Electronic Supplementary Information

Directing Nitrogen-doped Carbons Support Chemistry for Improved Aqueous Phase Hydrogenation Catalysis

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1. N_2 adsorption analysis

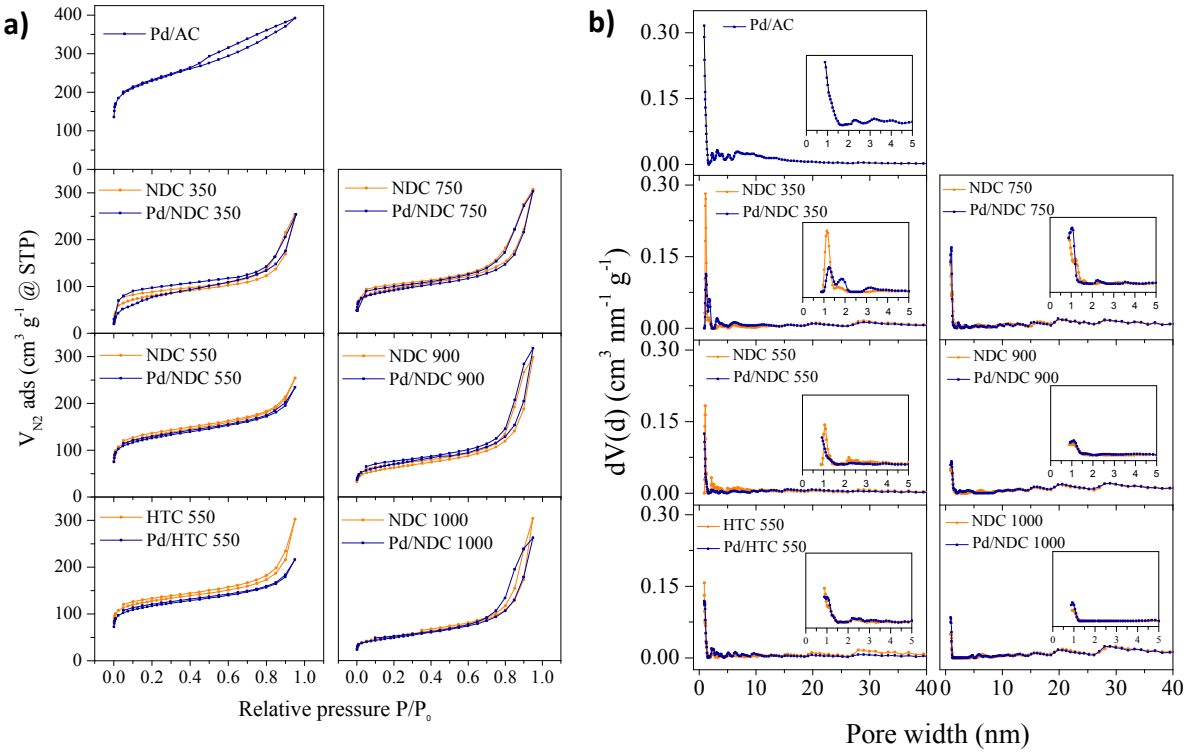
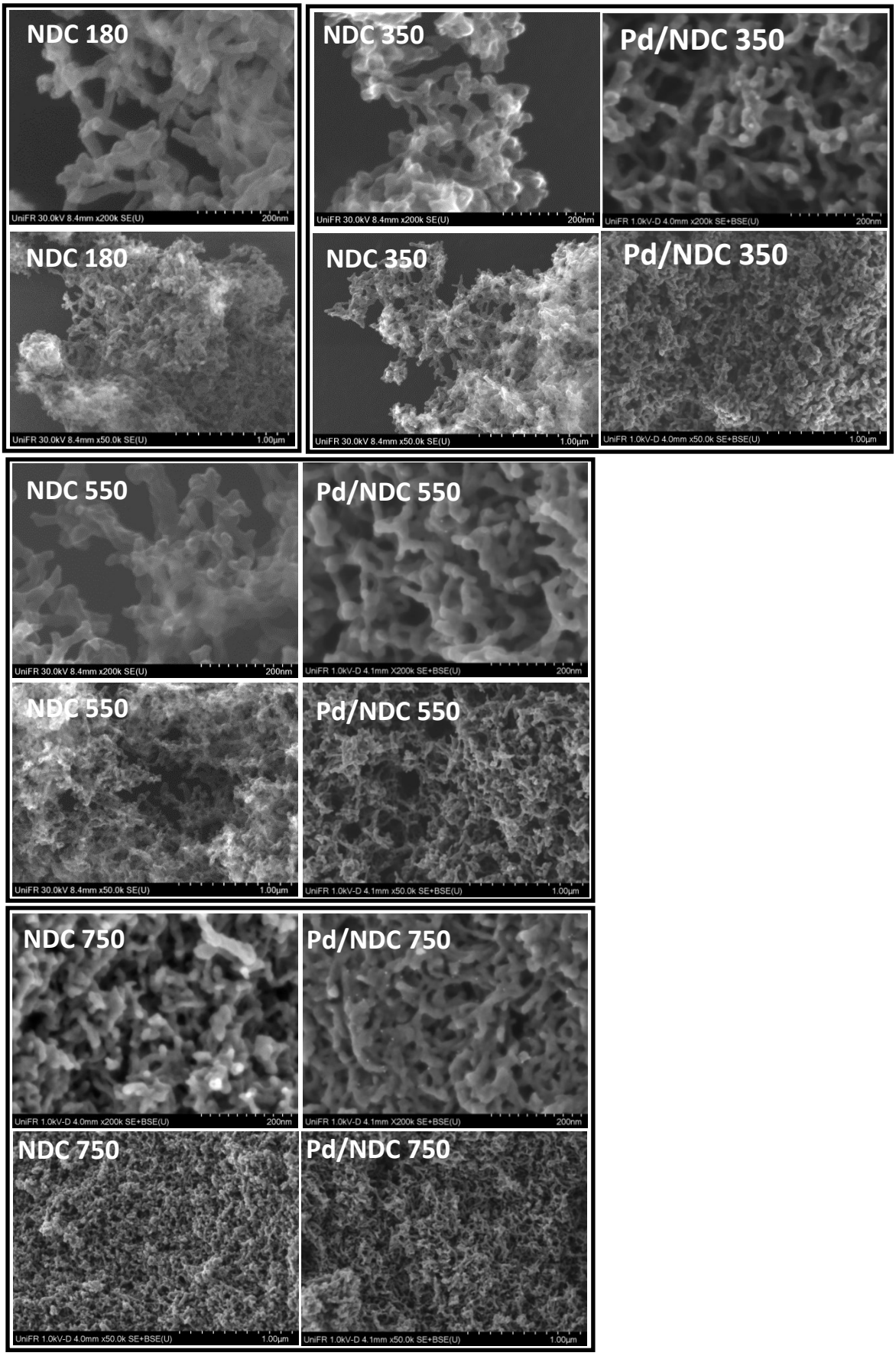


