Electronic Supplementary Material (ESI) for Catalysis Science & Technology

The structural and electronic promoting effect of nitrogen-doped carbon nanotubes on supported Pd nanoparticles for selective olefin hydrogenation

Supporting Information

1. TEM

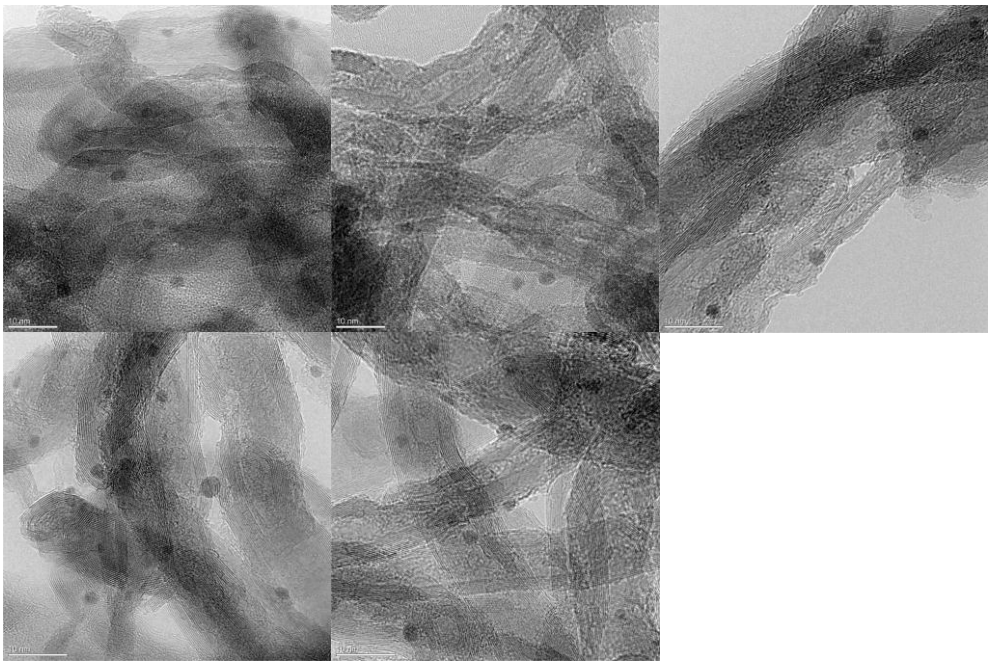


Fig. S 1 Representative TEM images of Pd/NCNT. The scale bars refer to 10 nm in all the images.

