Electronic Supplementary Material (ESI) for Catalysis Science & Technology.


# Disintegrative Activation of Pd Nanoparticles on Carbon Nanotube for Catalytic Phenol Hydrogenation

## Experimental

### Preparation of Pd/CNT catalyst

400 mg carbon nanotubes (CNTs) were dispersed into 25 ml water by sonicating for 30 min. Then $Pd(NO_3)_2$ solution were added dropwise into the CNTs suspension. After stirring for 8 h at room temperature, water was removed using a rotary evaporator at 60 ˚C under vacuum. After drying at 80 °C for 8 h in vacuum oven, the powder were reduced at 200 °C for 2 h with $H_2$.

The annealed Pd/CNT were obtained by annealing the Pd/CNT at 500 °C for 4 h in Ar atmosphere.

### Redisperse annealed Pd/CNT

#### 1. Redisperse annealed Pd/CNT with $HNO_3$ vapor

100-400 mg annealed Pd/CNT were put into a silica cup, which holds some small pores on the cup bottom and wall. Then this cup was placed in a hydrothermal autoclave, which contained some amounts of concentrated $HNO_3$. The sealed autoclave were put into a heated oven with 80-120 °C. After 1-6 h, the autoclave were taken out and cooled to room temperature. The Pd/CNT power were washed, dried and reduced with $H_2$.

#### 2. Redisperse annealed Pd/CNT with oxygen and nitrogen oxide

100-400 mg were put into a Teflon-lined stainless-steel reactor which was filled with oxygen/nitrogen oxide. Then the autoclave was heated to a given temperature. After 6 h, the autoclave cooled to room temperature. The Pd/CNT power were washed, dried and reduced with $H_2$.

### Characterization of catalysts

Transmission electron microscopy (TEM) images and scanning transmission electron microscopy (STEM) images were obtained by using an FEI Tecnai G2 F20 microscope operated at 200 kV. The X-ray Photoelectron Spectroscopy (XPS) were carried out at

ESCALAB 250 instrument with Al Kα X-rays (1489.6 eV, 150 W, 50.0 eV pass energy). The XRD patterns of the Pd/CNT catalysts were collected by using an X-ray diffractometer (D/MAX-2400) using a Cu Kα source at a scan rate of 2° • min-1.

**Selective Phenol Hydrogenation**

The reaction was conducted in a Schlenk flask (20 ml) with a graham condenser. A typical procedure was as follows: phenol (0.5 mmol), catalyst (10 mg), and water 2 ml were placed in a flask. The flask was purged with H2 to remove the air for 3 times, the reaction was then stirred at 80 ˚C under 1 bar of H2. During the reaction H2 was continuously supplied to maintain the pressure.