Figure S1 a) N_2 adsorption isotherms and b) pore size distribution of supports and Pd NP catalysts supported on different NDC T_c and HTC 550 supports in comparison to commercial Pd/AC catalyst. Note: T_c is the carbonisation temperature.

2. SEM of NDC T_c supports carbonised at different temperatures (T_c) and HTC support in comparison to Pd catalysts supported on these materials and commercial Pd/AC catalyst.



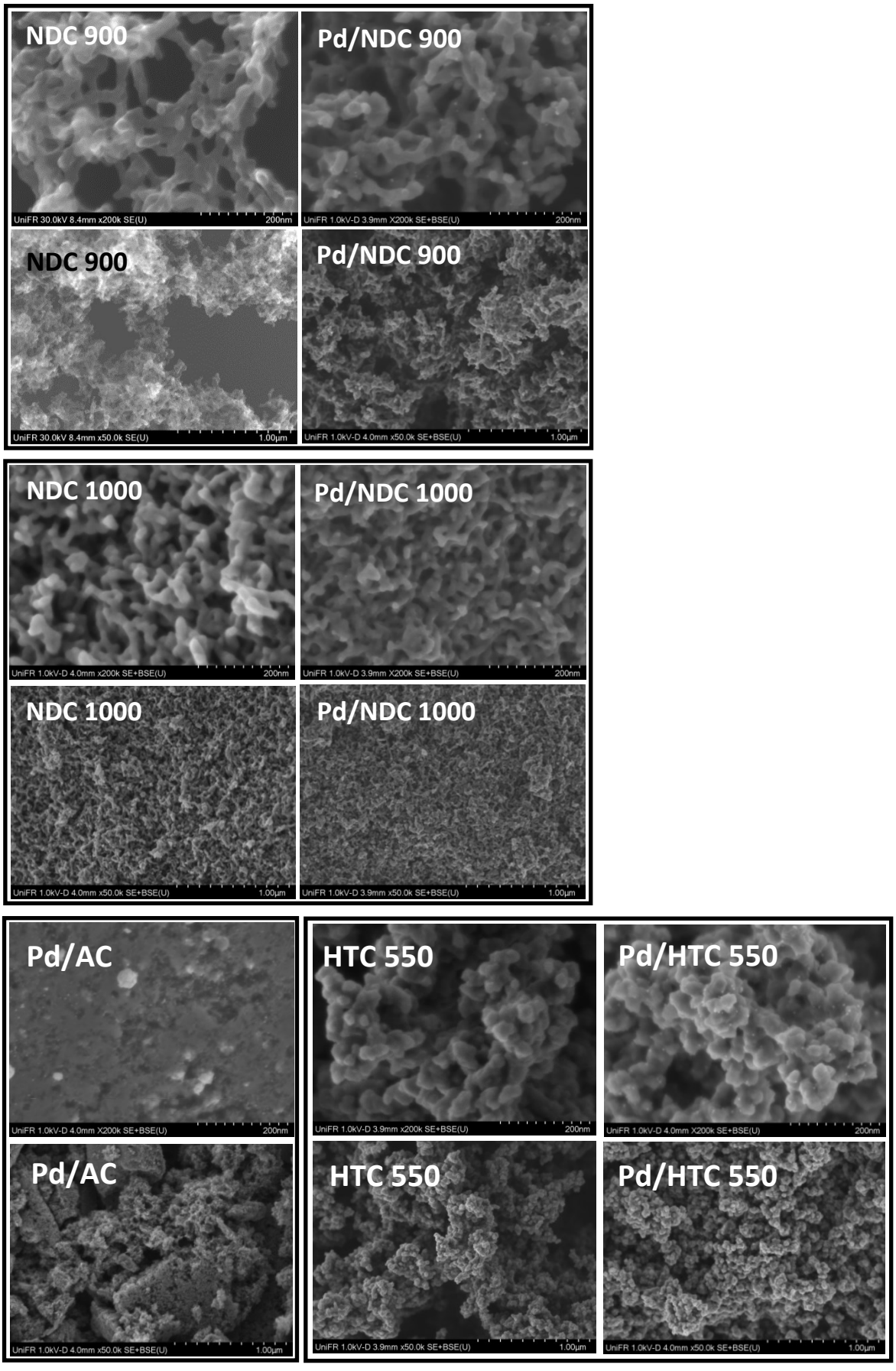


Figure S2 SEM images of NDC supports carbonised at different temperatures and HTC support in comparison to Pd catalysts supported on these materials and to commercial Pd/AC catalyst.

