

Supporting Information

Nitrogen-Doped Carbons with Hierarchical Porosity *via* Chemical Blowing Towards Long-lived Metal-free Catalysts for Acetylene Hydrochlorination

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Catalyst Synthesis

The N-doped carbons, NC-I- T_C , were synthesized *via* a chemical blowing approach, using ammonium chloride as blowing agent and hexamethylene tetraamine (HMT, 99.0%, Sigma-Aldrich) as the C/N-precursor.^[1] Typically, a mixture of 1 g HMT and 1 g NH_4Cl was finely mixed and subsequently carbonized at varying temperatures ($T_C = 773$ - 1273 K, heating rate 3 K min^{-1} , 6 h, N_2 atmosphere), as indicated in the respective sample code. For the preparation of NC-II and NC-III, magnesium acetate (1 g $\text{Mg}(\text{OAc})_2 \cdot 4 \text{ H}_2\text{O}$, MERCK) or calcium carbonate (1 g CaCO_3 (PlasmaChem GmbH) were respectively added to the mixture of HMT and NH_4Cl , before carbonization at 973 K (heating rate 3 K min^{-1} , 6 h, N_2 atmosphere, for simplicity $T_C = 973$ is omitted in the sample code). The obtained products were stirred in 1 M H_2SO_4 (NC-II) and 1 M HCl (NC-III) for 24 h and subsequently in deionized water (24 h) to remove Mg and Ca residues, respectively. Finally, the solids were filtered (deionized water, 1 L g^{-1}), dried ($T = 373$ K, 24 h, static air), and ground and sieved into particles (0.4-0.6 mm).

Catalyst Characterization

Elemental analysis was performed on a Flash EA 2000 Series. Powder X-ray diffraction (XRD) was measured using a Rigaku Ultima IV multi-purpose high power X-ray diffractometer. The data was recorded in the 5 - 70° 2θ range. Argon sorption was measured at 77 K in a Micromeritics 3Flex instrument, after evacuation of the samples at 373 K for 24 h. The pore size distribution was determined *via* Nonlocal Density Functional Theory (NLDFT). Static volumetric chemisorption of acetylene was performed in a Micromeritics 3Flex Chemi instrument at 303 K. Temperature-programmed desorption of acetylene (C_2H_2 -TPD) was performed in a Micromeritics Autochem II 2920 unit equipped with a thermal conductivity detector (TCD) and a Pfeiffer Vacuum OmniStar GSD 320 O MS. The sample (amount fixed to 100 mg) was loaded into a U-shaped quartz micro-reactor, pre-dried in He ($T = 473$ K, 2 h, $F_T = 20 \text{ cm}^3 \text{ min}^{-1}$, heating rate 5 K min^{-1}), cooled to 323 K, and subsequently saturated with acetylene ($T = 323$ K, 20 min, $F_T = 10 \text{ cm}^3 \text{ min}^{-1}$). After purging with He ($T = 323$ K, 60 min, $F_T = 20 \text{ cm}^3 \text{ min}^{-1}$), the desorption was initiated by increasing the temperature to 673 K using a ramp of 5 K min^{-1} , while monitoring the desorbed C_2H_2 by MS. Thermogravimetric analysis (TGA) was performed using a Linseis STA PT1600 system coupled to a Pfeiffer Vacuum Thermo-Star GSD 320 T1 mass spectrometer (MS). TGA of the as-prepared catalysts and after use in acetylene hydrochlorination was carried out in diluted oxygen (20% O_2/Ar , $100 \text{ cm}^3 \text{ min}^{-1}$), heating the samples (amount fixed to 20 mg) from 298 to 1273 K at 10 K min^{-1} to quantify the amount of coke deposits in the used catalysts. TGA-differential scanning calorimetry (DSC) to monitor the synthesis of NC-I, NC-II, and NC-III was conducted in Ar atmosphere (heating rate 3 K min^{-1} , $T = 973$ K). Raman spectroscopy was carried out in a confocal Raman microscope (WITec CRM 200) using a 532 nm diode laser. The microscope was operated in the backscattering mode with a $100\times$ objective lens and 4 mW power. Bright field transmission electron microscopy (TEM) and high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) coupled with energy dispersive X-ray spectroscopy (EDX) were performed using a Talos F200X instrument operated at 200 kV and equipped with a FEI SuperX detector. The carbon powder was dispersed dry onto holey-carbon coated copper grids. Scanning electron microscopy (SEM) was acquired on a Tescan Mira3 LM FE. X-ray photoelectron spectroscopy (XPS) was carried out using a PHI VersaProbe II scanning XPS microprobe (Physical

Instruments AG, Germany) with a monochromatic Al-K α X-ray source of 24.8 W power with a beam size of 100 μ m. The detailed fitting parameters are given in **Table S2**.

Catalyst Testing

Steady-state hydrochlorination of acetylene was studied at atmospheric pressure in a continuous-flow fixed-bed micro-reactor (**Figure S1**).^[2] The gases C₂H₂ (PanGas, purity 2.6), HCl (Air Liquide, purity 2.8, anhydrous), Ar (PanGas, purity 5.0, internal standard), and He (PanGas, purity 5.0, carrier gas), were fed using digital mass-flow controllers (Bronkhorst) to the mixing unit, equipped with a pressure indicator. A quartz micro-reactor of 10 mm inner diameter was loaded with the catalyst ($W_{\text{cat}} = 0.25$ g, particle size 0.4–0.6 mm) and placed in a homemade electrical oven. A K-type thermocouple fixed in a coaxial quartz thermowell with the tip positioned in the center of the catalyst bed was used to control the temperature during the reaction. Prior to testing, the catalyst was heated in a He flow to the desired temperature ($T_{\text{bed}} = 473\text{--}623$ K) and allowed to stabilize for at least 30 min before the reaction mixture (40 vol.% C₂H₂, 44 vol.% HCl, and 16 vol.% Ar) was fed at a total volumetric flow of $F_T = 15$ cm³ STP min⁻¹. Carbon-containing compounds (C₂H₂ and C₂H₃Cl) and Ar were quantified on-line *via* a gas chromatograph equipped with a GS-Carbon PLOT column coupled to a mass spectrometer (GC-MS, Agilent, GC 7890B, Agilent MSD 5977A). Since vinyl chloride (VCM) was the only product detected in all our tests, the catalytic activity is presented as the yield of VCM, $Y(\text{VCM})$, calculated according to Eq. 1,

$$Y(\text{VCM}) = \frac{n(\text{VCM})^{\text{outlet}}}{n(\text{C}_2\text{H}_2)^{\text{inlet}}} \times 100, \% \quad \text{Eq. 1}$$

where $n(\text{VCM})^{\text{outlet}}$ and $n(\text{C}_2\text{H}_2)^{\text{inlet}}$ denote the respective molar flows of VCM and C₂H₂ at the reactor outlet and inlet. The error of the carbon balance, ε_C , determined using Eq. 2, was less than 5% in all experiments, *i.e.*, the carbon mass balance was closed at $\geq 95\%$.