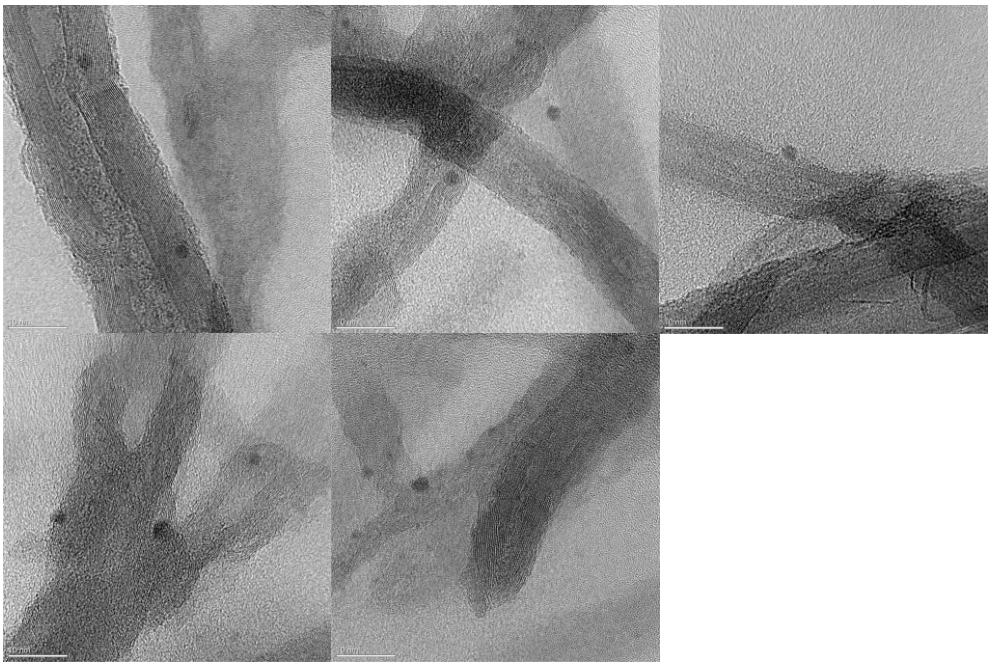


Fig. S 2 Representative TEM images of Pd/OCNT. The scale bars refer to 10 nm in all the images.

2. XPS

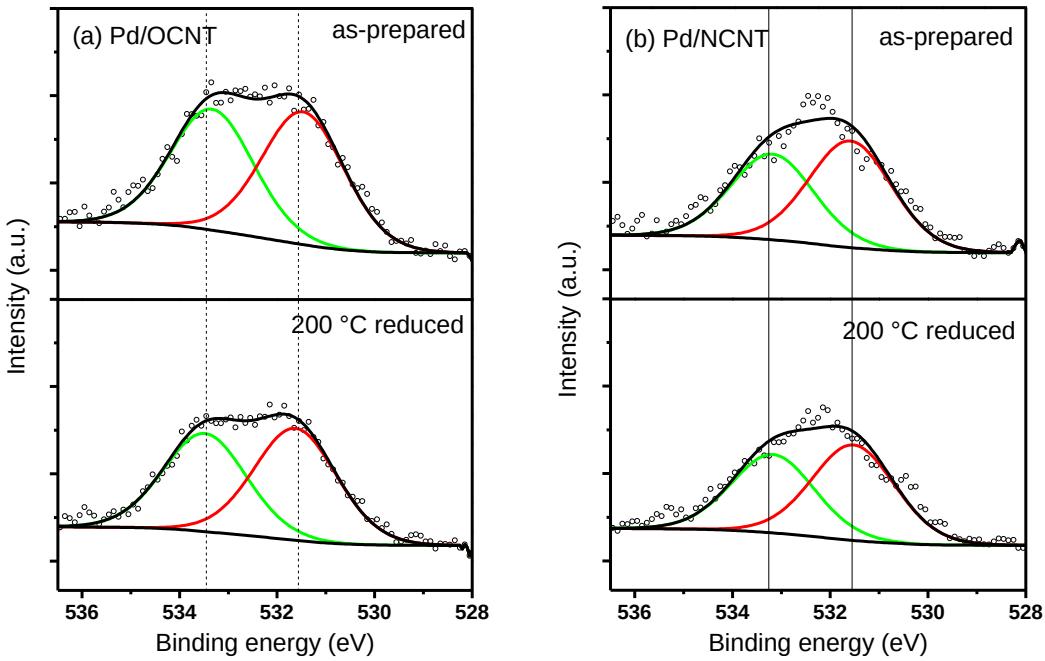


Fig. S 3 XP O 1s spectra of (a) Pd on OCNTs and (b) Pd on NCNT as prepared and after reduction in H_2 at 200 °C

