The role of surface deformation on responsivity of the pillared layer metal-organic framework DUT-8(Ni)

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Content

1 PXRD patterns

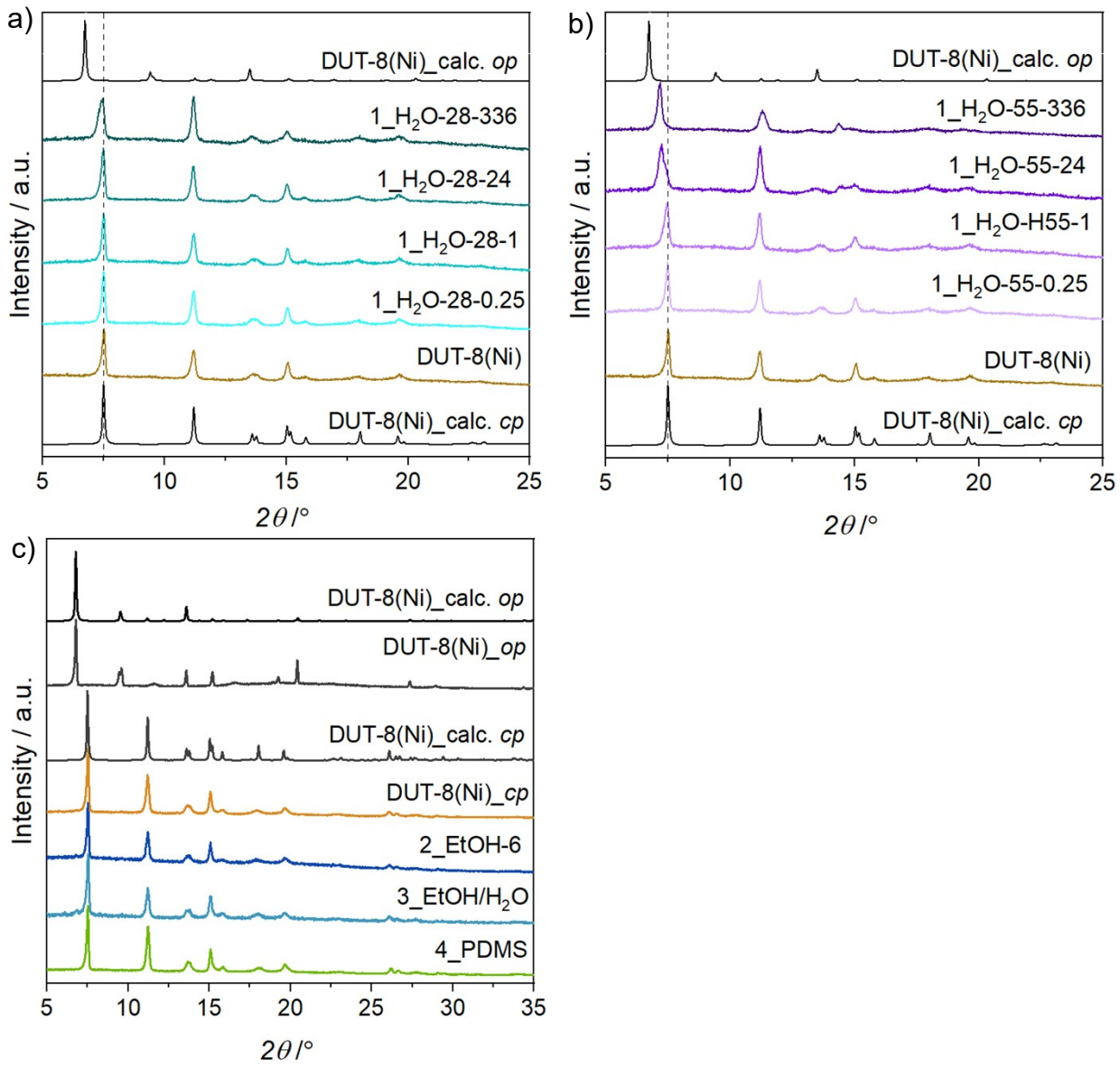


Figure S1. PXRD patterns of DUT-8(Ni) samples exposed to humid air with a) 28 % and b) 55% humidity, c) treated with ethanol, treated with the mixture of ethanol and water, and treated with PDMS.