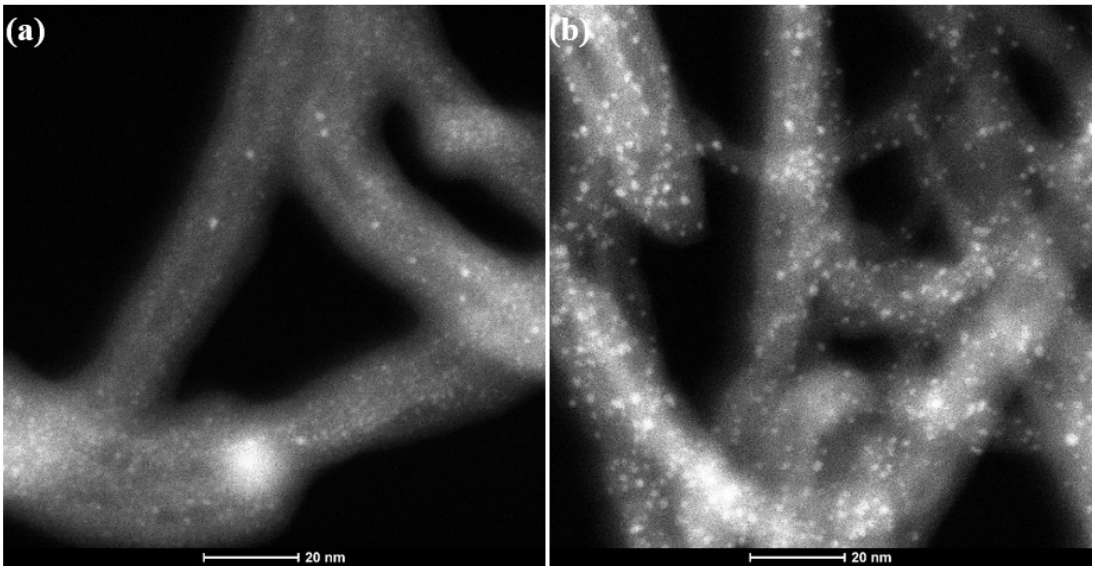


**Figure S1.** STEM images of GO treated Pd/CNT before (a) and after (b) reduction.

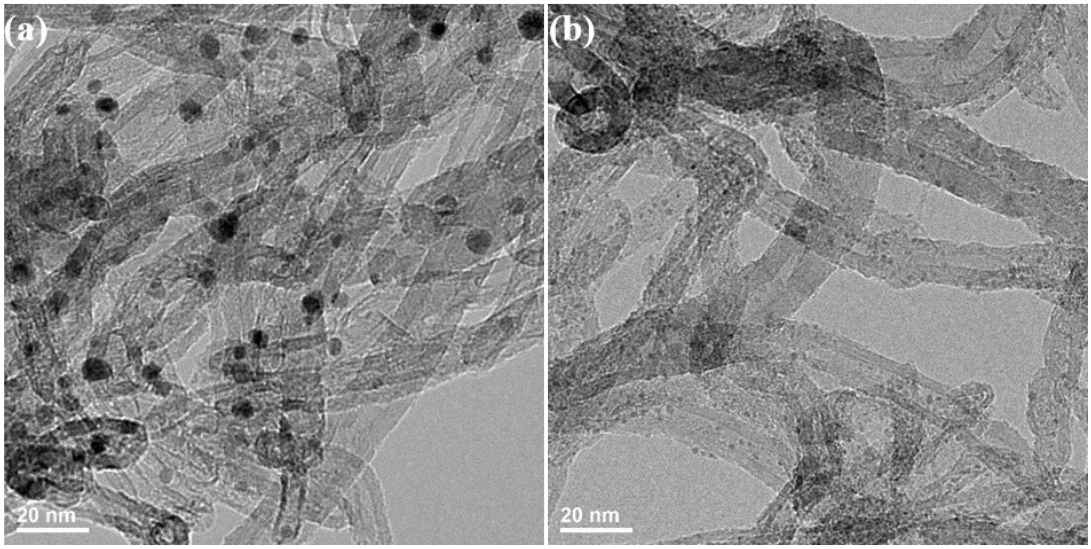


**Figure S2.** TEM images of (a) Annealed Pd/CNT, (b) Pd/CNT-GO at 120 ˚C for 6 h.

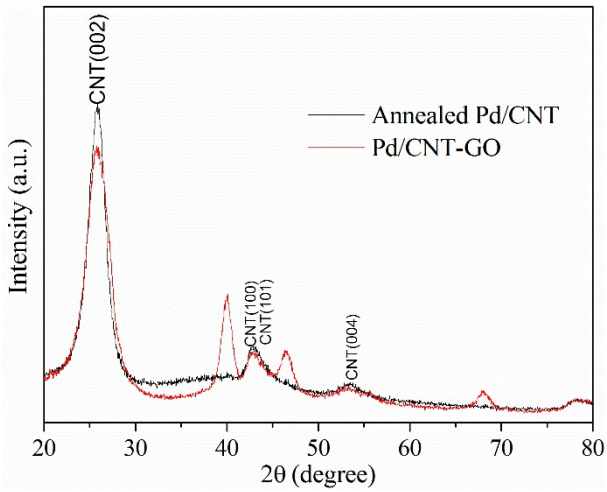


