Support Information

Structural Effects of Microcrystalline Cellulose-Derived Carbon Supports on Catalytic Performance of the $Pd(OH)_2/C$ Catalysts for the Hydrogenolytic Debenzylation of Hexanitrohexaazaisowurtzitane Derivatives

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Additional Figures and Data

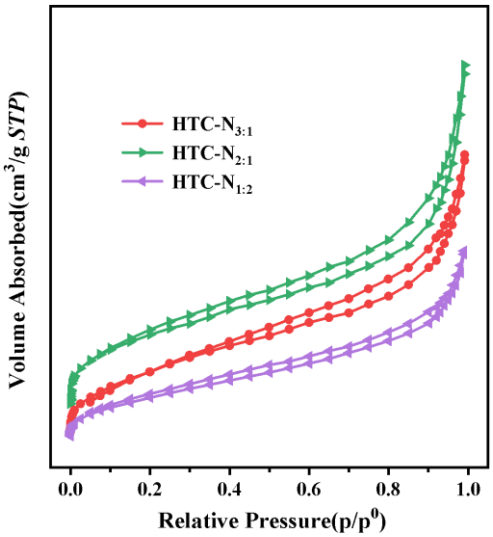

Figure S1. N_2 absorption-desorption isotherms of the HTC-$N_{3:1}$, HTC-$N_{2:1}$, HTC-$N_{1:2}$ samples.

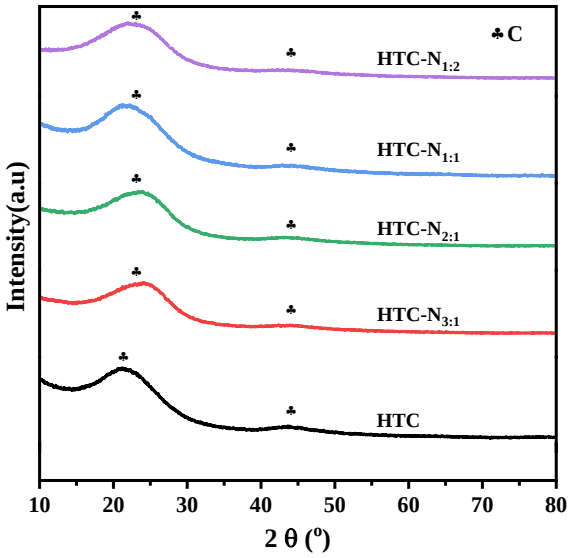

Figure S2. XRD patterns of the carbon supports.

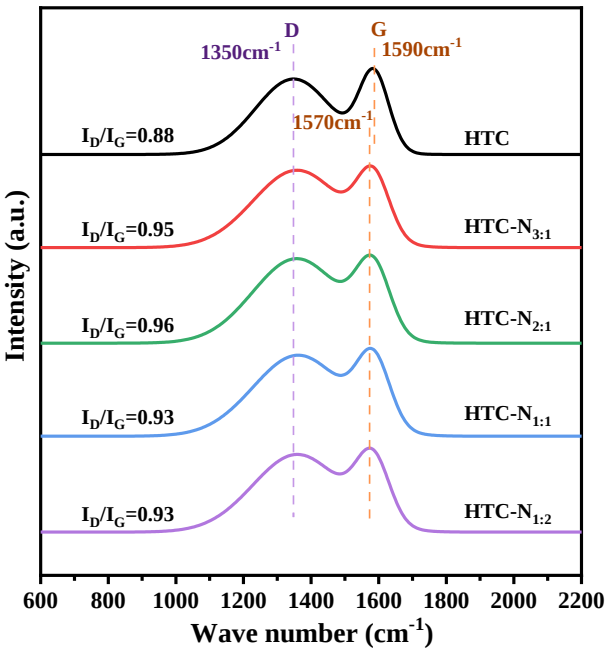

Figure S3. Raman spectra of the carbon supports.