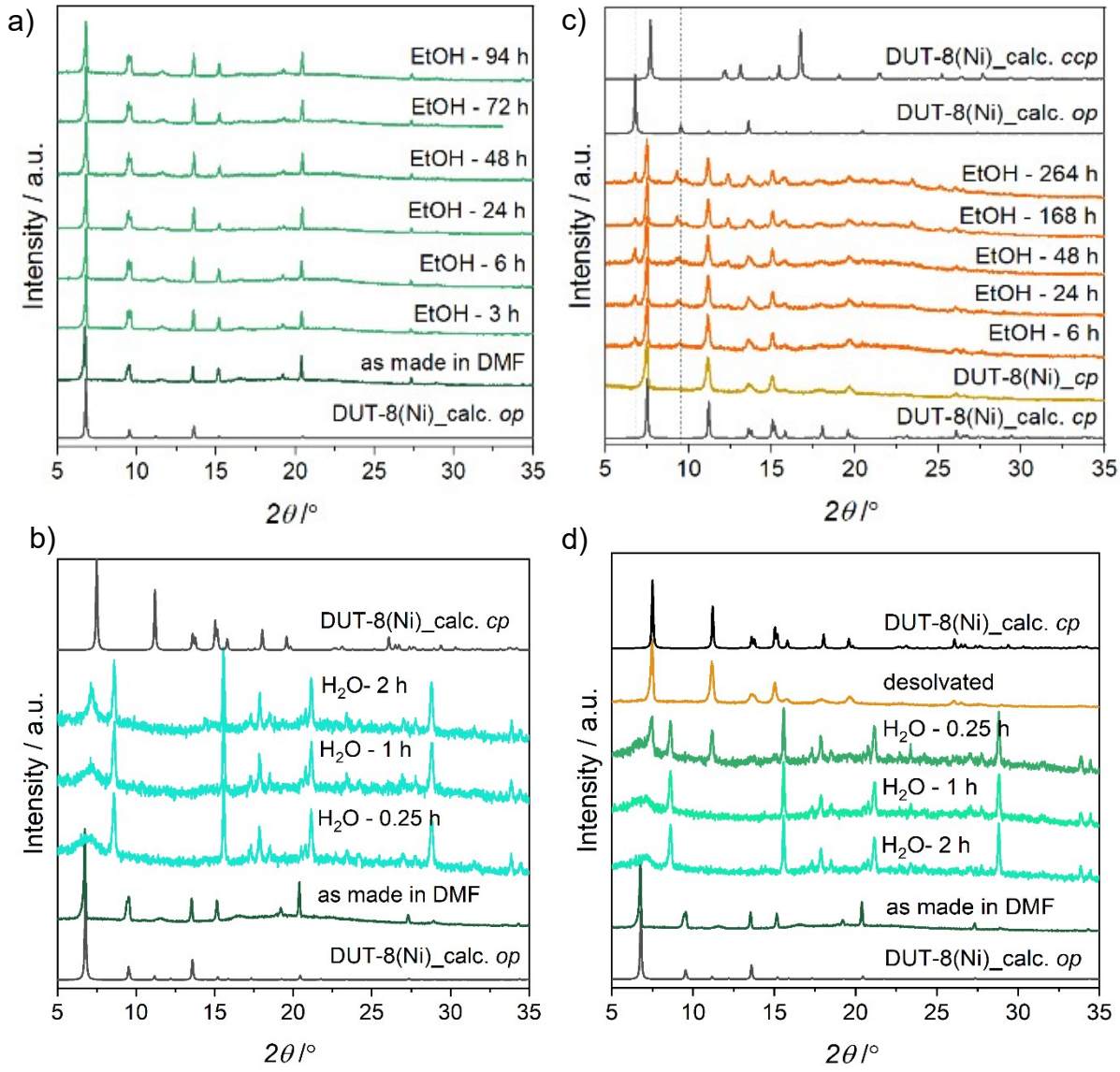


Figure S2. Stability of DUT-8(Ni)_*op* a) EtOH, b) H_2O and DUT-8(Ni)_*cp* in c) EtOH, d) H_2O.