**Figure S3.** XRD patterns of (a) Annealed Pd/CNT, (b) Pd/CNT-GO at 120 ˚C for 6 h with reduction.

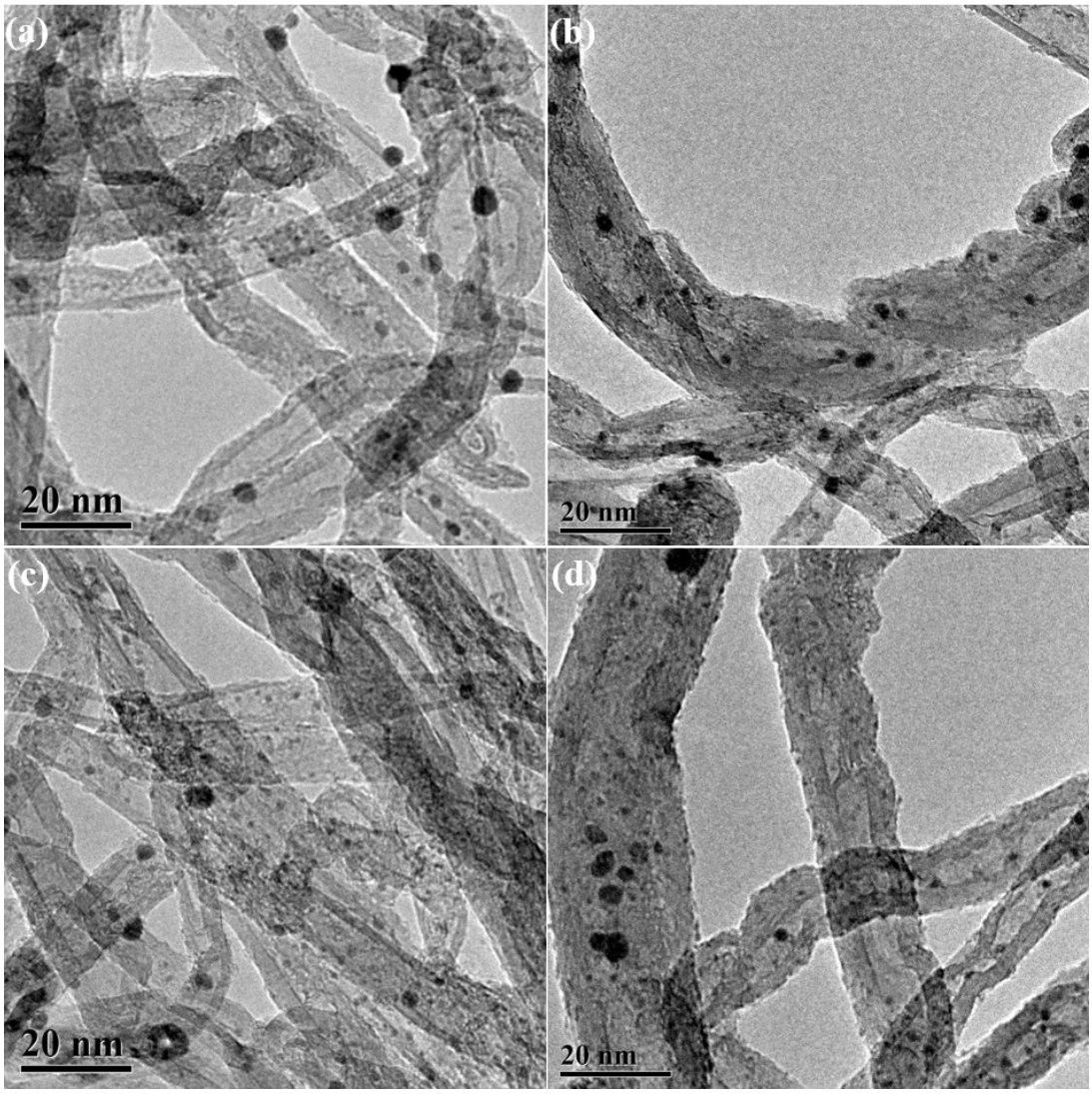


**Figure S4.** TEM images of Pd/CNT after GO treatment at (a) 80 ˚C for 6 h, (b) 100 ˚C for 6 h, (c) 120 ˚C for 1 h, (d) 120 ˚C for 3 h.

