

Supporting information

Size-Dependent Halogenated Nitrobenzene Hydrogenation Selectivity of Pd Nanoparticles

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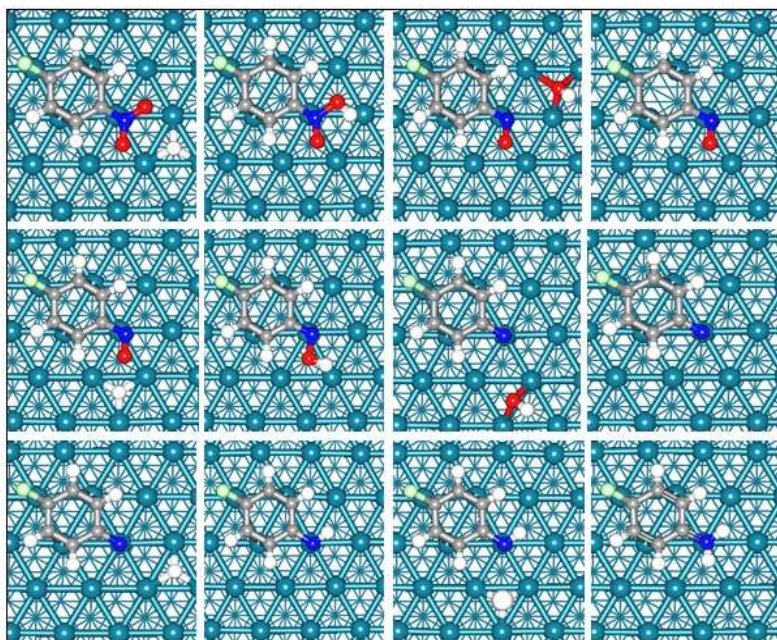


Figure S1. The optimized structures for the corresponding species in elementary step of *p*-CAN formation from *p*-CNB hydrogenation on Pd(111) surface.

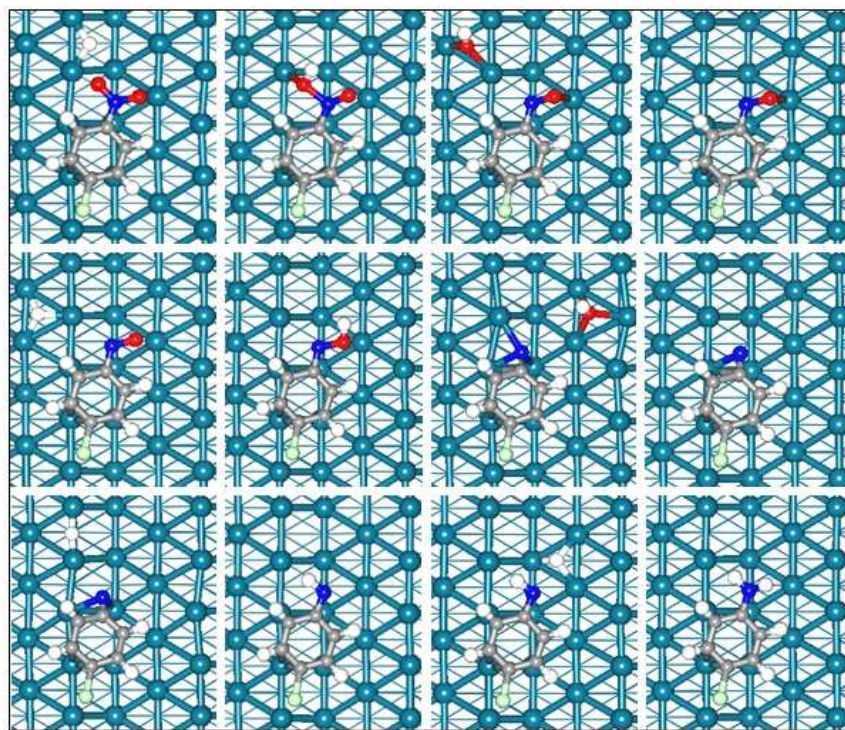


Figure S2. The optimized structures for the corresponding species in elementary step of *p*-CAN formation from *p*-CNB hydrogenation on Pd(211) surface.

