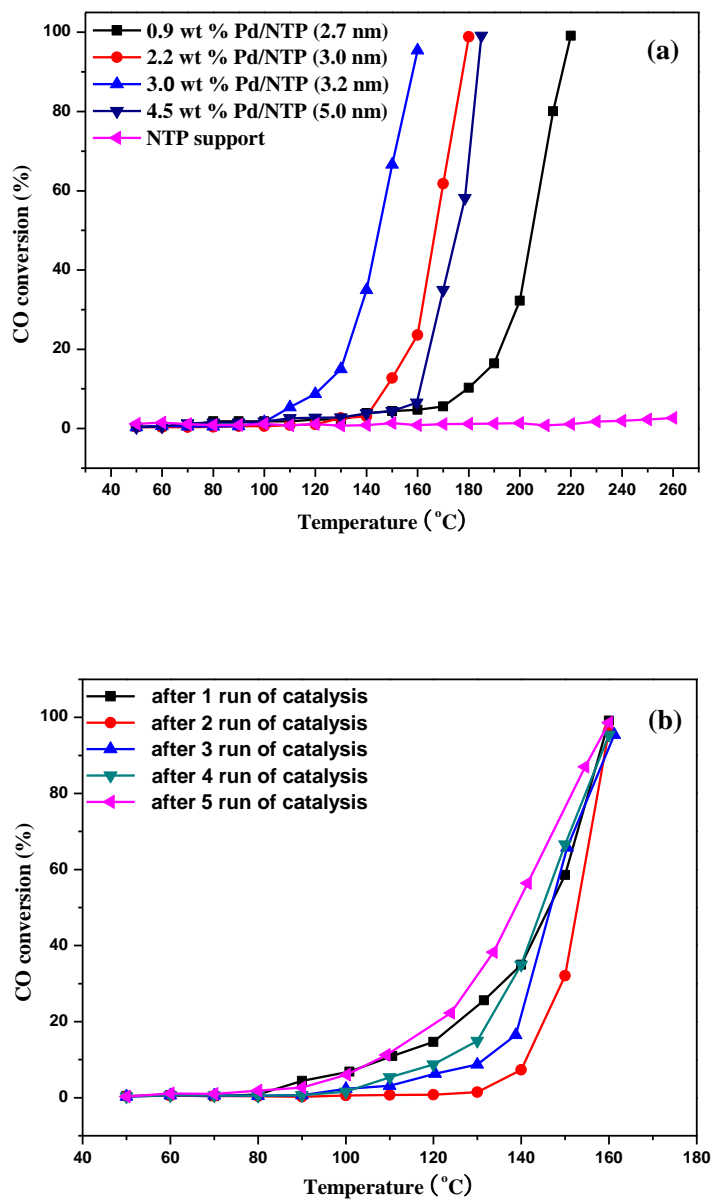


Figure S8. (a) Conversion-temperature curves for CO oxidation over Pd/NTP catalysts with different Pd loadings and (b) over 3.0 wt% Pd/NTP (3.2 nm) for repeated catalytic runs.

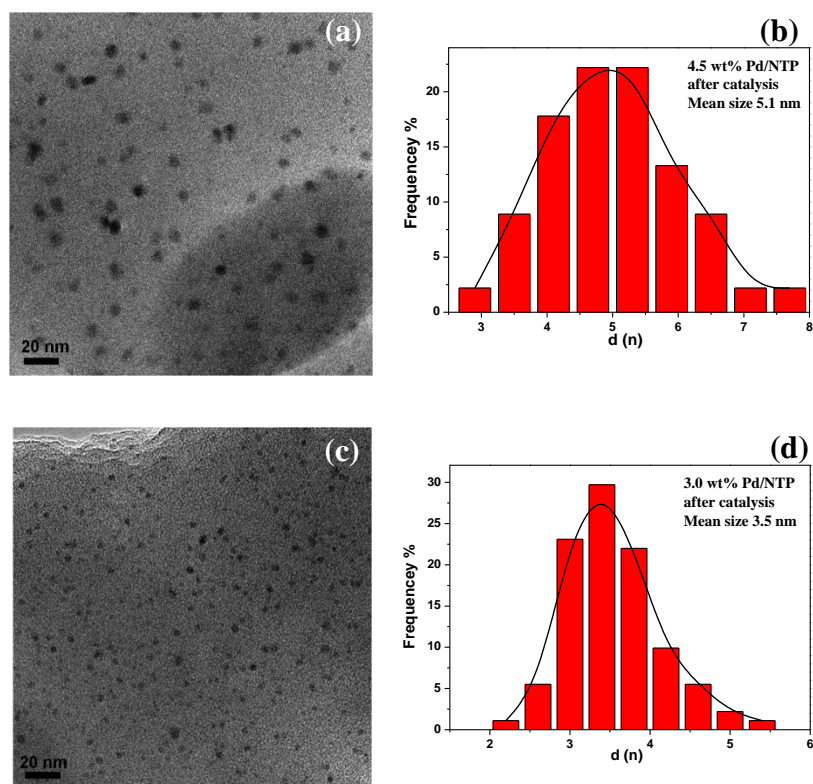


Figure S9. TEM images of the used 4.5 wt% (a), 3.0 wt% (c) Pd/NTP and corresponding Pd NPs size distributions in 4.5 wt% (b), 3.0 wt% (d) Pd/NTP

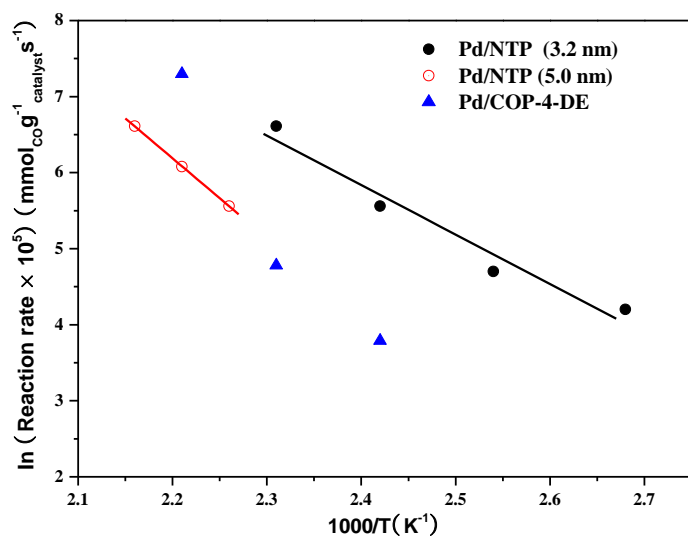


Figure S10. Arrhenius plots for the reaction activation energy on 3.0 wt% Pd/NTP (3.2 nm), 4.5 wt% Pd/NTP (5.0 nm) and Pd/COP-4-DE.

Reference

- 1 J. H. Chong and M. J. MacLachlan, *Inorg. Chem.*, 2006, **45**, 1442.
- 2 C. Zhang and C. -F. Chen, *J. Org. Chem.*, 2006, **71**, 6626.