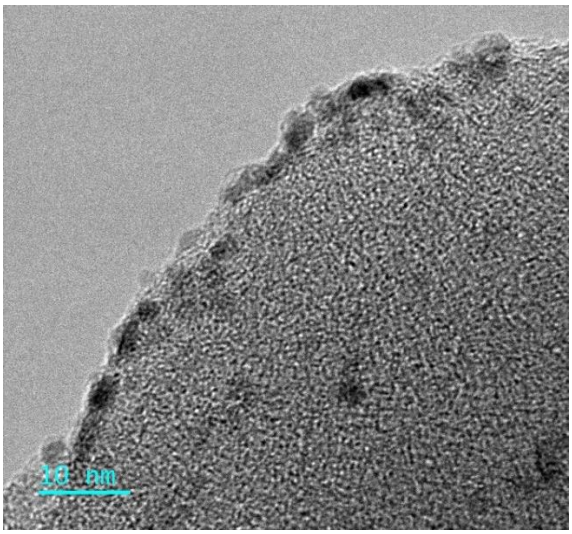

Figure S4. TEM bright field image of Pd/HTC-N1:1.

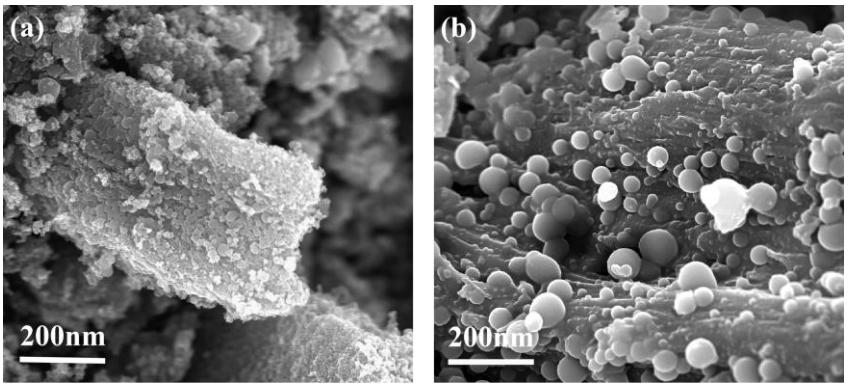

Figure S5. SEM images of the recovered Pd/HTC(a) and Pd/HTC-$N_{1:1}$(b) samples after three cycles in the hydrogenolysis reaction of TADB.

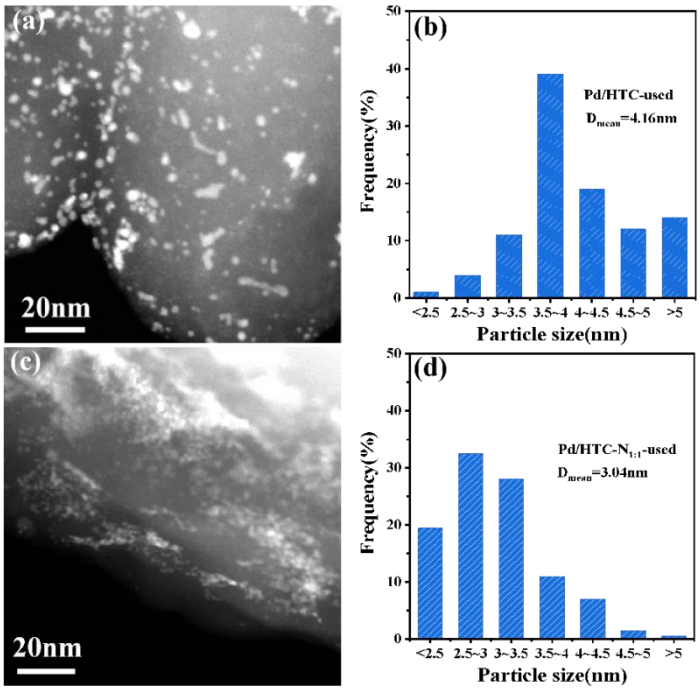

Figure S6. STEM images and the Pd particle size distributions of Pd/HTC (a and b) and Pd/HTC-$N_{1:1}$ (c and d) after three cycles in the hydrogenolysis reaction of TADB.