3. XPS C 1s of catalysts

C 1s core levels were fitted to Lorentzian (LA) line shape after subtraction of a Shirley background. Binding energies (BEs) of C=C, sp^2 were fixed at 284.8 eV. The full-width at half-maximum (FWHM) of C 1s was constrained between 1.1 eV and 1.5 eV depending on the species, and for the π-π* peak between 1.8 eV and 2.3 eV.

Table S1 XPS C 1s of Pd/NDCs, Pd/HTC 550 and Pd/AC catalysts.

	C1 (C=C)		**C2** (C-C/C-H_x)		**C3** (C-N/C-O)		**C4** (C=O/C=N)		**C5** (O-C=O)		**C6** (π-π*)	
Catalyst	**B.E. (eV)**	**at%**	**B.E. (eV)**	**at%**	**B.E. (eV)**	**at%**	**B.E. (eV)**	**at%**	**B.E. (eV)**	**at%**	**B.E. (eV)**	**at%**
Pd/NDC 350	284.8	21.9	285.7	34.7	286.7	24.5	287.9	10.5	289.3	4.5	291.1	4.0
Pd/NDC 550	284.8	66.4	285.7	15.9	286.7	7.1	287.9	4.5	289.4	3.6	291.1	2.6
Pd/HTC 550	284.8	75.9	285.7	3.9	286.6	7.0	287.9	3.8	289.4	3.4	291.2	3.9
Pd/NDC 750	284.8	66.4	285.7	15.9	286.7	7.1	287.9	4.5	289.4	3.6	291.1	2.6
Pd/NDC 900	284.8	63.3	285.7	12.9	286.6	9.9	287.9	5.6	289.3	3.6	291.1	4.8
Pd/NDC 1000	284.8	64.1	285.7	12.0	286.6	9.4	287.8	5.5	289.2	3.6	291.0	5.4
Pd/AC	284.8	68.6	285.7	7.9	286.5	8.7	287.7	5.5	289.1	4.1	290.8	8.7

Table S2 Full-width at half-maximum (FWHM) values of C 1s for all Pd catalysts.

	FWHM					
	C1 (C=C)	**C2** (C-C/C-H_x)	**C3** (C-N/C-O)	**C4** (C=O/C=N)	**C5** (O-C=O)	**C6** (π-π*)
Pd/NDC 350	1.2	1.2	1.3	1.4	1.4	2.3
Pd/NDC 550	1.2	1.2	1.3	1.4	1.4	1.8
Pd/HTC 550	1.2	1.2	1.3	1.4	1.4	2.0
Pd/NDC 750	1.2	1.2	1.3	1.4	1.4	2.0
Pd/NDC 900	1.2	1.2	1.3	1.4	1.4	2.1
Pd/NDC 1000	1.1	1.1	1.2	1.3	1.3	2.1
Pd/AC	1.1	1.1	1.2	1.3	1.3	2.1

4. XPS O 1s

O 1s core level peaks of support materials were fitted after a Shirley background subtraction and core level spectra were calibrated *vs.* the C 1s peak BE = 284.8 eV (C=C, sp^2). Peaks were fitted to Lorentzian (LA) line shape. The full-width at half-maximum (FWHM) of O 1s was constrained between 1.5 eV and 2.2 eV.

Table S3 XPS O 1s of NDCs and HTC 550 supports.

	O1 (C=O)		**O2** (CO(OH))		**O3** (C-OH/C-O-C)		**O4** (CO/CO_2)	
Catalyst	**B.E. (eV)**	**at%**	**B.E. (eV)**	**at%**	**B.E. (eV)**	**at%**	**B.E. (eV)**	**at%**
NDC 350	531.2	18.9	532.4	36.1	533.7	39.4	535.9	5.7
NDC 550	531.2	13.5	532.3	36.9	533.5	42.6	536.1	6.9
HTC 550	531.3	10.5	532.6	32.0	533.9	49.8	536.1	7.7
NDC 750	531.1	15.9	532.6	46.4	533.7	30.4	536.3	7.3
NDC 900	530.9	12.3	532.6	47.7	533.7	32.1	536.2	7.9
NDC 1000	531.0	14.6	532.6	46.8	533.7	30.6	536.2	7.9

Table S4 FWHM values of O 1s core level spectra.