Table 1. The content of surface oxygen and surface atomic ratio of fresh and GO treated Pd/CNT catalysts without reduction, obtained from XPS analysis.

| Catalyst | Temperature/˚C | Time/ h | Atomic ratio(Pd/C) | C(At. %) | N(At. %) | O(At. %) | Pd(At. %) |
|---|---|---|---|---|---|---|---|
| Annealed Pd/CNT | - | - | 3.7 $e^{-3}$ | 94.87 | 0 | 4.78 | 0.35 |
| Pd/CNT-GO | 80 | 6 | 4.7$e^{-3}$ | 93.12 | 0.56 | 5.86 | 0.46 |
| | 100 | 6 | 4.9$e^{-3}$ | 92.15 | 0.74 | 6.68 | 0.43 |
| | 120 | 1 | 5.3$e^{-3}$ | 92.88 | 0.54 | 6.09 | 0.49 |
| | 120 | 3 | 5.5$e^{-3}$ | 90.88 | 0.81 | 7.8 | 0.50 |
| | 120 | 6 | 5.7$e^{-3}$ | 89.78 | 0.78 | 8.93 | 0.51 |

Table 2. The content of surface oxygen and surface atomic ratio of fresh and GO treated Pd/CNT catalysts without reduction, obtained from XPS analysis.

| Gas | $P_{Gas}$(MPa) | Temperature/˚C | Time/h | C(At.%) | N(At.%) | O(At. %) | Pd(At. %) |
|---|---|---|---|---|---|---|---|
| 40% $O_2$ | 1 | 120 | 6 | 94.02 | 1.07 | 4.58 | 0.34 |
| 40% $O_2$ | 1 | 200 | 6 | 94.21 | 0.39 | 4.97 | 0.44 |
| 5% $NO_2$ | 0.6 | 120 | 6 | 92.77 | 0.62 | 5.66 | 0.53 |
| 5% $NO_2$ flow | 0.1 | 120 | 6 | 94.11 | 0.48 | .91 | 0.51 |