2 Surface treatment by linear alcohols

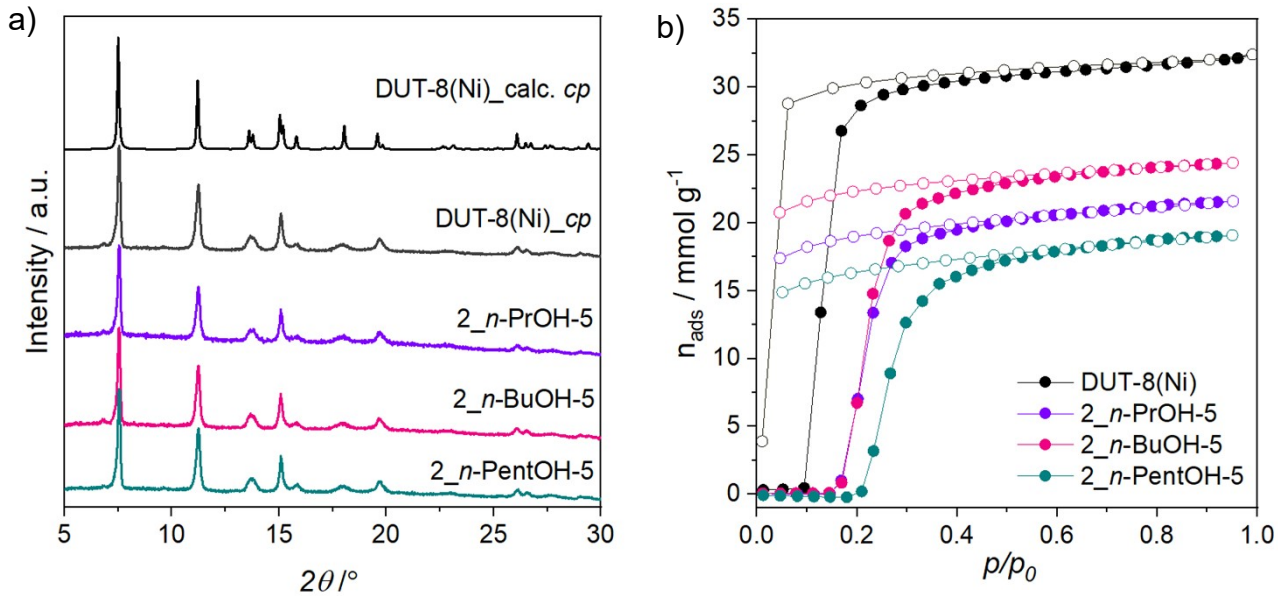