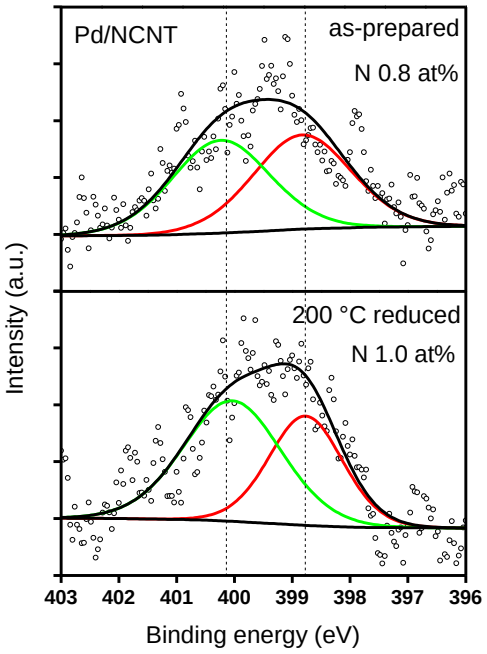


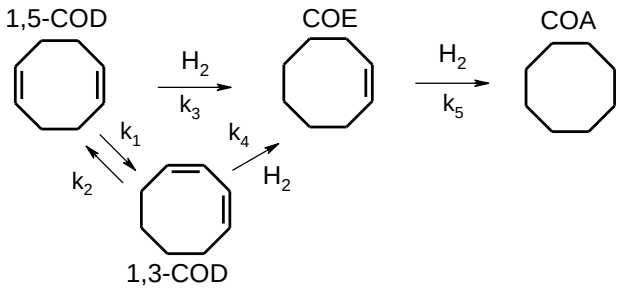
Fig. S 4 XP N 1s spectra of Pd on NCNT as prepared and after reduction in H_2 at 200 °C

Lower overall XP O 1s intensity was observe after reduction in H_2 at 200 °C than in the as-prepared samples (Fig. S 33), which can be attributed to the reductive removal of either oxygen related to Pd in oxidized state or oxygen groups on CNT surface.

As compared to the as-prepared Pd/NCNT sample, relatively higher surface concentration of nitrogen was detected over the reduced Pd/ NCNT. Considering the low nitrogen contents on CNT surface and the low sensitivity factor of nitrogen in XPS, further studies using Pd/NCNT samples with higher nitrogen contents (for example, catalytically grown NCNTs) will be performed.

3. Kinetic simulation using Athena software

Kinetic model



Scheme S 1 Reaction network of 1,5-COD hydrogenation

$$COD \longrightarrow COE \longrightarrow COA \qquad \text{(S1)}$$

$$1,5-COD \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 1,3-COD \qquad \text{(S2)}$$

$$1,5-COD + H_2 \xrightarrow{k_3} COE \qquad \text{(S3)}$$

$$1,3-COD + H_2 \xrightarrow{k_4} COE \qquad \text{(S4)}$$

$$COE + H_2 \xrightarrow{k_5} COA \qquad \text{(S5)}$$

Reaction rate for 1,5-COD,

$$r_{1,5-COD} = -k_1 C_{1,5-COD} + k_2 C_{1,3-COD} - k_3 C_{1,5-COD} C_{H_2} \quad \text{(S6)}$$

Reaction rate for 1,3-COD,

$$r_{1,3-COD} = k_1 C_{1,5-COD} - k_2 C_{1,3-COD} - k_4 C_{1,3-COD} C_{H_2} \quad \text{(S7)}$$

Reaction rate for COE,

$$r_{COE} = k_3 C_{1,5-COD} C_{H_2} + k_4 C_{1,3-COD} C_{H_2} - k_5 C_{COE} C_{H_2} \quad \text{(S8)}$$

Reaction rate for COA,

$$r_{COA} = k_5 C_{COE} C_{H_2} \quad \text{(S9)}$$

Reaction rate for H_2,

$$r_{H_2} = -k_3 C_{1,5-COD} C_{H_2} - k_4 C_{1,3-COD} C_{H_2} - k_5 C_{COE} C_{H_2} \quad \text{(S10)}$$

The simulation of COD hydrogenation performed using the Athena visual studio engineering software was based on consecutive reaction pathway. COD is hydrogenated to COE and subsequently converted to COA (Eq. 1). The reactions shown in Scheme S1 were assumed to be all first-order. Eq. S2-S5 describe the elementary steps of the COD hydrogenation. The reaction rates of the consumption of 1,5-COD, 1,3-COD, COE, COA and H_2 are expressed in Eq. S6, S7, S8, S9, and S10, respectively.