$$\varepsilon_C = \frac{n(\text{C}_2\text{H}_2)^{\text{inlet}} - (n(\text{C}_2\text{H}_2)^{\text{outlet}} + n(\text{VCM})^{\text{outlet}})}{n(\text{C}_2\text{H}_2)^{\text{inlet}}} \times 100, \% \quad \text{Eq. 2}$$

After the tests, the reactor was quenched to room temperature in He flow and the catalyst was retrieved for further characterization. All catalytic data points were determined as an average of at least two measurements. The evaluation of the dimensionless moduli based on the criteria of Carberry, Mears, and Weisz–Prater confirmed that all the catalytic tests were performed in the absence of mass and heat transfer limitations.^[3] The deactivation constants, k_D , were derived *via* a simple linear regression of the initial time-on-stream (*tos*) performances of selected catalysts (linear regime). For clarity, the considered data ranges are indicated by the respective trend lines in **Figures 3** and **S9**.

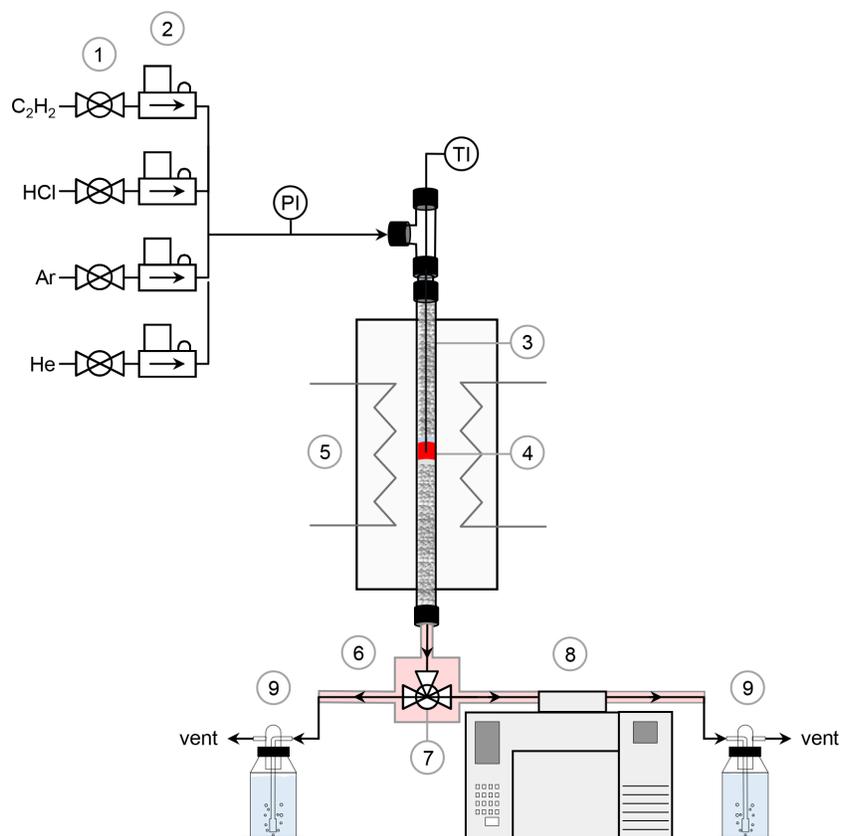


Figure S1. Scheme of the laboratory set-up used for acetylene hydrochlorination. 1: two-way on-off valves, 2: mass flow controllers, 3: quartz reactor, 4: catalyst bed, 5: oven, 6: heat tracing (red background), 7: three-way sampling valve, 8: gas chromatograph coupled to a mass spectrometer, 9: NaOH scrubbers, PI: pressure indicator, and TI: temperature indicator.

Table S1. Characterization data of N-doped carbon catalysts.

Sample	C ^a (at.%)	O ^a (at.%)	N ^a (at.%)	V _{total} ^b (cm ³ g ⁻¹)	V _{micro} ^c (cm ³ g ⁻¹)	S _{BET} ^d (m ² g ⁻¹)
NC-I-773	73.4	2.9	23.7	0.00	0.00	4
NC-I-873	77.4	2.9	19.8	0.08	0.03	207
NC-I-973	84.5	2.8	12.7	0.10	0.06	245
NC-I-1073	86.4	2.9	10.7	0.10	0.06	238
NC-I-1173	91.3	3.6	5.2	0.08	0.03	170
NC-I-1273	93.5	2.5	4.1	0.01	0.00	4
NC-II ^e	75.6	6.3	17.9	0.29	0.22	643
NC-III ^e	78.7	4.3	16.8	0.70	0.42	1290

^aXPS analysis. ^bVolume of Ar adsorbed at $p/p_0 = 0.98$. ^c t -plot method. ^dBET method. ^eCarbonized at 973 K.

Table S2. Fitting parameters derived from the N 1s XPS spectra of as-prepared N-doped carbons and after use in acetylene hydrochlorination.