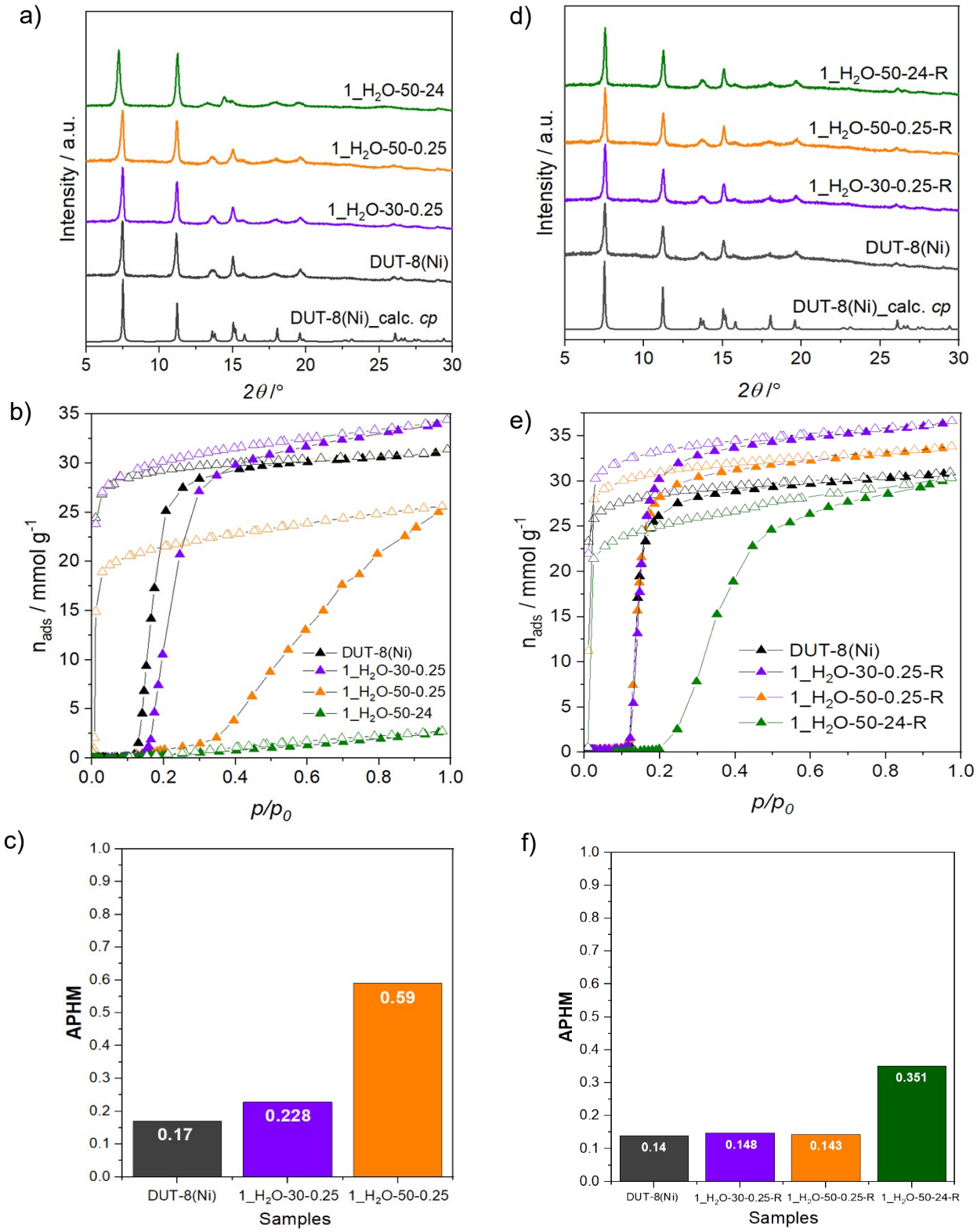