	FWHM			
Support	**O1** (C=O)	**O2** (CO(OH))	**O3** (C-OH/C-O-C)	**O4** (CO/CO_2)
NDC 350	1.9	1.7	1.7	2.9
NDC 550	2.2	2.0	2.0	3.4
HTC 550	1.9	1.6	1.5	3.6
NDC 750	2.2	2.0	2.0	3.0
NDC 900	2.2	2.0	2.0	3.0
NDC 1000	2.2	2.0	2.0	3.0

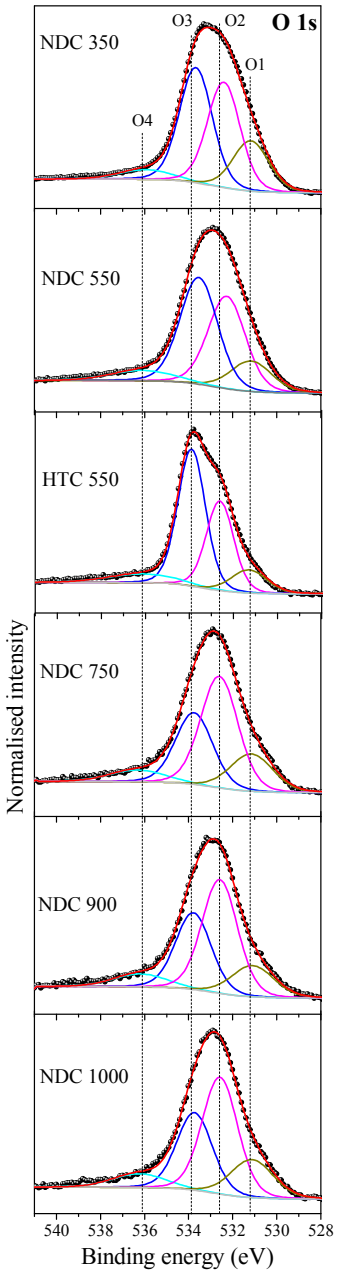


Figure S3 High-resolution XPS scans of O 1s region of HTC 550 and NDC supports.

5. XPS N 1s

N 1s core level peaks were fitted after a Shirley background subtraction and core level spectra were calibrated *vs.* the C 1s peak BE = 284.8 eV (C=C, sp^2). Peaks were fitted to Lorentzian (LA) line shape. Peaks were not constrained. The full-width at half-maximum (FWHM) of N 1s was constrained between 1.5 eV and 1.6 eV, for amine at 1.9 eV and for the pyr-N-oxide peak between 2.6 eV and 3.0 eV.

Table S5 FWHM values of N 1s core level spectra.

	FWHM					
Catalyst/ Support	**N1** (amine, $R\text{-}NH_2$)	**N2** (pyridine, C_6H_5N)	**N3** (N-Pd)	**N4** (pyrrole, C_4H_5N)	**N5** (quaternary N, $[N\text{-}R_4]^+$)	**N6** (pyr-N-oxide, $C_5H_5N^+O^-$)
NDC 350	1.9			1.6	1.7	
Pd/NDC 350	1.9	-	-	1.6	1.6	2.6
NDC 550		1.5		1.5	1.5	3.0
Pd/NDC 550	-	1.5	-	1.5	1.5	2.7
NDC 750		1.6	-	-	1.6	2.9
Pd/NDC 750	-	1.6	1.6	-	1.6	2.9
NDC 900	-	1.6	-	-	1.6	3.0
Pd/NDC 900	-	1.6	1.6	-	1.6	3.0
NDC 1000		1.6	-	-	1.6	2.9
Pd/NDC 1000	-	1.6	1.6	-	1.6	2.9

6. XPS Pd $3d_{5/2}$ and Pd $3d_{3/2}$

The core level peaks were fitted after a Shirley background subtraction and core level spectra were calibrated vs. the C 1s peak BE = 284.8 eV (C=C, sp^2). Core levels were fitted to Gaussian-Lorentzian (GL) line shape with a ratio of 70 % Gaussian. For analysis of Pd^0 species via XPS, area transitions were constrained to the theoretical value of 3:2 and the distance between the two spin-orbit splitting is set to 5.26 eV. FWHM of Pd^0 3d was fixed between 1.1 eV and 1.2 eV, for Pd^{2+} between 1.4 eV and 1.6 eV and for Pd^{4+} between 1.8 eV and 2.2 eV. The peak position was not constrained.

Table S6 FWHM values of Pd $3d_{5/2}$ and Pd $3d_{3/2}$for all Pd catalysts.

	FWHM					
	Pd 3d $_{5/2}$			**Pd 3d $_{3/2}$**		
	Pd^0	**Pd^{2+}**	**Pd^{4+}**	**Pd^0**	**Pd^{2+}**	**Pd^{4+}**
Pd/NDC 350	1.2	1.6	2.3	1.2	1.6	2.2
Pd/NDC 550	1.2	1.5	1.9	1.2	1.5	1.9
Pd/HTC 550	1.1	1.4	1.8	1.1	1.4	1.8
Pd/NDC 750	1.2	1.5	2.0	1.2	1.4	2.0

Pd/NDC 900	1.2	1.6	2.0	1.2	1.5	2.0
Pd/NDC 1000	1.2	1.5	2.0	1.2	1.5	2.0
Pd/AC	1.2	1.6	2.3	1.2	1.6	2.1

7. Correlation between Pd and quaternary N in Pd/NDC catalysts.

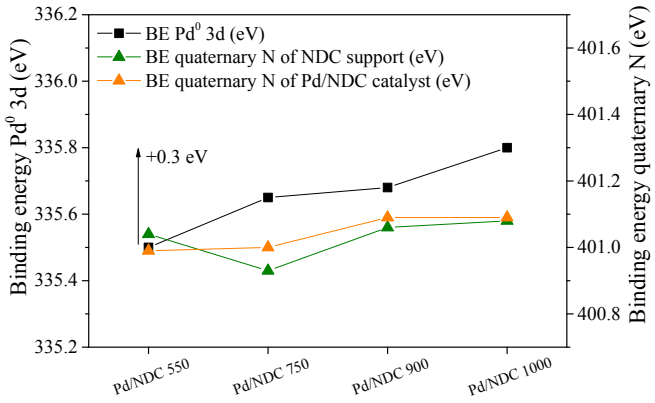


Figure S4 No significant differences in BE of quaternary N in NDC support compared to BE of quaternary N in Pd/NDC catalysts. Therefore, no charge transfer between the quaternary N and Pd^0 3d is assumed.