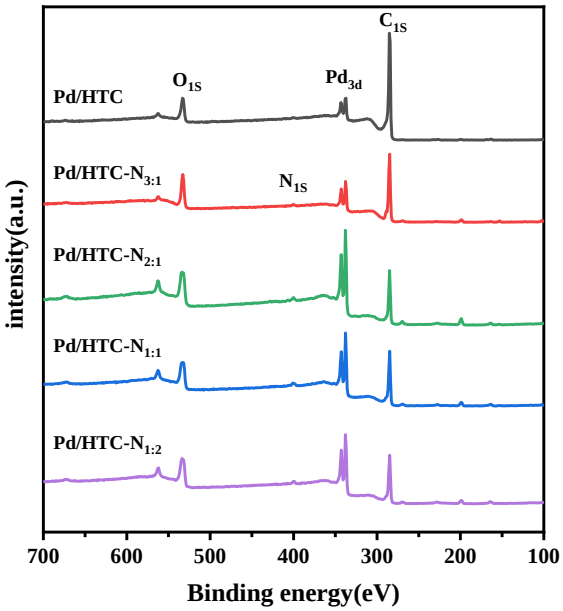

Figure S7. XPS survey spectrum of various catalysts: Pd/HTC, Pd/HTC-$N_{3:1}$, Pd/HTC-$N_{2:1}$, Pd/HTC-$N_{1:1}$ and Pd/HTC-$N_{1:2}$.

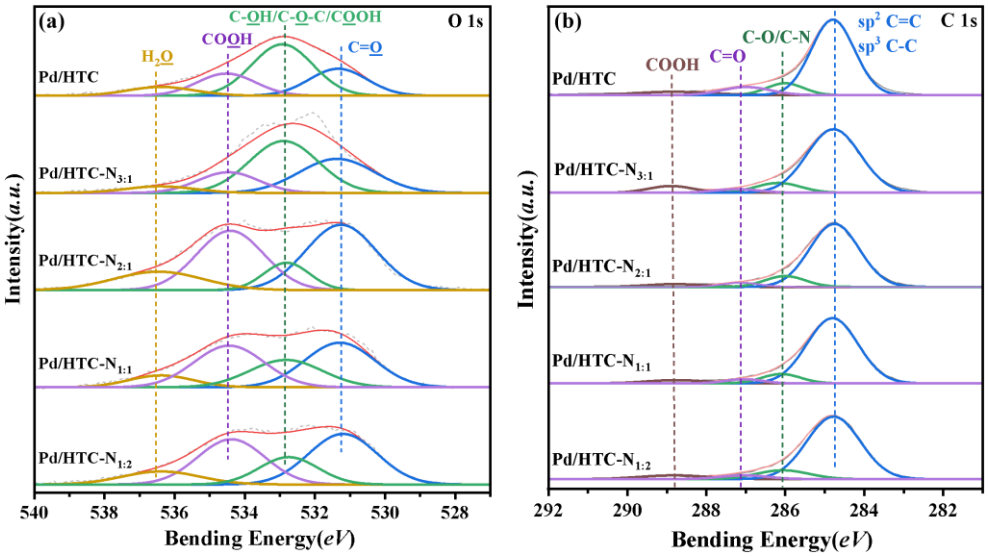

Figure S8. High-resolution of O 1s (a) and C 1s (b) XPS spectra of the Pd/HTC, Pd/HTC-$N_{3:1}$, Pd/HTC-$N_{2:1}$, Pd/HTC-$N_{1:1}$ and Pd/HTC-$N_{1:2}$ catalysts.

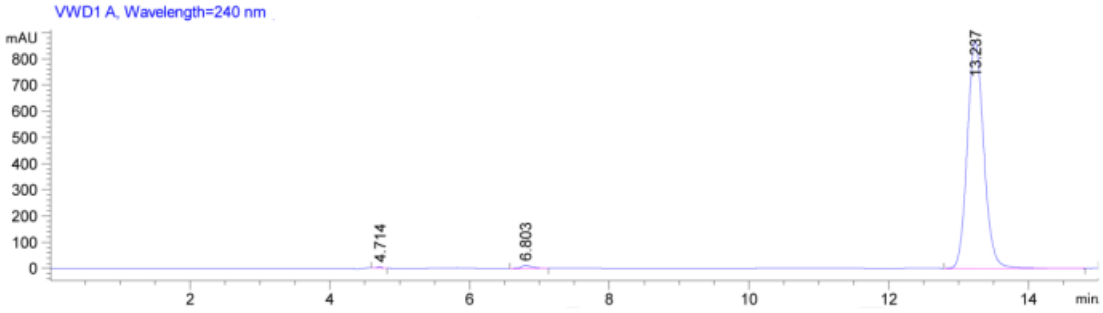

Figure S9. HPLC data of TADB crude product. Condition: C18 column, 70% methanol aqueous solution as mobile phase, velocity of flow 0.4mL/min.