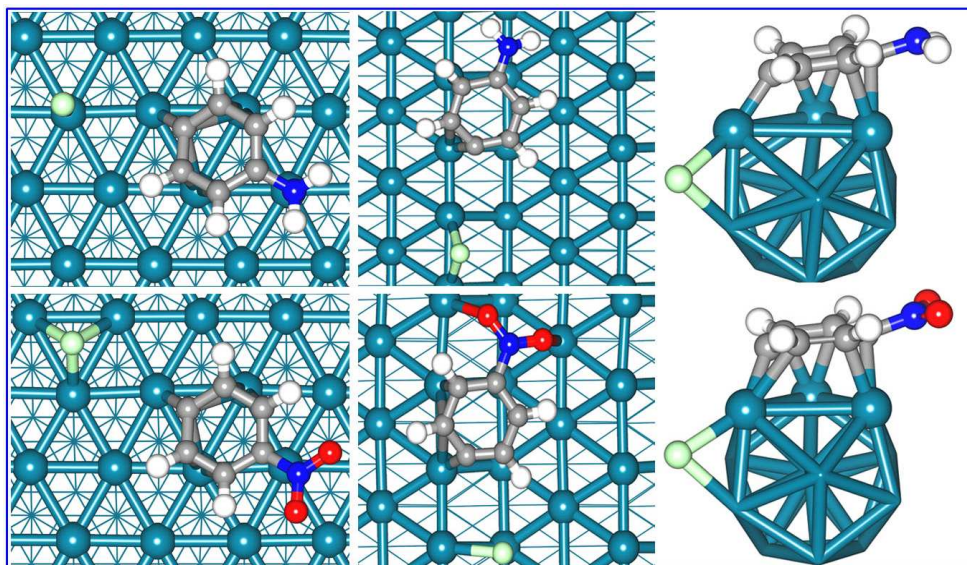


Figure S3. The optimized structures for the final states of dechlorination of *p*-CAN and *p*-CNB on Pd(111), Pd(211) surfaces and Pd₁₃ clusters.

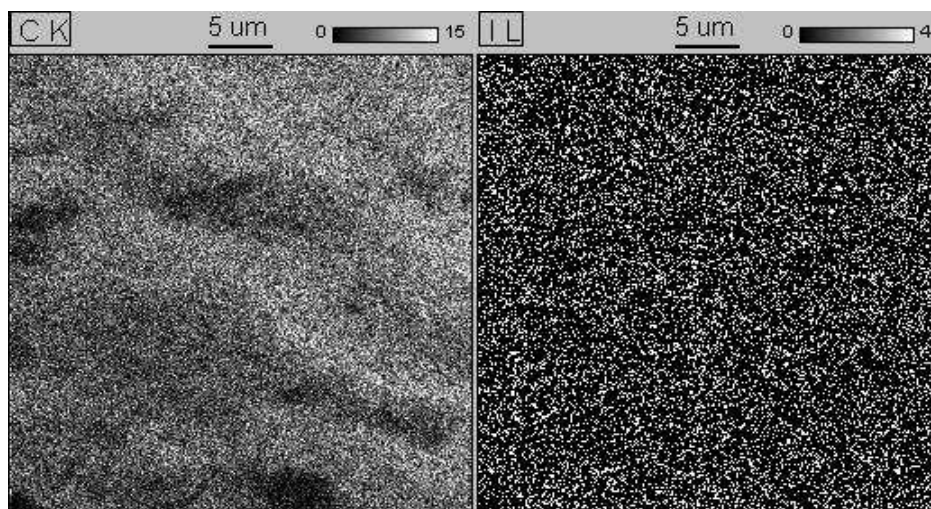


Figure S4 Distribution of halogen ions on the surface of activated carbon measured by EDS

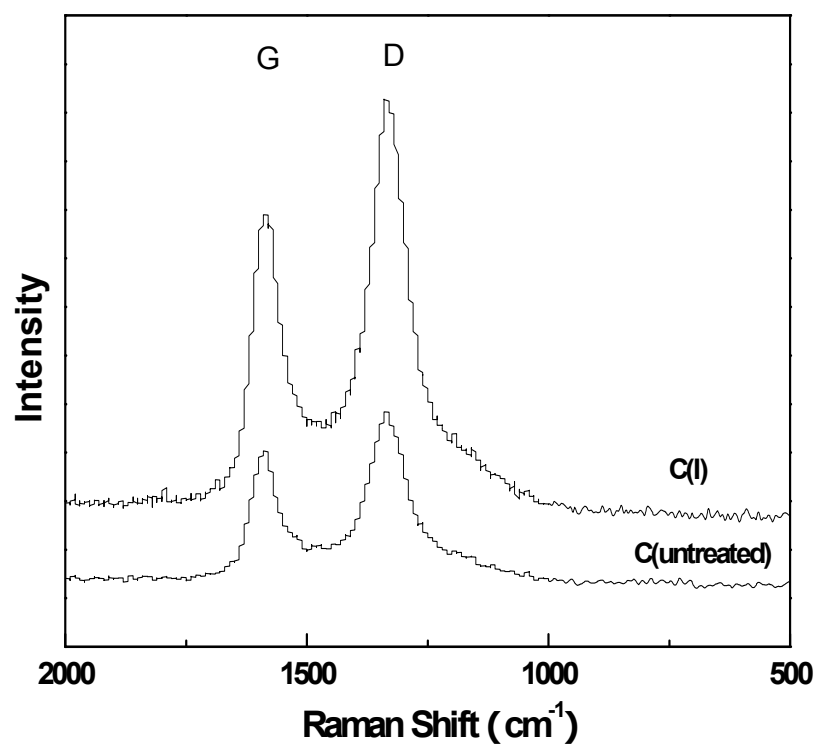


Figure S5 Raman spectra of activated carbons preadsorbed with various halogen ions