Figure S3. a) PXRD patterns of reference DUT-8(Ni)_cp sample and patterns of the samples treated with alcohols, b) Corresponding nitrogen physisorption isotherms at 77 K.



3 Reactivation

Figure S4. a) PXRD patterns, b) nitrogen physisorption isotherms at 77 K and c) corresponding APHM values for samples exposed to humid air in comparison with non-treated sample DUT-8(Ni), d) PXRD patterns, e) nitrogen physisorption isotherms at 77 K and f) corresponding APHM values for samples exposed to reactivation procedure. The difference in uptake most likely originates from the relatively small sample amount used for the measurements (approximately 15 mg) and

the associated uncertainty in sample weighing. Therefore, we decided not to emphasise the treatment-dependent variation in uptake and instead focused on analysing the APHM, which is unaffected by uncertainties in sample weight.

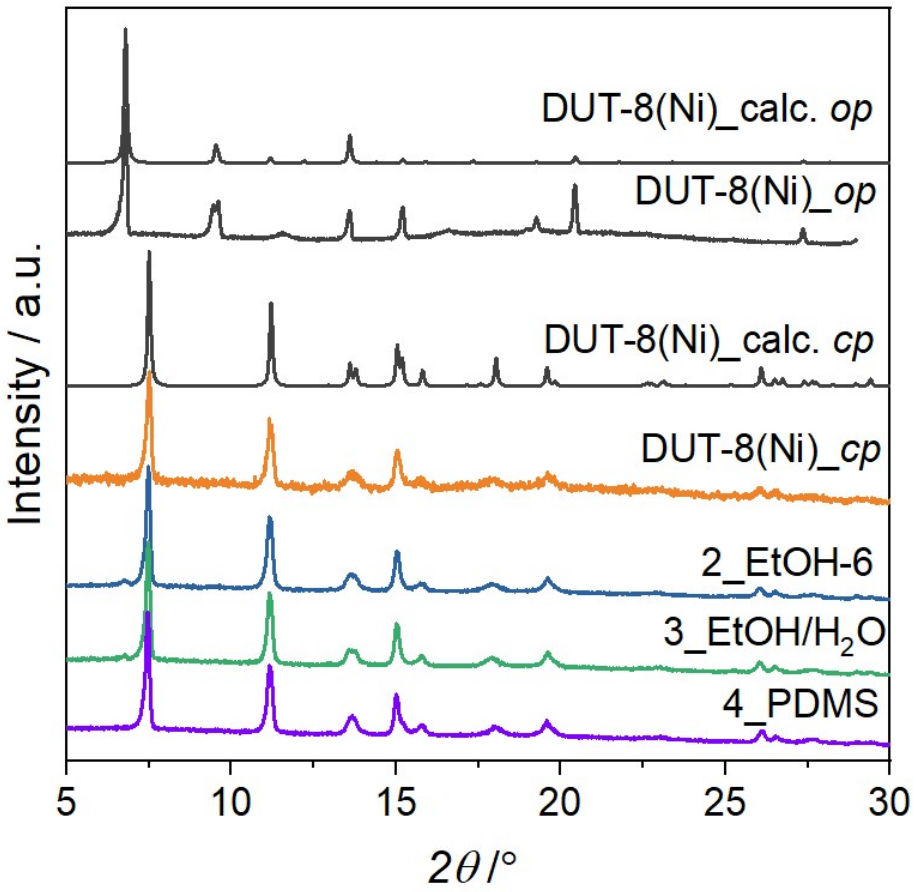


Figure S5. PXRD patterns of treated samples for reactivation.