Catalyst	N6 ^a			N5 ^a			N3 ^a			N0 ^a		
	Position (eV)	FWHM ^b (eV)	Area (%)	Position (eV)	FWHM ^b (eV)	Area (%)	Position (eV)	FWHM ^b (eV)	Area (%)	Position (eV)	FWHM ^b (eV)	Area (%)
NC-I-773	398.2	1.6	52.7	400.1	1.7	38.3	401	1.6	7.1	402.9	2.0	1.8
NC-I-873	398.2	1.7	50.1	400.1	1.4	23.9	400.9	1.7	19.4	402.9	2.6	6.6
NC-I-973	398.2	1.5	38.1	400.2	1.8	26.0	401.1	1.8	26.7	403.3	2.4	9.2
NC-I-1073	398.3	1.8	39.5	400.4	1.8	25.3	401.1	1.6	28.8	402.9	1.7	6.3
NC-I-1173	398.4	2.3	18.3	400.5	2.4	13.2	401	2.2	45.6	402.9	2.2	22.8
NC-I-1273	398.5	1.0	10.6	400.4	2.5	10.9	401.2	1.7	64.8	403.1	2.5	13.6
NC-II	398.3	1.7	44.1	400.2	1.7	30.0	401.3	1.7	17.6	403.2	1.7	8.3
NC-III	398.1	1.5	43.2	400.2	1.8	28.5	401.0	1.9	22.2	403.1	1.8	6.1
NC-I-12h	398.3	1.6	40.4	400.3	1.6	40	401.3	1.6	17.3	403.1	1.6	2.3
NC-II-12h	398.3	1.6	40.4	400.1	1.6	33.2	401.2	1.6	20.8	403.1	1.6	5.6
NC-III-12h	398.3	1.5	41.1	400.1	1.5	45.3	401.3	1.7	8.8	403.1	1.6	4.8

^aAssigned based on reference values.^[2] N6: pyridinic-N, N5: pyrrolic-N, N3: graphitic-N, N0: oxidized-N.

^bFWHM: full width at half maximum.

Table S3. Deactivation constants (k_D) of selected catalysts in acetylene hydrochlorination.

Catalyst	tos^a (h)	k_D (h^{-1})	Reference
NC-I	1	20	This work
NC-II	1	7	This work
NC-III	12	0.3	This work
NC	1	14	This work and [2]
Au/NC	12	1.2	[4]
Au/AC	12	0.8	[4]
Ru/NC	12	1.3	[5]

^aTime-on-stream. Reaction conditions: $T_{bed} = 473$ K and 523 K for metal-c and metal-free catalysts, respectively, $F_{tot} = 15$ cm³ min⁻¹, C₂H₂:HCl:Ar = 44:40:16, $W_{cat} = 0.25$ g. ^bLinear regression of the data range indicated by dashed lines in **Figure S9**.

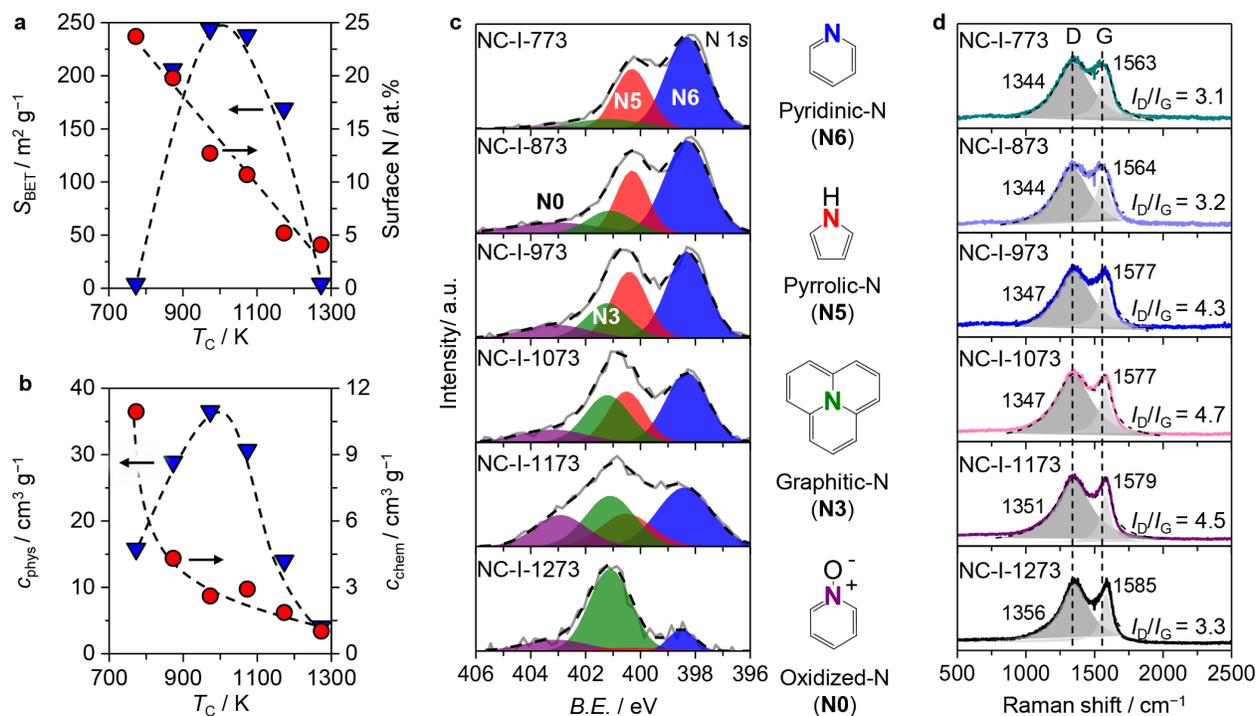


Figure S2. **a**, Evolution of the surface area and the surface N-content, as derived from N 1s XPS analysis, as a function of the carbonization temperature T_C . The former passes through a maximum in the temperature range of 900-1100 K, which is well in line with previous literature reports.² In the temperature range of 900-1100 K, cross-linking reactions take place, leading to an expansion of the carbon material which corresponds to the development of a more porous structure with high surface area. At increasingly higher temperatures these linkages degrade, accompanied by the oxidation of the carbon material, which causes the collapse of the pore structure and loss in specific surface area.^[6] **b**, physisorption and chemisorption of acetylene as a function of T_C . **c**, N 1s XPS spectra, accompanied by the structures of all N-species observed. **d**, Raman spectra of the NC-I- T_C series, confirming the common amorphous carbon structure. The shift of the D and G-band and the ratio of their intensities (I_D/I_G) indicates that the carbonization temperature marginally affects the total content of defects in the carbon structure, reaching a maximum for $T_C = 1073$ K ($I_D/I_G = 4.7$). Notably, the concentration of surface defects in the material, associated with higher electrical conductivity, has been reported as a catalytic descriptor of N-doped carbons in acetylene hydrochlorination.^[2]