Simulation approach

Modeling with ordinary differential equations option was selected to simulate the experimental data in batch reactor mode. Differential model is usually used to model unsteady-state processes such as batch or semi-batch reactors [M. Caracotsios, Athena Visual Studio, www.athenavisual.com]. The inputs to the model are the initial and the experimentally determined concentrations of 1,5-COD, 1,3-COD, COE, COA and H_2. The software solves concurrently five differential equations for the reaction rates (Eq. S6-S10). Consequently, the numerical results obtained show the experimentally determined and simulation predicted concentration of 1,5-COD, 1,3-COD, COE, COA and H_2, and also the estimated reaction rate constants.

Modeling results

Table S 1 Athena simulation results based on the observed kinetic data over Pd nanoparticles supported on OCNTs using purified CNTs as starting material

(a) 1,5-COD

Time on stream (min)	Observed	Simulated	Residual
0	1.00E+00	1.00E+00	0.00E+00
2	4.81E-01	5.10E-01	-2.91E-02
4	2.98E-01	2.73E-01	2.47E-02
6	1.71E-01	1.51E-01	1.99E-02
8	8.30E-02	8.52E-02	-2.21E-03
10	5.20E-02	4.86E-02	3.37E-03
12	0.00E+00	2.80E-02	-2.80E-02

(b) 1,3-COD

Time on stream (min)	Observed	Simulated	Residual
0	0.00E+00	0.00E+00	0.00E+00
2	2.36E-01	2.46E-01	-1.03E-02
4	2.26E-01	2.18E-01	7.91E-03
6	1.69E-01	1.50E-01	1.88E-02
8	9.00E-02	9.48E-02	-4.85E-03
10	5.40E-02	5.76E-02	-3.62E-03
12	0.00E+00	3.43E-02	-3.43E-02

(c) COE

Time on stream (min)	Observed	Simulated	Residual
0	0.00E+00	0.00E+00	0.00E+00
2	3.26E-01	2.38E-01	8.85E-02
4	5.27E-01	4.82E-01	4.49E-02
6	7.21E-01	6.41E-01	8.03E-02
8	8.98E-01	7.24E-01	1.74E-01
10	9.38E-01	7.58E-01	1.80E-01
12	9.09E-01	7.60E-01	1.49E-01
14	8.74E-01	7.46E-01	1.28E-01
16	8.32E-01	7.21E-01	1.11E-01
18	7.94E-01	6.92E-01	1.02E-01
20	7.56E-01	6.61E-01	9.46E-02
22	7.18E-01	6.30E-01	8.80E-02
26	6.40E-01	5.69E-01	7.09E-02
36	4.46E-01	4.38E-01	8.08E-03
46	2.69E-01	3.37E-01	-6.78E-02
56	0.00E+00	2.59E-01	-2.59E-01
76	1.54E-01	1.54E-01	0.00E+00
96	9.17E-02	9.17E-02	0.00E+00

(d) COA

Time on stream (min)	Observed	Simulated	Residual
0	0.00E+00	0.00E+00	0.00E+00
2	6.50E-02	6.07E-03	5.89E-02
4	6.90E-02	2.65E-02	4.25E-02
6	7.40E-02	5.80E-02	1.60E-02
8	8.20E-02	9.56E-02	-1.36E-02
10	1.09E-01	1.36E-01	-2.71E-02
12	1.44E-01	1.77E-01	-3.32E-02
14	1.82E-01	2.18E-01	-3.58E-02
16	2.19E-01	2.57E-01	-3.83E-02
18	2.57E-01	2.95E-01	-3.82E-02
20	2.96E-01	3.31E-01	-3.53E-02
22	3.34E-01	3.66E-01	-3.18E-02
26	4.12E-01	4.30E-01	-1.75E-02
36	5.93E-01	5.62E-01	3.10E-02
46	7.70E-01	6.63E-01	1.07E-01
56	9.22E-01	7.41E-01	1.81E-01
76	9.80E-01	8.46E-01	1.34E-01
96	9.78E-01	9.08E-01	6.97E-02