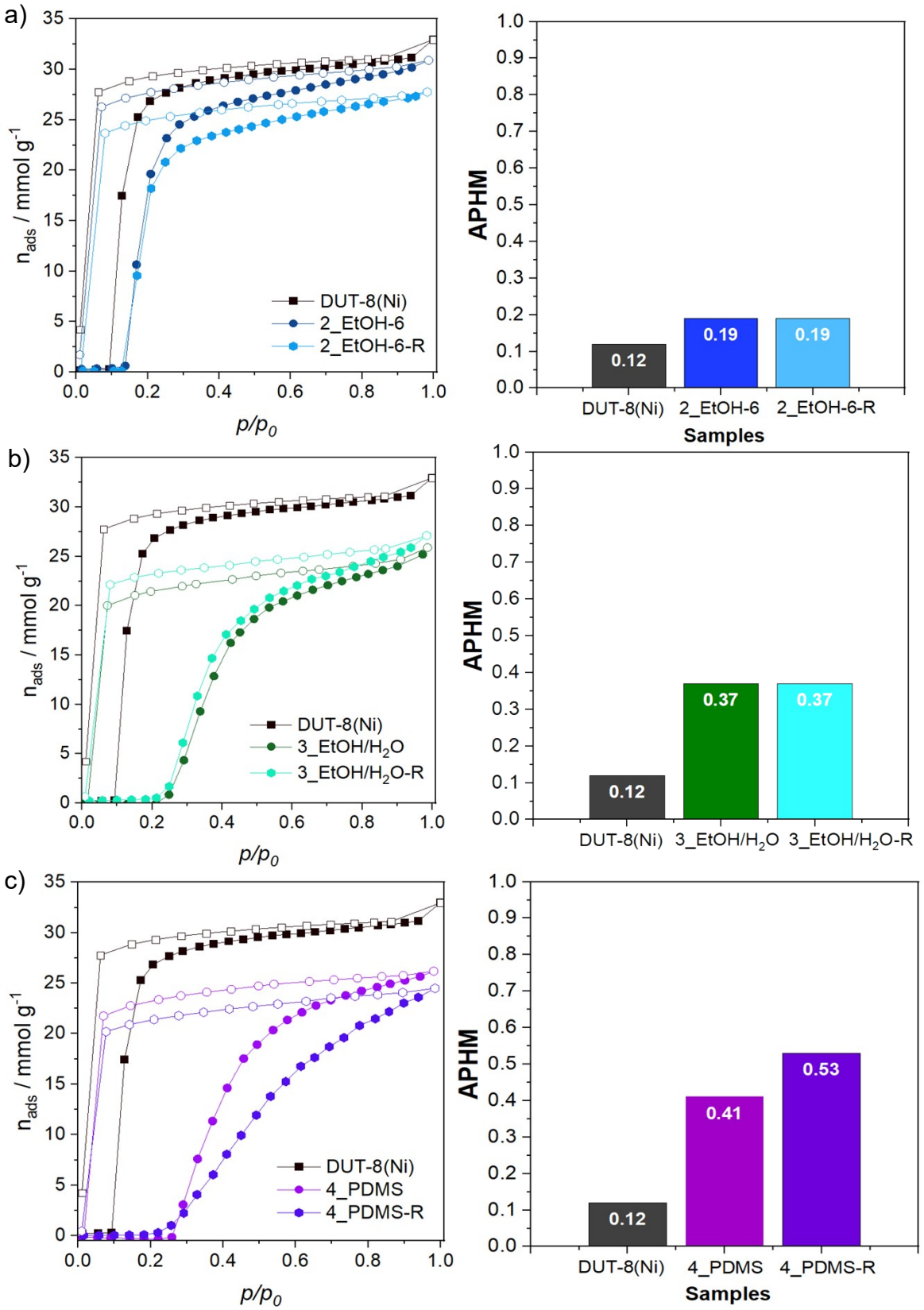


Figure S5. Nitrogen physisorption isotherms at 77 K for a) sample treated by ethanol 2_EtOH-6, sample after reactivation 2_EtOH-6-R, b) sample treated by ethanol/water mixture 3_EtOH/H_2O and sample after reactivation 3_EtOH/H_2O-R, c) sample coated with PDMS, sample after reactivation in comparison with non-treated DUT-8(Ni), as well as corresponding APHM values.