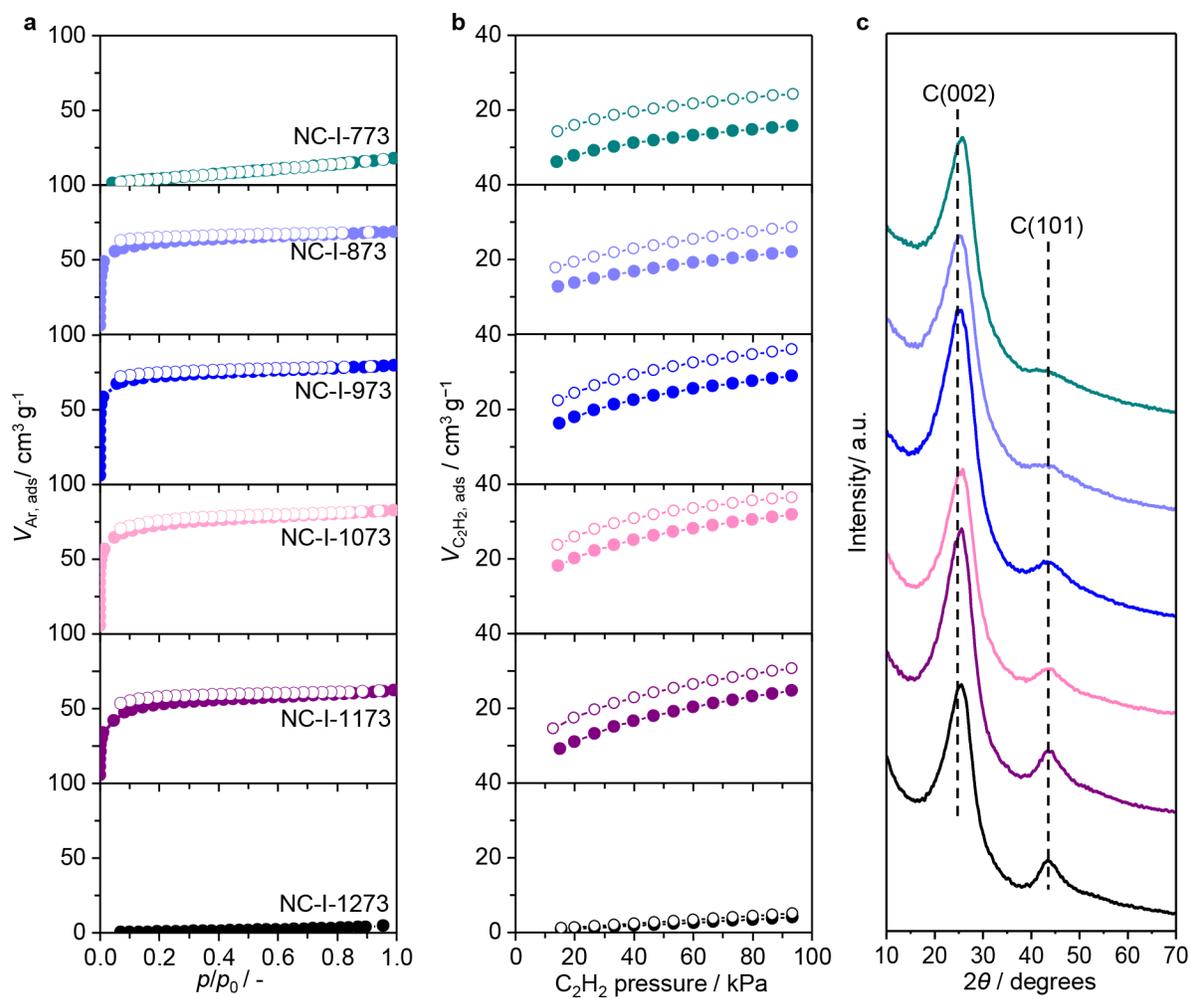


Figure S3. **a**, Ar isotherms. **b**, Acetylene chemisorption isotherms. **c**, X-ray diffraction pattern. In each sample a broad diffraction peak at $25.4^\circ 2\theta$ is visible, indicating the (002) plane of graphitic carbon. With increasing calcination temperature an additional peak at $27.5^\circ 2\theta$ develops, corresponding to the (101) plane of graphitic carbon.