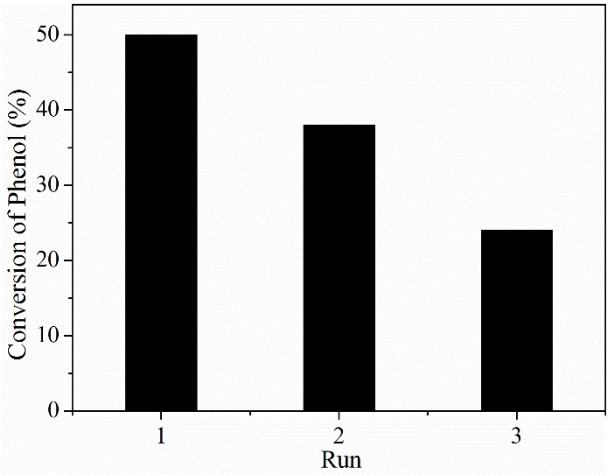


**Figure S5.** The recyclability of the re-dispersed catalyst.

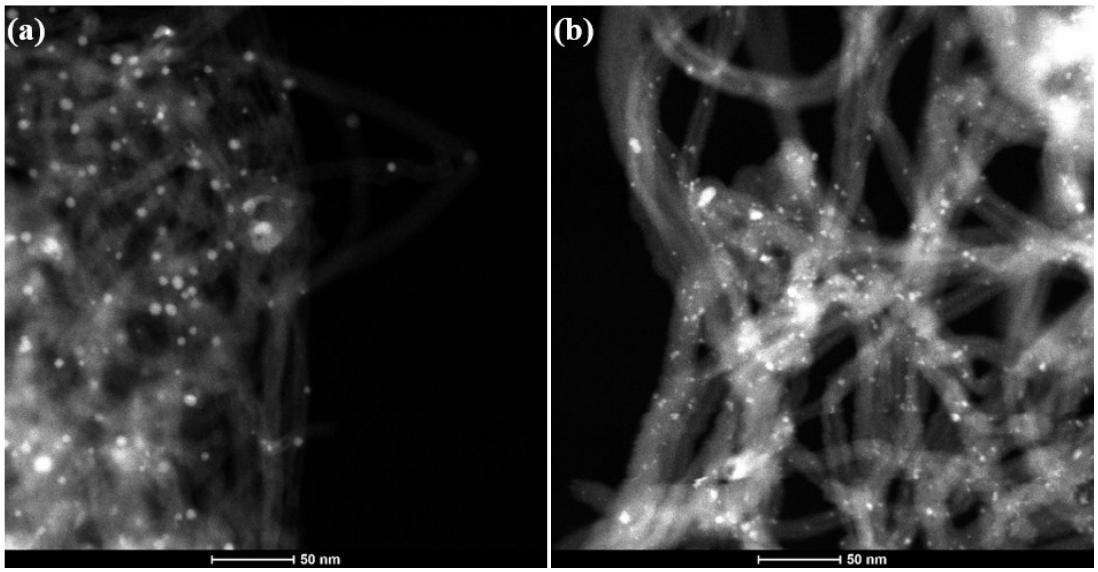


**Figure S6.** STEM images of Pd/CNT after GO treatment with 40% $O_2$ under 1 MPa (a) at 120 ˚C for 6 h (b) at 200 ˚C for 6 h without reduction.

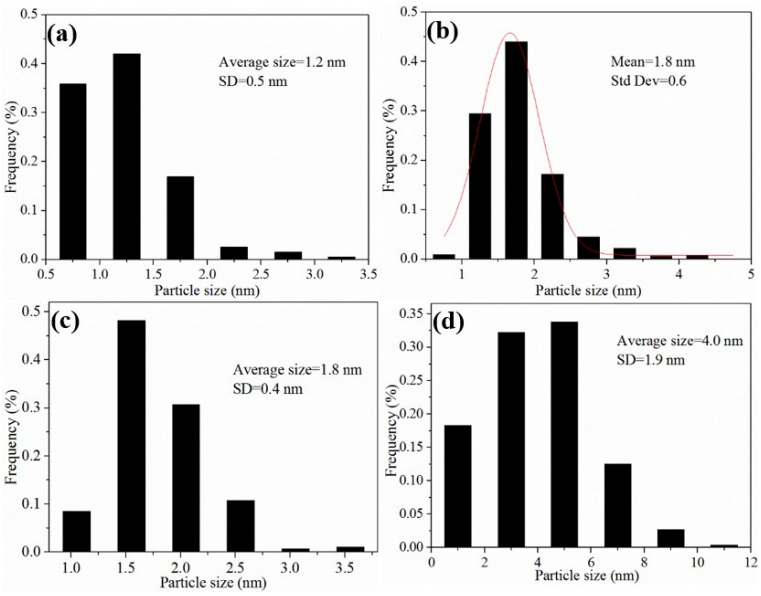


**Figure S7.** PSD patterns of Pd NPs of (a) 5% $NO_2$/He(0.6 MPa) without reduction, (b) with reduction, (c) 5% $NO_2$/He flow (ambient pressure) without reduction, (d) with reduction.

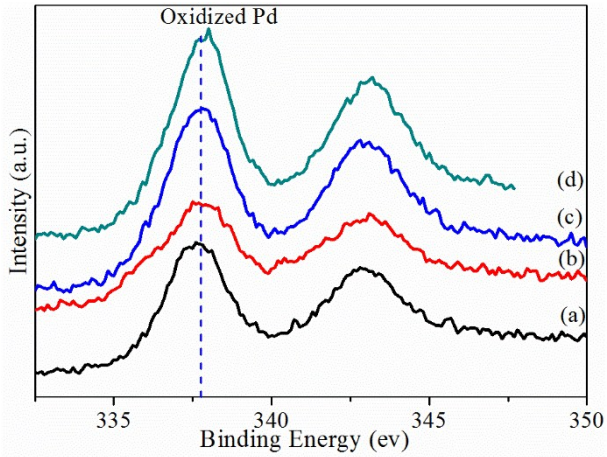


**Figure S8.** XPS Pd 3d spectra recorded on Pd/CNT after GO treatment at (a) 80 ˚C for 6 h, (b) 100 ˚C for 6 h, (c) 120 ˚C for 1 h, (d) 120 ˚C for 3 h without reduction.