8. H_2O adsorption analysis and hydrophilicity index (HI)

Hydrophilicity index (HI) was calculated according to the reference[1] developed by Thommes and his co-workers. HI is the comparison of the adsorption isotherms of an adsorptive that is sensitive to surface chemistry and does not completely wet the adsorbent surface (i.e. water) with an adsorptive that does completely wet the surface (such as nitrogen at their boiling temperatures) at a given relative pressure (here P/P_0 = 0.93). HI of 1 indicates complete pore filling with H_2O. The corresponding volumes of N_2 and H_2O were calculated using a Gurvich rule by assuming that the pores are filled with the liquid adsorptive at P/P_0 = 0.93.[38] The greater the deviation from 1, the greater is the surface hydrophobicity of the catalysts. The calculation of the liquid volume of N_2 and H_2O is based on the Gurvich rule (Eq. 1). The Gurvich rule allows conversion of the adsorbed amount (at a relative pressure of 0.93) into a pore volume by assuming that the pores are filled with the liquid adsorptive (at P/P_0 =0.93 all micro- and mesoporous are filled with the liquid adsorptive).
Volume of liquid adsorbed (V_p) was calculated using Equation 1:

$$V_p = V_1/22414 \times M_1/\rho_1 \quad \textbf{(1)}$$

Where M_1 is molecular weight of the adsorptive gas and ρ_1 is density of adsorptive.
Having ρ_{N2}= 0.808 g/cm³ and ρ_{H2O}=0.997 g/cm³
Thus:
V_p (nitrogen) = V_1 (nitrogen) × 0.001547
V_p (water) = V_1 (water) × 0.0008055

The H-index is then:

$$\text{H-index} = V_p water/V_p nitrogen \quad \textbf{(2)}$$

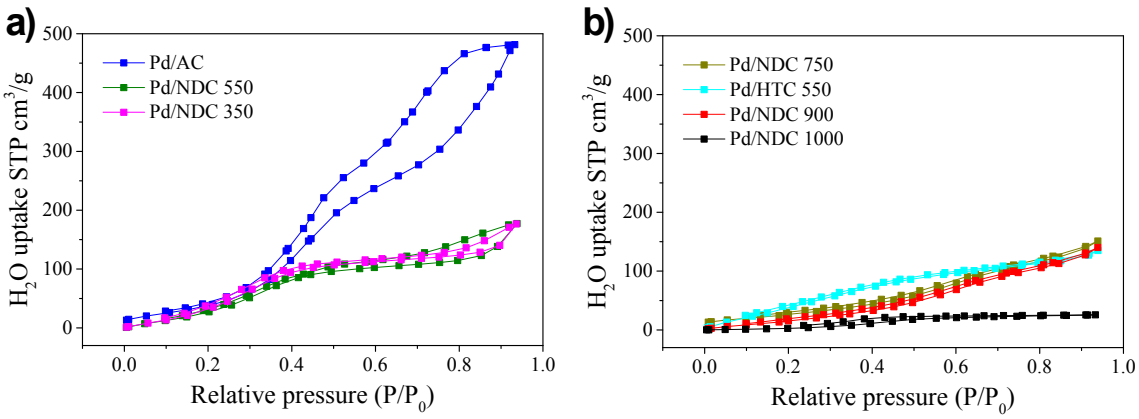


Figure S5 H_2O adsorption-desorption isotherms (measured at 40 °C) for all catalysts.

9. Impact of N and O content in the Pd/NDC catalysts on hydrophilicity (H-index). N and O contents were determined by the XPS analysis (survey spectra).

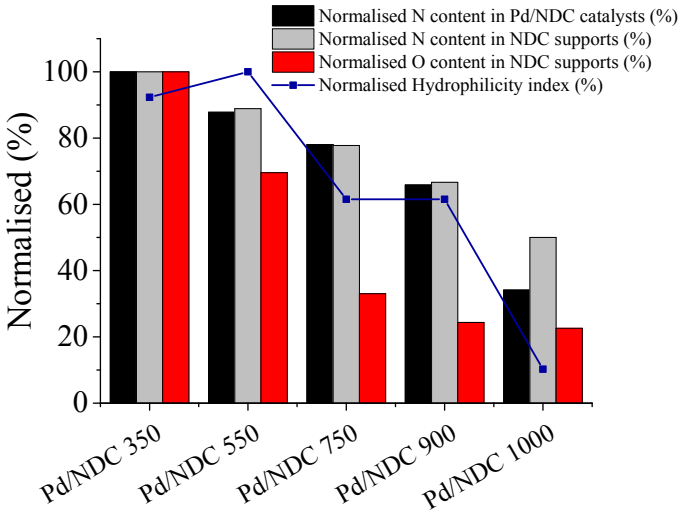


Figure S6 Correlation between the normalised hydrophilicity index and normalised N content in Pd/NDC catalysts and NDC supports as well as normalised O content in the NDC support.

10. XPS Pd $3d_{5/2}$ and Pd $3d_{3/2}$ of spent Pd/NDC 900 and Pd/AC catalysts.

Table S7 XPS Pd $3d_{5/2}$ and Pd $3d_{3/2}$ of spent Pd/NDC 900 and Pd/AC catalysts in comparison to fresh catalysts.