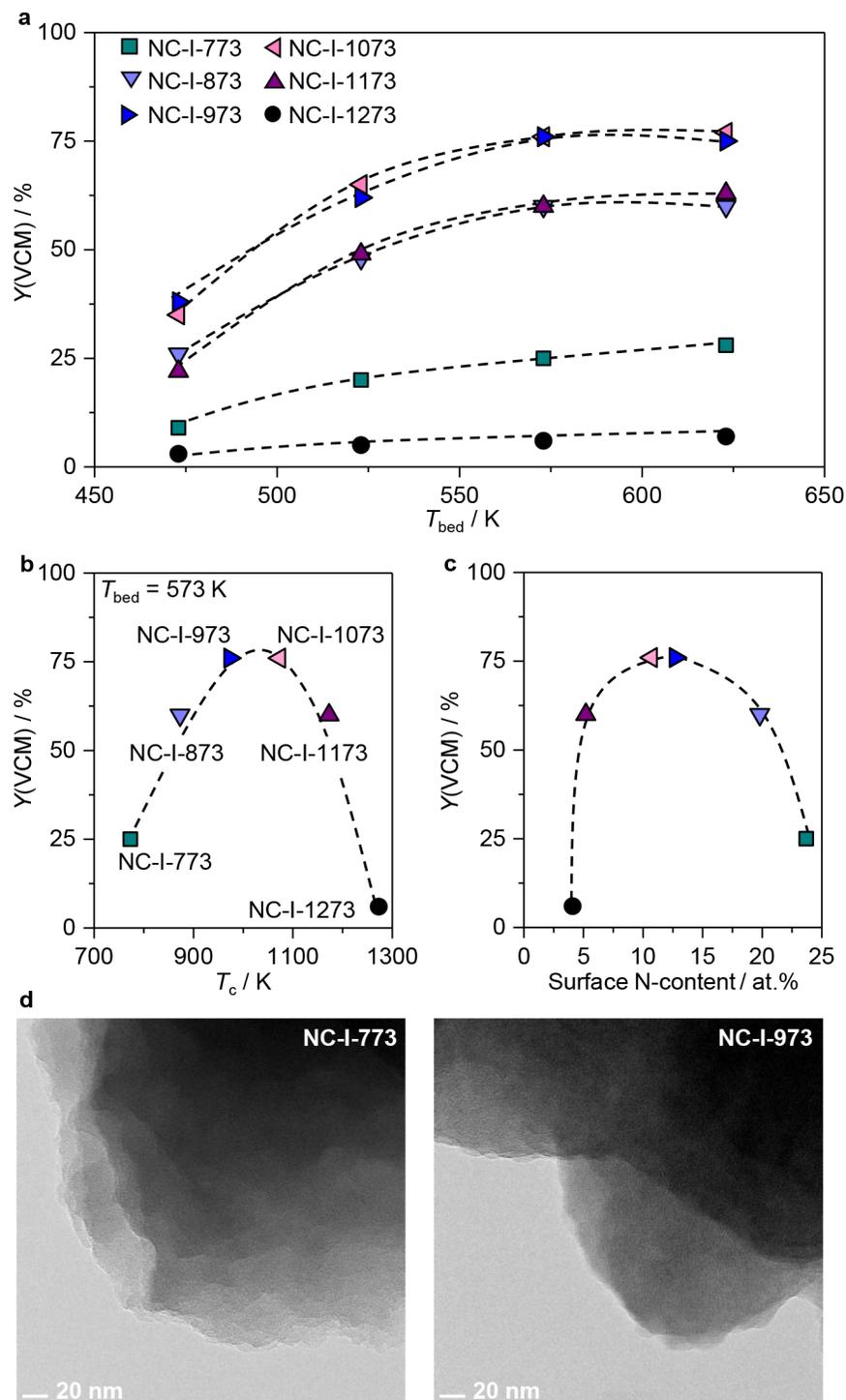


Figure S4. a-c, Initial acetylene hydrochlorination activity of the NC-I- T_C series, expressed as the yield of vinyl chloride, $Y(\text{VCM})$ as a function of the catalyst bed temperature (T_{bed} , **a**), the carbonization temperature (T_C , **b**), and the surface N-content, as derived from XPS (**c**). Reaction conditions: $T_{bed} = 473\text{--}623$ K (**a**) and 573 K (**b**, **c**), $F_T = 15$ cm³ min⁻¹, HCl:C₂H₂:Ar = 44:40:16, $W_{cat} = 0.25$ g, $P = 1$ bar. **d**, Bright field TEM images of selected as-prepared NC-I catalysts.

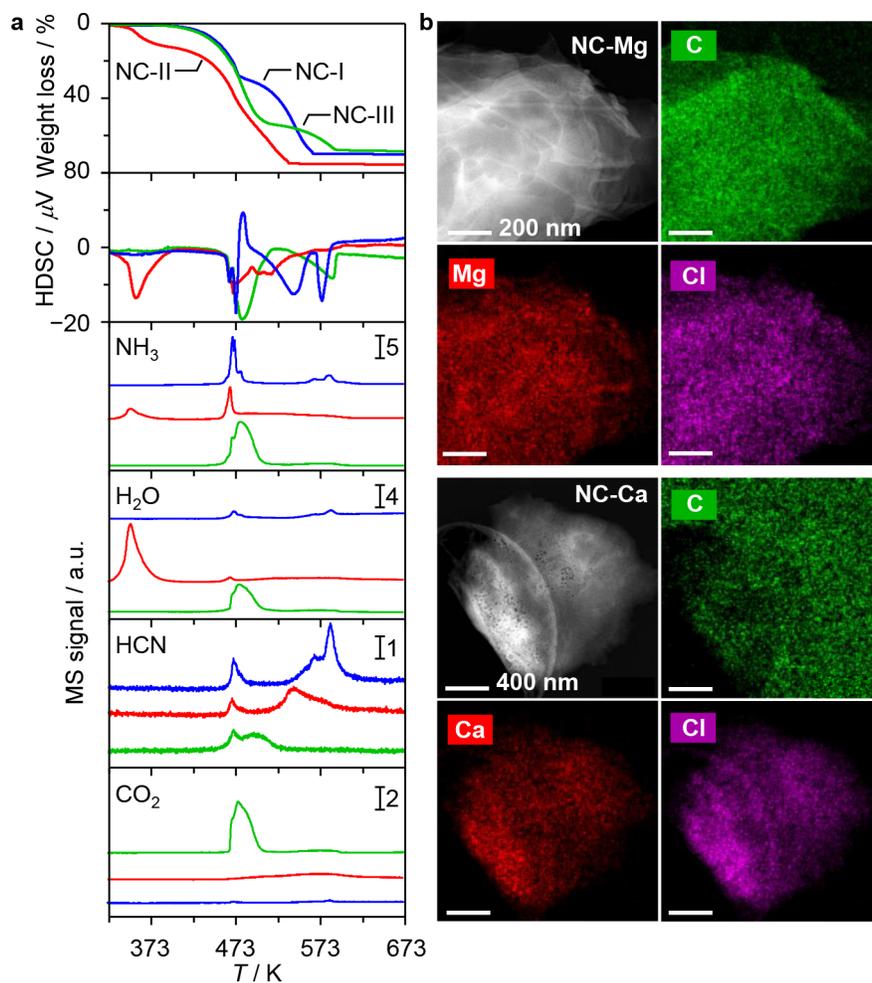


Figure S5. TGA/DSC-MS analysis of the reaction between HTM and NH_4Cl without any additives (blue) and in the presence of $\text{Mg}(\text{OAc})_2$ (red) and CaCO_3 (green) in Ar atmosphere, to monitor the synthesis of NC-I, NC-II, and NC-III, respectively. HAADF-STEM images and corresponding elemental maps of NC-II and NC-III before removal of the Mg and Ca residues, indicating the formation of MgCl_2 and CaCl_2 from the respective templates during the chemical blowing process.