Table S 2 Athena simulation results based on the observed kinetic data over Pd nanoparticles supported on NCNTs using purified CNTs as starting material

(a) 1,5-COD

Time on stream (min)	Observed	Simulated	Residual
0	1.00E+00	1.00E+00	0.00E+00
2	4.10E-02	-9.83E-02	1.39E-01
4	0.00E+00	-3.20E-02	3.20E-02

(b) 1,3-COD

Time on stream (min)	Observed	Simulated	Residual
0	0.00E+00	0.00E+00	0.00E+00
2	4.10E-02	2.04E-01	-1.63E-01
4	0.00E+00	-3.70E-02	3.70E-02

(c) COE

Time on stream (min)	Observed	Simulated	Residual
0	0.00E+00	0.00E+00	0.00E+00
2	9.15E-01	7.79E-01	1.36E-01
4	7.67E-01	7.01E-01	6.60E-02
6	6.13E-01	4.50E-01	1.63E-01
8	4.53E-01	3.36E-01	1.17E-01
10	3.09E-01	2.50E-01	5.94E-02
12	1.85E-01	1.83E-01	1.98E-03
14	8.30E-02	1.35E-01	-5.19E-02
16	4.20E-02	9.96E-02	-5.76E-02
18	0.00E+00	7.35E-02	-7.35E-02

(d) COA

Time on stream (min)	Observed	Simulated	Residual
0	0.00E+00	0.00E+00	0.00E+00
2	1.49E-01	1.15E-01	3.41E-02
4	3.07E-01	3.68E-01	-6.09E-02
6	4.71E-01	5.42E-01	-7.10E-02
8	6.28E-01	6.62E-01	-3.39E-02
10	7.73E-01	7.51E-01	2.17E-02
12	9.03E-01	8.17E-01	8.61E-02
14	1.01E+00	8.65E-01	1.40E-01
16	1.05E+00	9.00E-01	1.49E-01
18	1.04E+00	9.27E-01	1.17E-01

Table S 3 Estimated rate constants of 1,5-COD hydrogenation obtained by modeling the experimental data assuming first-order reactions (s^{-1}). Pd nanoparticles supported on OCNTs and NCNTs (Pd/OCNT and Pd/NCNT) using non-purified CNTs as starting material were employed as catalysts.

Sample	Pd/OCNT	Pd/NCNT
k_1	0.406	1
k_2	0	0
k_3	0.006	0.004
k_4	0.049	0.114
k_5	0.001	0.009

Table S 4 Athena simulation results based on the observed kinetic data over Pd nanoparticles supported on OCNTs using non-purified CNTs as starting material

(a) 1,5-COD

Time on stream (min)	Observed	Simulated	Residual
0	1.00E+00	1.00E+00	0.00E+00
2	4.01E-01	3.97E-01	3.60E-03
4	1.64E-01	1.70E-01	-6.32E-03
6	7.60E-02	7.58E-02	1.89E-04
8	5.90E-02	3.44E-02	2.46E-02
10	0.00E+00	1.57E-02	-1.57E-02
12	7.22E-03	7.22E-03	0.00E+00

(b) 1,3-COD

Time on stream (min)	Observed	Simulated	Residual
0	5.70E-02	0.00E+00	5.70E-02
2	2.26E-01	2.23E-01	3.15E-03
4	1.50E-01	1.44E-01	6.18E-03
6	7.30E-02	7.43E-02	-1.28E-03
8	5.30E-02	3.59E-02	1.71E-02
10	4.90E-02	1.69E-02	3.21E-02
12	7.86E-03	7.86E-03	0.00E+00