	Pd 3d $_{5/2}$						
Catalyst	**B.E. Pd^0**	**Peak area (%)**	**B.E. Pd^{2+}**	**Peak area (%)**	**B.E. Pd^{4+}**	**Peak area (%)**	**Ratio $Pd^0/Pd^{\delta+}$**
Pd/NDC 900	335.7	38.4	336.6	12.3	338.2	8.5	1.8
Pd/NDC 900 spent	335.7	37.3	336.6	15.1	338.3	5.9	1.8
Pd/AC	335.8	31.9	337.2	21.7	338.8	6.6	1.1
Pd/AC	336.0	48.5	337.0	4.1	338.4	6.1	4.8

spent							

Catalyst	Pd 3d $_{3/2}$						
	B.E. Pd^0	Peak area (%)	B.E. Pd^{2+}	Peak area (%)	B.E. Pd^{4+}	Peak area (%)	Ratio $Pd^0/Pd^{\delta+}$
Pd/NDC 900	341.0	25.6	341.8	10.0	343.3	5.7	1.6
Pd/NDC 900 spent	341.0	24.9	341.8	12.5	343.3	4.3	1.5
Pd/AC	341.0	21.3	342.3	10.1	342.3	10.1	1.1
Pd/AC spent	341.2	32.3	342.2	5.2	343.5	3.8	3.6

Table S8 FWHM values of Pd $3d_{5/2}$ and Pd $3d_{3/2}$ for spent Pd/NDC 900 and Pd/AC catalysts in comparison to fresh catalysts.

	FWHM					
	Pd 3d $_{5/2}$			Pd 3d $_{3/2}$		
	Pd^0	Pd^{2+}	Pd^{4+}	Pd^0	Pd^{2+}	Pd^{4+}
Pd/NDC 900	1.2	1.6	2.0	1.2	1.5	2.0
Pd/NDC 900 spent	1.2	1.5	2.1	1.2	1.5	2.0
Pd/AC	1.2	1.6	2.3	1.2	1.6	2.1
Pd/AC spent	1.2	1.6	2.0	1.2	1.6	1.8

Characterisation

N_2 adsorption

N_2 adsorption analysis was performed using a QuadraSorb Station 2 device (at 77.3 K). Prior to measurements, samples were degassed at 120 °C for 24 h. Specific surface areas were determined using N_2 adsorption data and the BET (Brunauer, Emmett, and Teller) method and calculated using a minimum of 5 points in the BET plot ($R^2 > 0.995$). Pore size distributions were obtained using N_2 adsorption data and the Quenched Solid Density Functional Theory (QSDFT) method as this evaluation model takes into account the effects of surface roughness and chemical heterogeneity of the material surfaces. N_2 adsorption isotherms and pore size distribution data were exported and processed using Origin Pro 9.1G software.

SEM

SEM analysis was performed on a high-resolution scanning electron microscope (HRSEM - SU8200 from Hitachi High-Tech), operated at 1.0 kV. Prior to measurement, samples were dried under vacuum overnight at 80 °C. For analysis, material was fixed on aluminum sample holders with double-sided adhesive conductive carbon tape.

GC-FID

Unconverted phenol and reaction products were identified by GC-FID (Agilent 7890A) using a DB-5ms column (15 m, 0.25 mm, 0.25 µm) and He as a carrier gas. After 0.1 min of holding at 30 °C, the column was ramped at 1 °C/min up to 45 °C, hold for 0.1 min and then ramped at 5 °C/min up to 80 °C. In the last step, the column was heated to 217 °C at 70 °C/min ramping rate. Injection volume was 5 µL, split ratio was 230:1 and the temperatures of the injector and detector were fixed at 320

and 275 °C, respectively. Yields and conversions were determined based on the phenol/cyclohexanone/cyclohexanol GC peak areas.

TEM

Pd catalysts were analysed on a Zeiss (LEO) 912 Omega at an acceleration voltage of 120 kV. Particle sizes were measured with ImageJ 1.52h, National Institutes of Health. All particle size distributions are obtained from a total count of a minimum of 260 nanoparticles.

XPS

X-ray photoelectron spectroscopy (XPS) measurements were performed using a ThermoScientific K-Alpha$^+$ X-ray Photoelectron Spectrometer. All samples were analyzed using a microfocused, monochromated Al K α X-ray source (1486.68 eV; 400 µm spot size). The analyzer had a pass energy of 200 eV (survey), and 50 eV (high resolution spectra), respectively. To prevent any localised charge buildup during analysis the K-Alpha$^+$ charge compensation system was employed at all measurements. The samples were mounted on conductive carbon tape. The XPS fitting was done by CasaXPS 2.3.15 software. In a typical procedure, core levels were fitted to Lorentzian line shape after subtraction of a Shirley background. Binding energies were calibrated by taking the adventitious C 1s binding energy (284.8 eV) as a reference. Data were exported and processed using Origin Pro 9.1G software.

CHNS Elemental analysis

The amount of carbon, nitrogen and hydrogen in supported materials was determined by CHNS elemental analysis on a Vario-Micro-Cube, Elementar Analysensysteme GmbH. O content was calculated by a subtraction of detected C, H, and N wt% content from the total 100 wt% by CHNS elemental analysis. Before measurement, samples were carefully ground to a fine powder using a mortar and pestle and dried overnight under vacuum at 80 °C.