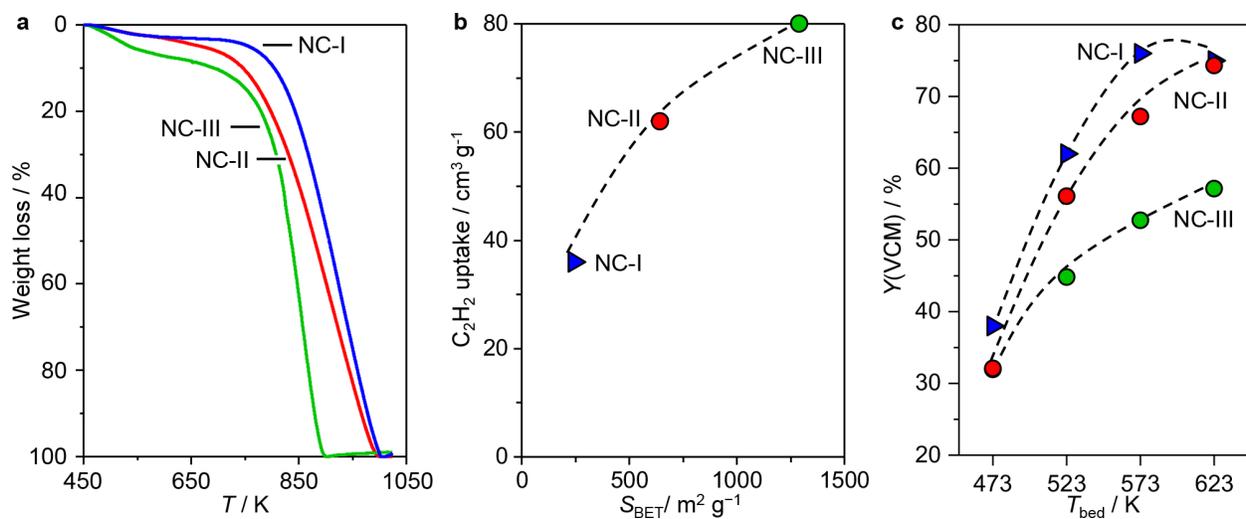


Figure S6. **a**, TGA in 20 vol.% O₂/Ar of as-prepared NC-I-III, showing distinct oxidation behaviour. **b**, positive correlation between acetylene uptake and surface area. **c**, Initial acetylene hydrochlorination activity, expressed as the yield of vinyl chloride, $Y(\text{VCM})$ at distinct catalyst bed temperatures (T_{bed}). Reaction conditions: $T_{\text{bed}} = 523 \text{ K}$, $F_T = 15 \text{ cm}^3 \text{ min}^{-1}$, $\text{HCl}:\text{C}_2\text{H}_2:\text{Ar} = 44:40:16$, $W_{\text{cat}} = 0.25 \text{ g}$, $P = 1 \text{ bar}$.