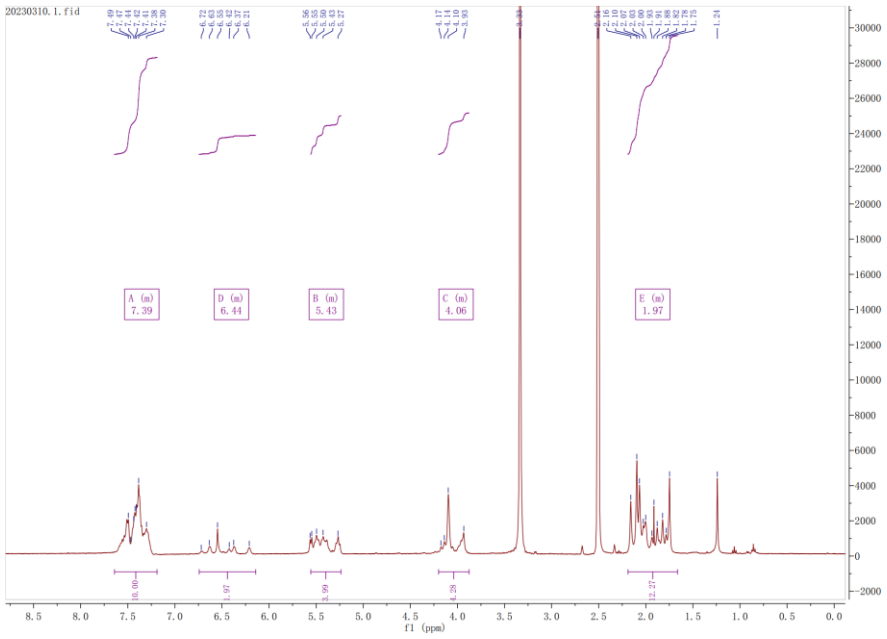

Figure S10. ^{1}H-NMR figure of TADB in DMSO.

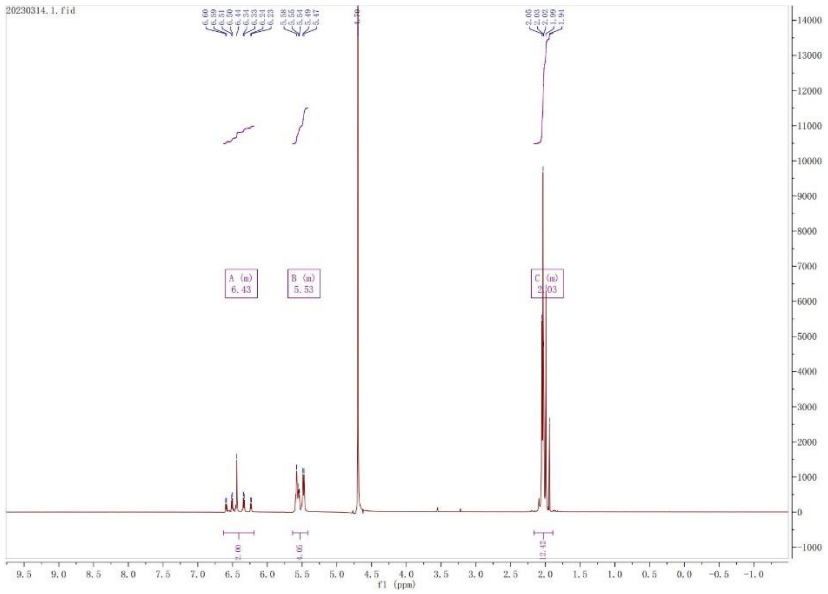

Figure S11. ^{1}H-NMR figure of TAIW in D_2O.

Table S1 Activities of Pd/HTC and Pd/HTC-$N_{1:1}$ in the three cycles of TADB debenzylation *.

Number	Catalysts	Number of cycles	TADB conversion%
1	Pd/HTC	Cycle-1	100
2	Pd/HTC	Cycle-2	76
3	Pd/HTC	Cycle-3	56
4	Pd/HTC-$N_{1:1}$	Cycle-1	100
5	Pd/HTC-$N_{1:1}$	Cycle-2	100
6	Pd/HTC-$N_{1:1}$	Cycle-3	86

* The Pd dosage was 2.6 ‰ comparing to substrate TADB.