ICP-OES

The amount of palladium in all catalysts was determined by inductive coupled plasma coupled with optical emission spectroscopy (Spectroblue EOP TI, Spectro Analytical Instruments GmbH). Solid samples (30-60 mg) were treated at room temperature with a mixture of hydrochloric acid (6 ml), hydrofluoric acid (2 ml) and nitric acid (2 ml) overnight. So prepared mixture was treated under microwaves and pressure in order to completely dissolve Pd in a CEM Discover SP-D, CEM. Ramp time was 4 min/K to reach 180 °C and the hold time was 10 min. For analysis the sample was filtered and deionized water was added to a volume of 100 ml.

Pulse H_2 Chemisorption

The metal dispersion and Pd surface area were evaluated by means of a H_2 chemisorption method and were carried out on a Thermo Scientific TPDRO 1100 equipped with a TCD from Thermo Fisher. Quartz wool was first put into the sample tube to keep the sample in place. The catalyst (ca. 50 mg) was loaded inside a sample holder, on which more quartz wool was placed to prevent it from being sucked into the instrument during evacuation. Catalyst was reduced in 5 % v/v H_2/Ar at 120 °C (heating ramp 2 K min^{-1}), with isothermal period of 20 min. After reduction the catalyst was heated to 150 °C in Ar (heating ramp 2 K min^{-1}) for another hour and cooled down to 35 °C at 2 K min^{-1} in Ar. The pulse-chemisorption was performed at 35 °C in 5 % v/v H_2/Ar. The gas flow was in all steps 20 mL/min. A metal/H_2 average stoichiometry of 2 was assumed to calculate the metal dispersion. The metal dispersion was calculated using the relationship:

$$Dispersion_{Pd} = \frac{n_{H2} \times S_f}{n_{Pd} \times 100} \quad \textbf{(3)}$$

Where n_{H2} is adsorbed amount of H_2 (mol), S_f is the stoichiometric factor (2), n_{Pd} is the mole of Pd in the sample (mol).

H_2O Adsorption

H_2O adsorption isotherms were measured in a volumetric apparatus VSTAR-Quantachrome vapour sorption analyser. Measurements were performed at 40 °C with 40 measured points between 0.05-0.99 P/P_0. Prior to measurements, samples were degassed at 200 °C for 3.5 h. H_2O adsorption isotherms data were exported and processed using Origin Pro 9.1G software.

XRD

XRD characterizations were carried out using a Rigaku MiniFlex600 diffractometer using Bragg-Brentano geometry and working with Cu-Kα radiation (λ = 0.15417 nm). The X-Ray gun was operated at 40 kV and 15 mA. Diffractograms were recorded over a 2θ range of 10 to 90° using a step width of 0.02° and step speed of 0.1°/min. The NIST SRM640e standard Si powder was used to determine the X-ray wavelength with precision.

Rietveld refinement

XRD measurements were done also in glass capillaries using Debye-Scherrer geometry and used for Rietveld refinement to determine the crystallite size of Pd. Measurements were performed using a STOE instrument with a Cu anode and Ge 111 monochromator operated at 40 kV and 30 mA. Diffractograms were recorded over a 2θ range of 10 to 106° using a step width of 0.5° and step time of 120 s.
Fig. S7a shows XRD patterns of Pd/NDCs catalysts and Fig. S6b XRD patterns of Pd/AC and Pd/HTC 550 catalysts measured in capillary using Debye-Scherrer geometry.
Fig. S8 shows fitting patterns obtained from Rietveld refinement for all Pd catalysts. For Rietveld calculation FullProf software was used.