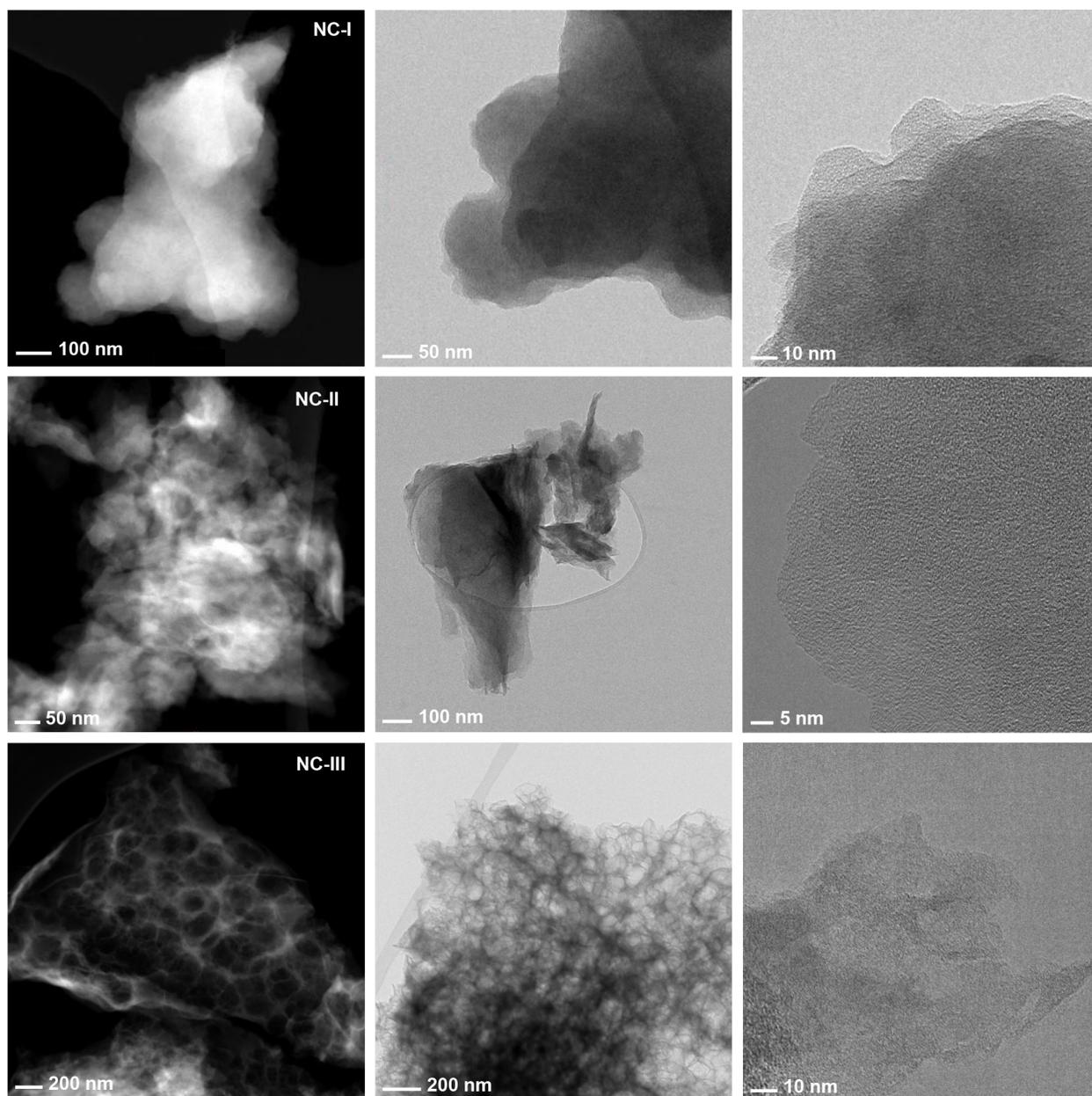


Figure S7. HAADF-STEM and bright field TEM images of selected N-doped carbons.

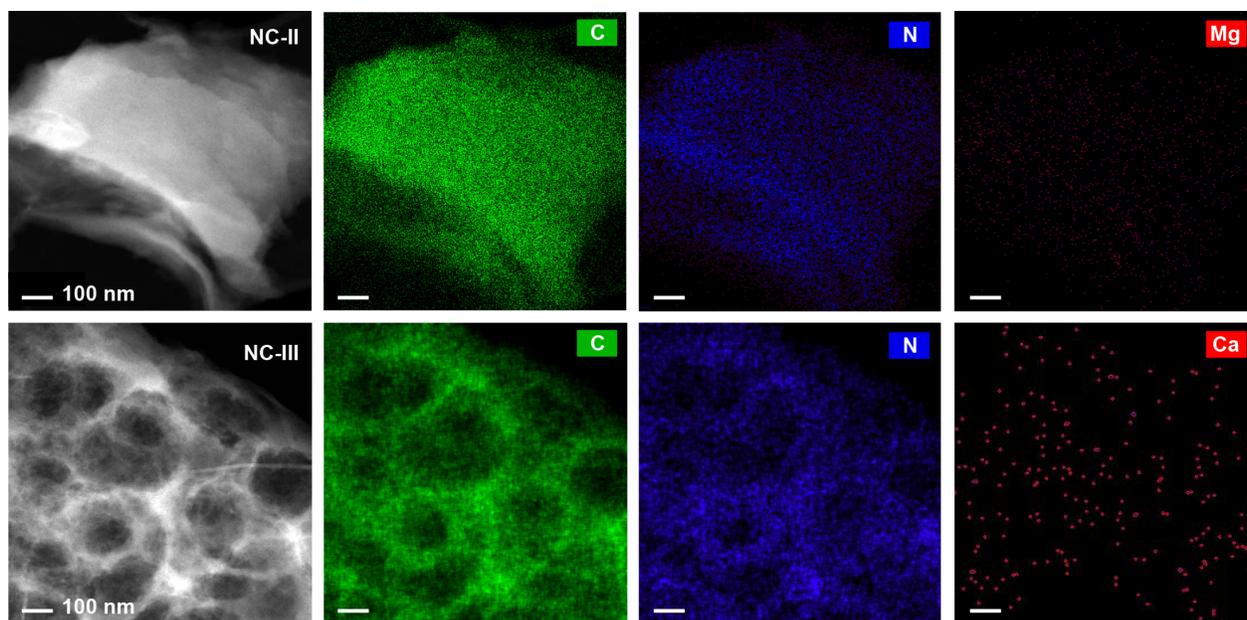


Figure S8. HAADF-STEM images and corresponding elemental maps of NC-II and NC-III.

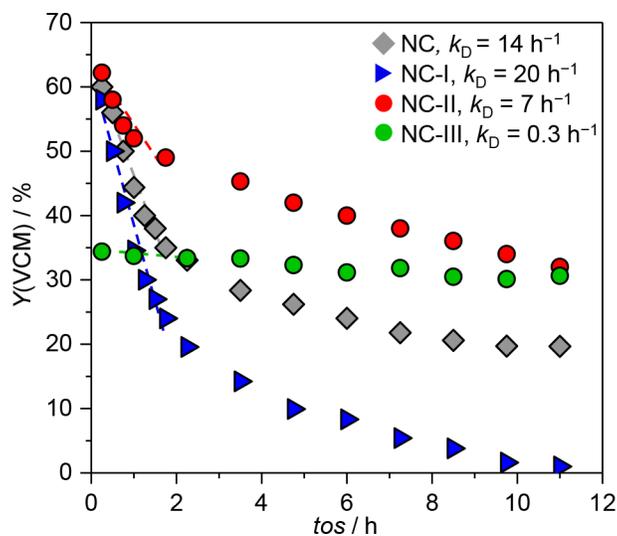


Figure S9. Time-on-stream (*tos*) performance of selected NCs in direct comparison to literature reported N-doped carbon (NC).^[2] The deactivation constants, k_D , were derived *via* a simple linear regression of the initial 2 h time-on-stream performances, as indicated by the dashed trend lines of equivalent color. Reaction conditions: $T_{bed} = 523$ K, $F_T = 15$ cm³ min⁻¹, HCl:C₂H₂:Ar = 44:40:16, $W_{cat} = 0.25$ g, $P = 1$ bar.