(c) COE

Time on stream (min)	Observed	Simulated	Residual
0	5.80E-02	0.00E+00	5.80E-02
2	4.03E-01	3.72E-01	3.06E-02
4	7.34E-01	6.57E-01	7.72E-02
6	9.00E-01	7.91E-01	1.09E-01
8	9.19E-01	8.38E-01	8.10E-02
10	9.01E-01	8.42E-01	5.91E-02
12	8.26E-01	8.26E-01	0.00E+00
14	8.50E-01	8.02E-01	4.82E-02
16	8.27E-01	7.74E-01	5.27E-02
18	7.96E-01	7.46E-01	5.02E-02
20	7.69E-01	7.18E-01	5.13E-02
22	7.46E-01	6.90E-01	5.58E-02
26	6.89E-01	6.38E-01	5.09E-02
36	5.67E-01	5.24E-01	4.26E-02
46	4.57E-01	4.31E-01	2.56E-02
56	3.53E-01	3.55E-01	-2.14E-03
76	1.80E-01	2.41E-01	-6.12E-02
96	6.50E-02	1.64E-01	-9.91E-02
116	0.00E+00	1.12E-01	-1.12E-01

(d) COA

Time on stream (min)	Observed	Simulated	Residual
0	4.90E-02	0.00E+00	4.90E-02
2	5.80E-02	7.39E-03	5.06E-02
4	6.40E-02	2.91E-02	3.49E-02
6	7.80E-02	5.88E-02	1.92E-02
8	1.00E-01	9.18E-02	8.23E-03
10	1.25E-01	1.25E-01	-4.76E-04
12	1.59E-01	1.59E-01	0.00E+00
14	1.78E-01	1.91E-01	-1.32E-02
16	2.05E-01	2.23E-01	-1.75E-02
18	2.30E-01	2.53E-01	-2.27E-02
20	2.56E-01	2.82E-01	-2.56E-02
22	2.81E-01	3.09E-01	-2.85E-02
26	3.28E-01	3.62E-01	-3.38E-02
36	4.42E-01	4.76E-01	-3.36E-02
46	5.51E-01	5.69E-01	-1.76E-02
56	6.47E-01	6.45E-01	2.14E-03
76	8.17E-01	7.59E-01	5.82E-02
96	9.30E-01	8.36E-01	9.41E-02
116	9.43E-01	8.88E-01	5.49E-02

Table S 5 Athena simulation results based on the observed kinetic data over Pd nanoparticles supported on NCNTs using non-purified CNTs as starting material

(a) 1,5-COD

Time on stream (min)	Observed	Simulated	Residual
0	1.00E+00	1.00E+00	0.00E+00
2	7.20E-02	7.66E-02	-4.55E-03
4	4.70E-02	2.52E-02	2.18E-02
6	0.00E+00	1.09E-02	-1.09E-02

(b) 1,3-COD

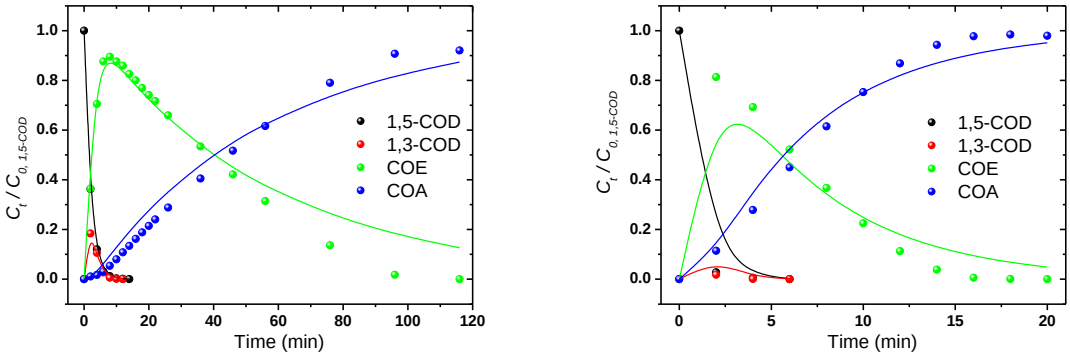
Time on stream (min)	Observed	Simulated	Residual
0	0.00E+00	0.00E+00	0.00E+00
2	6.10E-02	6.43E-02	-3.32E-03
4	4.30E-02	2.98E-02	1.32E-02
6	0.00E+00	1.31E-02	-1.31E-02