Table S2 Surface atomic contents of different catalysts.

Sample	C%	N%	O%	Pd%
HTC	89.15	—	9.3	1.55
HTC-$N_{3:1}$	72.34	2.57	22.26	2.83
HTC-$N_{2:1}$	55.78	4.53	32.03	7.66
HTC-$N_{1:1}$	62.22	4.66	27.27	5.85
HTC-$N_{1:2}$	60.39	4.79	28.64	6.18

Table S3 XPS binding energies of Pd species and the ratios in different catalysts.

Samples	Peak position (eV)						Ratio (%)		
	Pd^0		PdO		Pd^{2+}				
	$3d_{5/2}$	$3d_{3/2}$	$3d_{5/2}$	$3d_{3/2}$	$3d_{5/2}$	$3d_{3/2}$	Pd^0	PdO	Pd^{2+}
Pd/HTC	335.7	340.8	337.7	343.0	338.8	344.6	11.5	72.3	16.2
Pd/HTC-$N_{3:1}$	335.8	340.8	337.3	342.6	338.7	344.4	7.8	72.5	19.7
Pd/HTC-$N_{2:1}$	335.8	340.8	337.5	342.8	338.8	344.6	7.0	75.0	18.0
Pd/HTC-$N_{1:1}$	335.9	340.7	337.5	342.7	338.8	344.6	5.8	77.6	16.6
Pd/HTC-$N_{1:2}$	335.8	340.8	337.4	342.8	338.8	344.6	6.3	78.5	15.2

Table S4 XPS binding energies of N species and the ratios in different catalysts.

Samples	Peak position (eV)			Ratio (%)		
	N 1s					
	Pyridine	Pyrrole	Graphltic	Pyridine	Pyrrole	Graphltic
Pd/HTC-$N_{3:1}$	398.8	400.3	401.5	37.3%	46.7%	16.0%
Pd/HTC-$N_{2:1}$	398.7	400.2	401.4	38.6%	44.3%	17.1%
Pd/HTC-$N_{1:1}$	398.7	400.3	401.5	42.5%	42.4%	15.0%
Pd/HTC-$N_{1:2}$	398.7	400.1	401.3	40.5%	41.2%	18.3%

Table S5 Calculated surface pyridinic N contents and surface pyridinic N/Pd molar ratios.

Sample	Pyridinic N content (%)	Surface pyridinic N content (%)	Surface N/Pd ratio	Surface pyridinic N/Pd ratio
Pd/HTC-$N_{3:1}$	37.3%	0.96	0.91	0.34
Pd/HTC-$N_{2:1}$	38.6%	1.75	0.59	0.23
Pd/HTC-$N_{1:1}$	42.5%	1.98	0.8	0.34
Pd/HTC-$N_{1:2}$	40.5%	1.94	0.78	0.31

Table S6 Surface atomic concentrations of the oxygen species of various catalysts.

Samples	Ratio of O 1s (%)			
	C=O	C-OH C-O-C COOH	COOH	H_2O
	531.3	532.8	534.5	536.4
Pd/HTC	23.7	47.7	19.6	9.0
Pd/HTC-$N_{3:1}$	32.8	45.5	16.0	5.7
Pd/HTC-$N_{2:1}$	40.1	10.8	34.8	14.3
Pd/HTC-$N_{1:1}$	35.5	22.6	33.1	8.8
Pd/HTC-$N_{1:2}$	38.1	17.6	33.2	11.1

Table S7 Surface atomic concentrations of the carbon species of various catalysts.

Samples	Ratio of C 1s (%)			
	Sp^2 C=C Sp^3 C-C	C-O C-N	C=O	COOH
	284.8	286	287	288.8
Pd/HTC	75.1	10.1	9.0	5.8
Pd/HTC-$N_{3:1}$	79.2	10.2	3.7	6.9
Pd/HTC-$N_{2:1}$	80.3	11.3	4.1	4.3
Pd/HTC-$N_{1:1}$	82.6	8.9	3.7	4.8
Pd/HTC-$N_{1:2}$	79.4	10.8	4.0	5.8