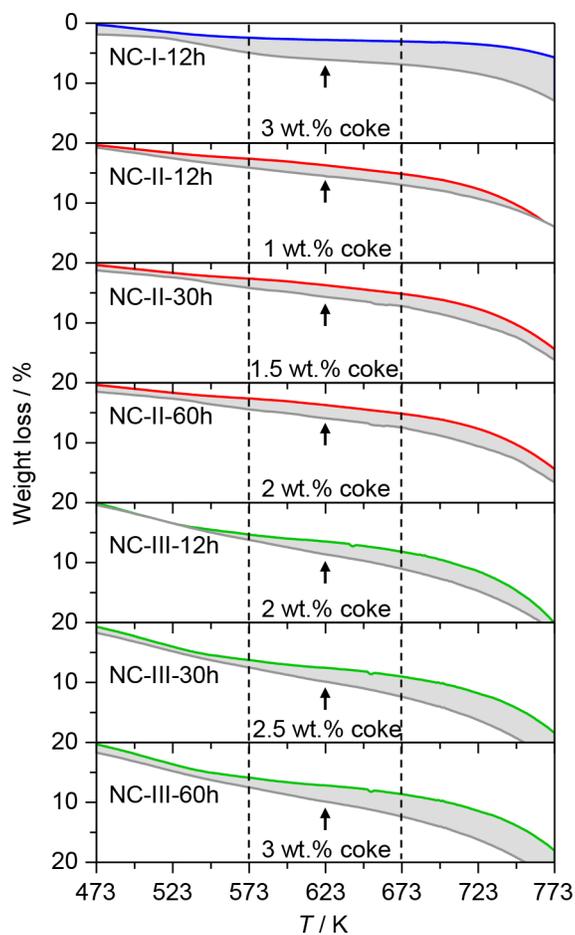


Figure S10. TGA analysis in 20 vol.% O₂/Ar of as-prepared NCs and after use in acetylene hydrochlorination for 12 h (grey curves). The difference in weight-loss between the fresh and used samples is highlighted by the grey coloured area. Quantification of coke in the used samples was assessed by integrating each TGA profile in reference to the as-prepared sample in the temperature region 573-673 K.

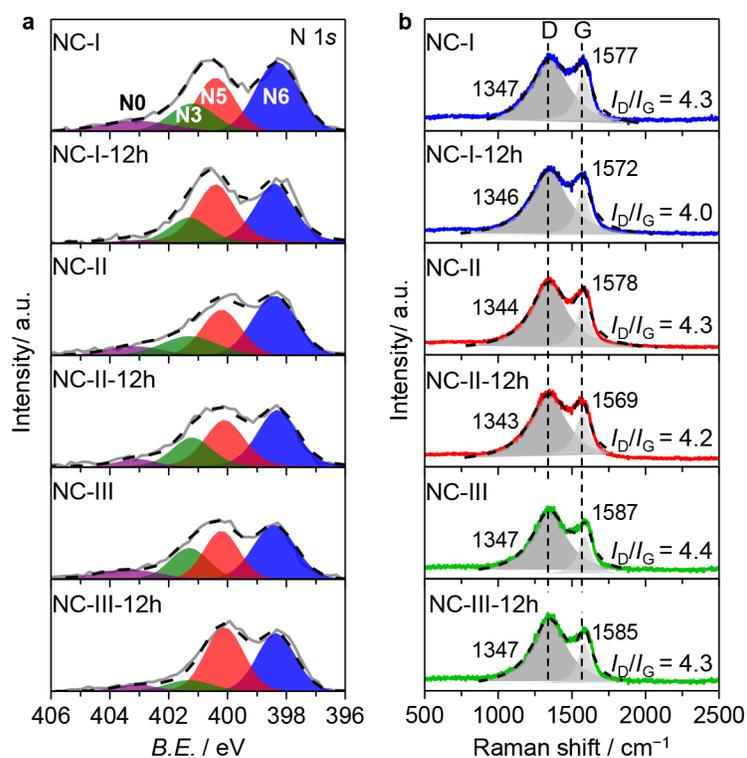


Figure S11. a,b, N 1s XPS and Raman spectra of as-prepared NCs and after use in acetylene hydrochlorination for 12 h. The shift of the D and G-band and the ratio of their intensities (I_D/I_G) indicates that the addition of templates does not alter the amount of defects nor the carbon structure.

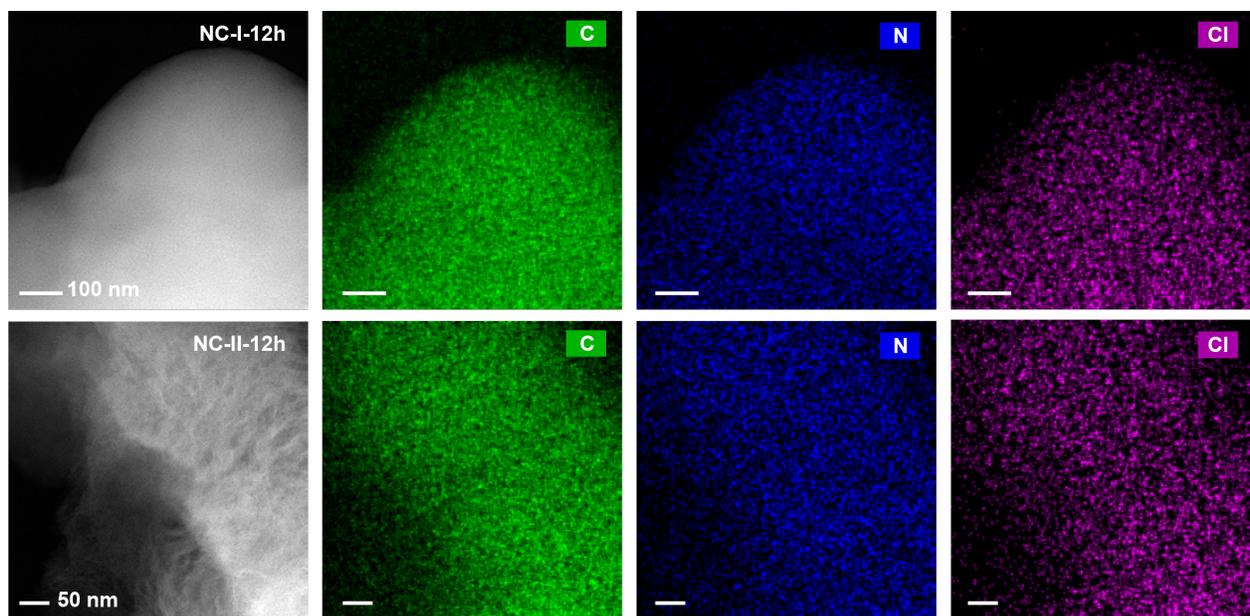


Figure S12. HAADF-STEM images and corresponding elemental maps of NC-I and NC-II after use in acetylene hydrochlorination for 12 h.

References

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