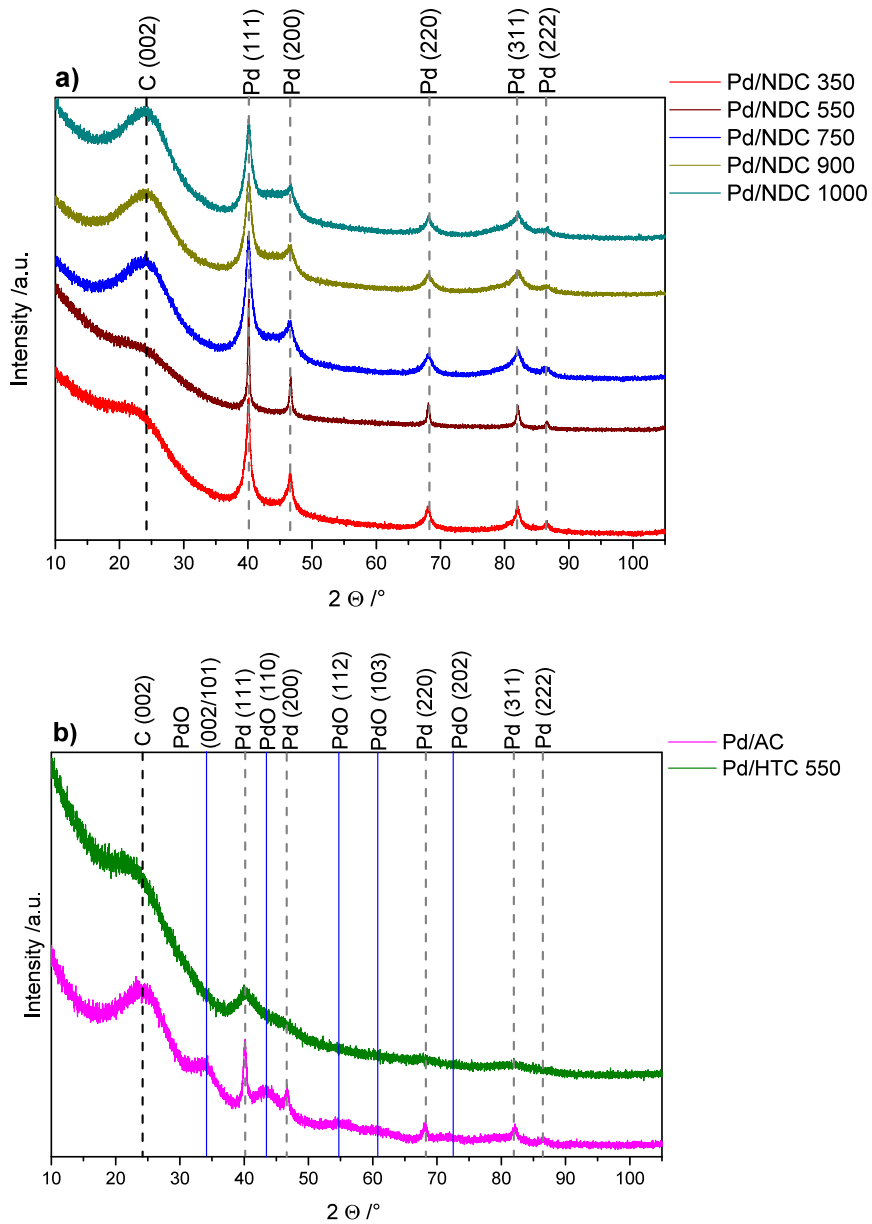


Figure S7 XRD patterns for a) Pd/NDC catalysts and b) Pd/HTC 550 and commercial Pd/AC catalysts.

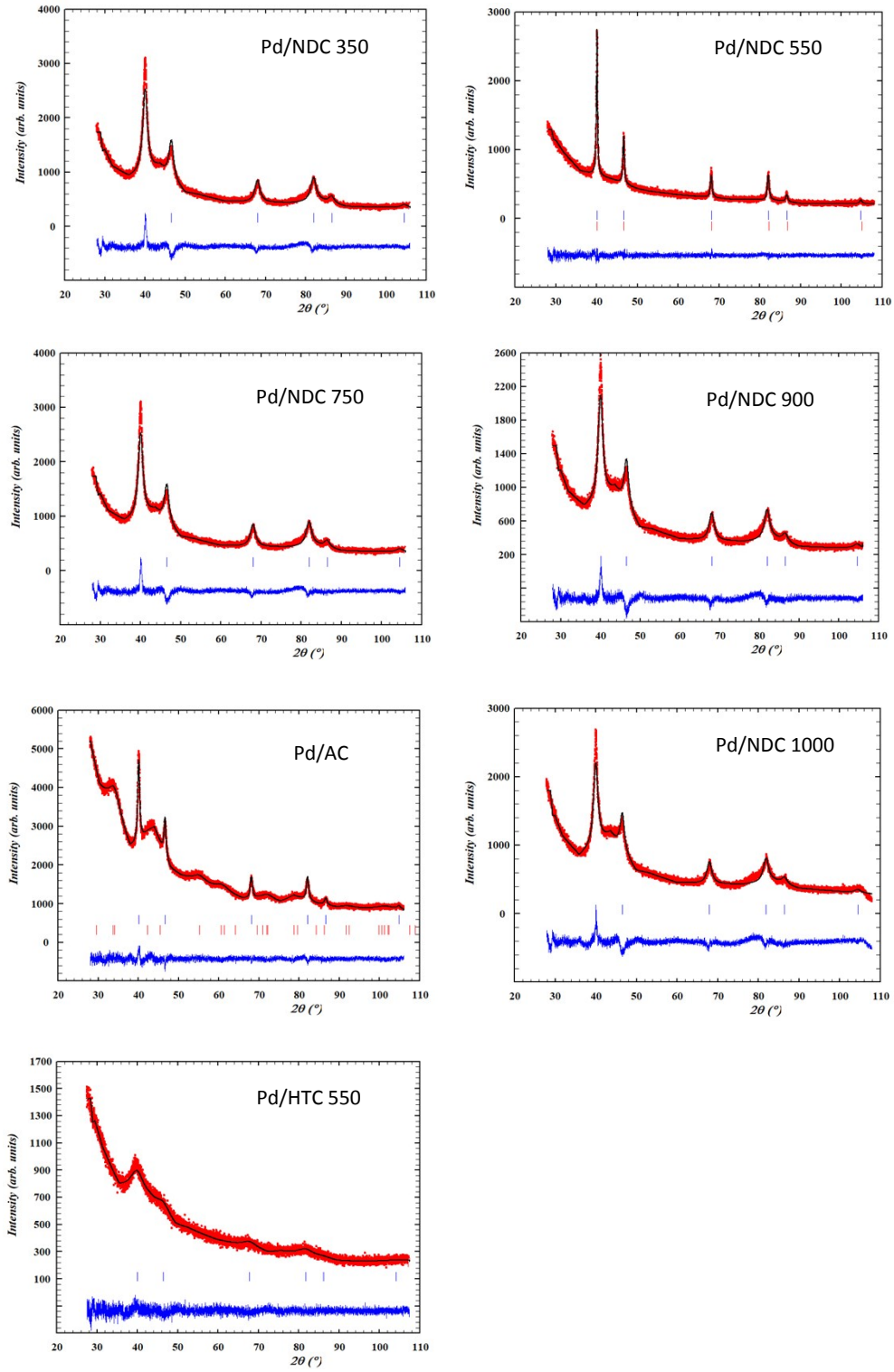


Figure S8 Structural analysis and patterns fit using Rietveld refinement method.

References:

[1] M. Thommes, S. Mitchell, J. Pérez-Ramírez, *J. Phys. Chem. C* **2012**, *116*, 18816–18823.