Table S1. Recycling of Pd/C(28.4 nm) catalyst for the selective hydrogenation of *p*-CNT under solvent-free conditions

Recycling time	Catalyst addition /g	Conversion /%	Time /min	Selectivity (%)	
				<i>P</i> -CAN	aniline
1	1.0	100	155	99.91	0.09
2	0.1	100	221	99.93	0.07
3	0	100	219	99.92	0.08
4	0	100	230	99.94	0.06
5	0	100	236	99.95	0.05
6	0.1	100	217	99.96	0.04
7	0	100	229	99.93	0.07
8	0	100	241	99.93	0.07
9	0	100	245	99.96	0.04
10	0	100	237	99.93	0.07
11	0	100	252	99.91	0.09
12	0.1	100	222	99.95	0.05
13	0	100	223	99.93	0.07
14	0	100	229	99.94	0.06
15	0	100	242	99.91	0.09
16	0	100	250	99.95	0.05
17	0	100	243	99.91	0.09
18	0.1	100	231	99.92	0.08
19	0	100	225	99.93	0.07
20	0	100	237	99.91	0.09

Reaction conditions: *p*-CNB, 200 g; Pd/C (28.4 nm), 1.0 g; speed of stirring, 1200 r/min. Note: the catalyst was separated and recycled by the same filter paper every time.

Table S2. Pilot experiment for Recycling of Pd/C (28.4 nm) catalyst for the hydrogenation of 6-chloro-2-nitrotoluene (6-CNT) under solvent-free conditions

Recycling time	6-CNT /Kg	Catalyst /Kg	Selectivity /%	
			Main product	By-products
1	1500	6.12	99.95	0.05
2	1250	5.98	99.96	0.04
3	1250	5.66	99.95	0.05
4	1250	5.41	99.91	0.09
5	1250	5.30	99.94	0.06
6	1250	4.20	99.98	0.02
7	1250	4.08	99.91	0.09
8	1250	3.96	99.91	0.09
9	1250	3.85	99.93	0.07
10	1250	4.00	99.92	0.08
11	1250	3.40	99.94	0.06
12	1250	3.30	99.95	0.05
13	1250	3.20	99.93	0.07
14	1250	3.25	99.91	0.09
15	1250	3.30	99.91	0.09
16	1250	3.50	99.92	0.08
17	1250	3.60	99.92	0.08
18	1250	4.60	99.92	0.08
19	1750	5.75	99.95	0.05
20	1750	5.60	99.96	0.04
21	1750	5.50	99.93	0.07
22	1750	5.40	99.93	0.07
23	1750	5.00	99.96	0.04

24	1750	4.90	99.98	0.02
25	2500	12.90	99.95	0.05
26	3000	12.80	99.94	0.06
27	3000	12.58	99.92	0.08
28	3000	12.46	99.91	0.09
29	3000	12.90	99.93	0.07
30	3000	12.66	99.92	0.08

Reaction conditions: 353~373 K, 1.0 MPa, 2000 L reactor (1~25th recycling) and 3000 L reactor (26~27th recycling).

1) The catalyst used from 2nd recycling to 25th recycling comes from the catalyst of the first experiment.

2) The catalyst used from 26nd recycling to 30th recycling is comprised of the catalyst of the first experiment (6.12 Kg) and fresh catalyst (6.78 Kg).

Table S3 Structural parameters of the activated carbon with different pretreatments

Pretreated Carbon	S_{BET} (m^2/g)	V_{micro} (cm^3/g)	V_{total} (cm^3/g)	D (nm)
un	1969	0.726	1.194	1.32
a	1949	0.752	1.335	1.37
b	1842	0.713	1.237	1.34
c	1794	0.698	1.203	1.34
d	1455	0.571	0.957	1.31
e	1175	0.554	0.863	1.25
f	1840	0.736	1.215	1.32

un: untreated carbon, a: 1 mol/L HNO_3 , b: 2 mol/L HNO_3 , c: 4 mol/L HNO_3 , d: 8 mol/L HNO_3 , e: 16 mol/L HNO_3 , f: 2.5 mol/L KI

Table S4 Surface oxides groups of the activated carbon with various pretreatments

pretreated Carbon	Carboxyl group (mmol/g)	Lactonic group (mmol/g)	Phenol group (mmol/g)
un	0.115	0.003	0.082
a	0.475	0.126	0.207
b	0.516	0.149	0.348
c	0.746	0.270	0.365
d	1.267	0.317	0.478
e	1.408	0.643	0.643
f	0.108	0.017	0.112

un: untreated carbon, a: 1 mol/L HNO₃, b: 2 mol/L HNO₃, c: 4 mol/L HNO₃, d: 8 mol/L HNO₃, e: 16 mol/L HNO₃, f: 2.5 mol/L KI