(c) COE

Time on stream (min)	Observed	Simulated	Residual
0	0.00E+00	0.00E+00	0.00E+00
2	9.19E-01	6.71E-01	2.48E-01
4	7.89E-01	5.48E-01	2.41E-01
6	6.05E-01	4.17E-01	1.88E-01
8	4.38E-01	3.10E-01	1.28E-01
10	2.84E-01	2.28E-01	5.63E-02
12	1.64E-01	1.66E-01	-1.94E-03
14	8.30E-02	1.20E-01	-3.74E-02
16	4.80E-02	8.72E-02	-3.92E-02
18	4.30E-02	6.30E-02	-2.00E-02
20	0.00E+00	4.55E-02	-4.55E-02
22	0.00E+00	3.29E-02	-3.29E-02

(d) COA

Time on stream (min)	Observed	Simulated	Residual
0	0.00E+00	0.00E+00	0.00E+00
2	1.65E-01	1.89E-01	-2.36E-02
4	3.42E-01	3.97E-01	-5.54E-02
6	5.28E-01	5.59E-01	-3.09E-02
8	7.05E-01	6.79E-01	2.57E-02
10	8.55E-01	7.68E-01	8.73E-02
12	9.79E-01	8.32E-01	1.47E-01
14	1.06E+00	8.79E-01	1.80E-01
16	1.10E+00	9.12E-01	1.84E-01
18	1.10E+00	9.37E-01	1.66E-01
20	1.10E+00	9.54E-01	1.45E-01
22	1.09E+00	9.67E-01	1.24E-01



(a) (b)

Fig. S 5 Observed (symbol) and simulated (line) evolution of 1,5-COD, 1,3-COD, COE and COA during the hydrogenation over Pd nanoparticles supported on (a) OCNTs and (b) NCNTs using as-received CNTs without purification by acid-washing as starting material (5 mg catalyst in 1g quartz sand, 1 vol% 1,5-COD and 6 vol% H_2 in the feed gas, N_2 as carrier gas, 50 °C, ambient pressure). Off-site reduction (200 °C, 10 vol% H_2 in He with a total flow of 100 ml min^{-1}, 2 h) and in situ activation (50 °C, 10 vol% H_2 in N_2 with a total flow of 200 ml min^{-1}, 20 min) were performed with the catalysts prior to the catalytic tests.

4. XRD

Parallel samples were synthesized on OCNTs and NCNTs using non-purified CNTs as starting materials. Similarly, Pd on NCNTs showed much weaker reflections.

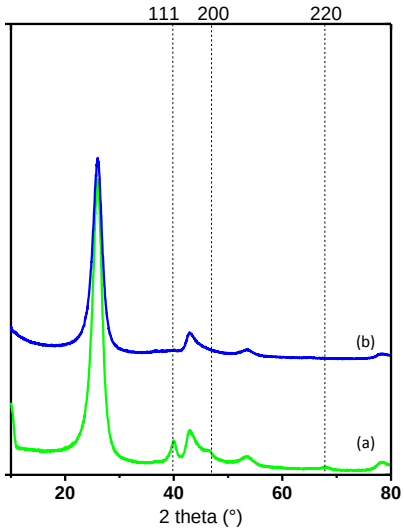


Fig. S 6 XRD patterns of Pd nanoparticles (after reduction in H_2 at 200 °C for 2 h) supported on (a) OCNTs and (b) NCNTs using non-purified CNTs as starting material.