4 Transmission and Scanning electron microscopy

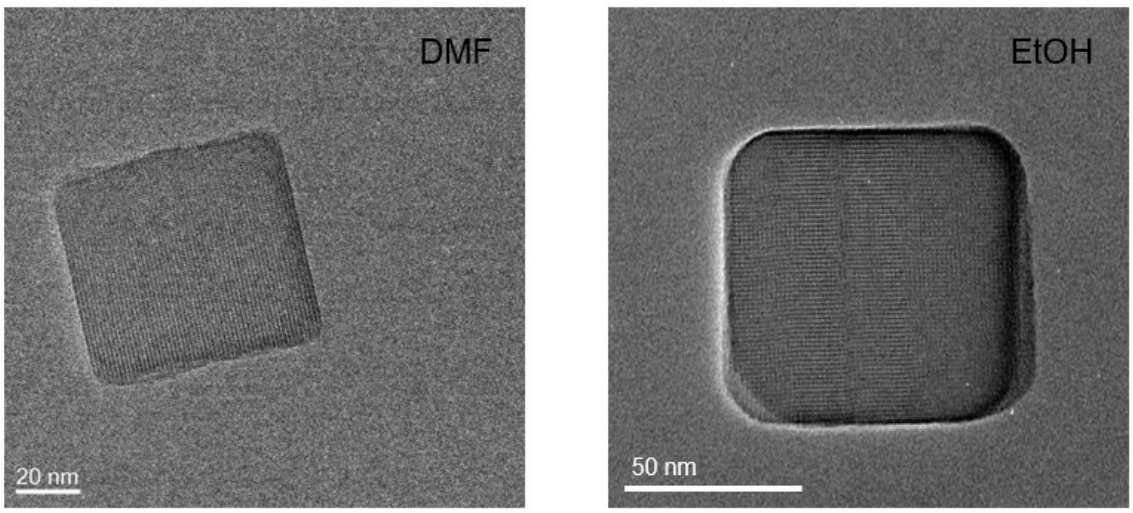
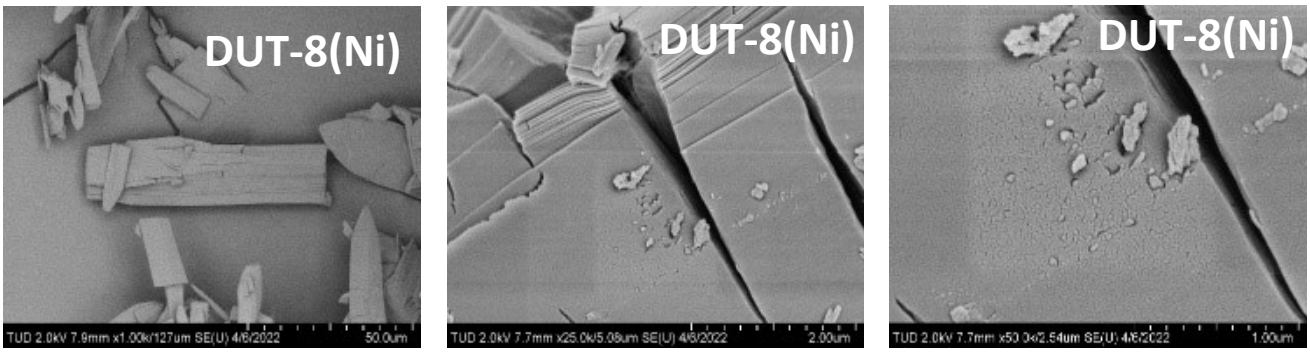
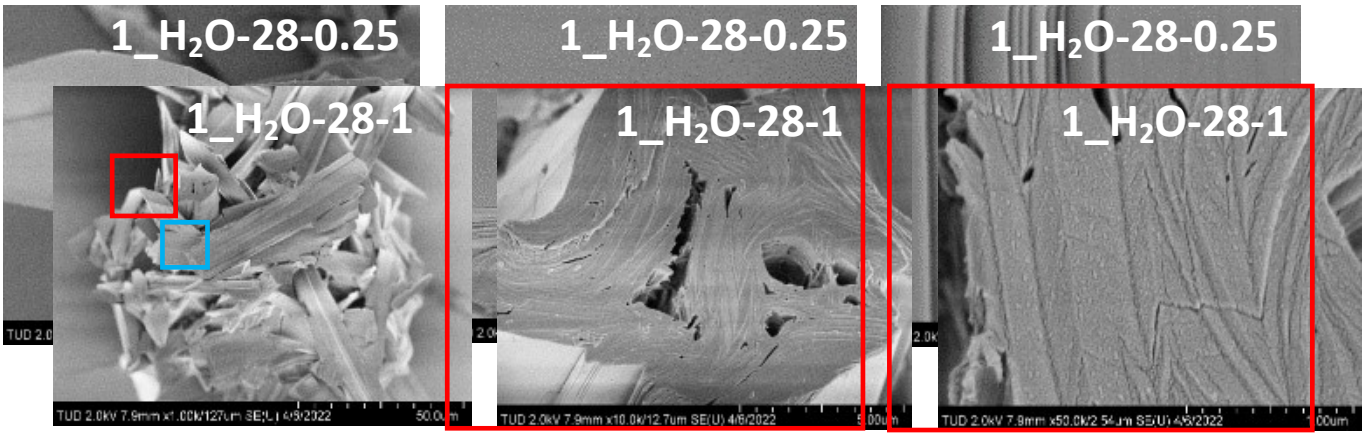


Figure S6. TEM images of as-made DUT-8(Ni) nanocrystals in DMF (left) and soaked in EtOH for 2 months (right).

a)


DUT-8(Ni)
DUT-8(Ni)
DUT-8(Ni)

b)


1_H2O-28-0.25
1_H2O-28-0.25
1_H2O-28-0.25
1_H2O-28-1
1_H2O-28-1
1_H2O-28-1


1_H2O-28-1
1_H2O-28-1
1_H2O-28-24
1_H2O-28-24
1_H2O-28-24

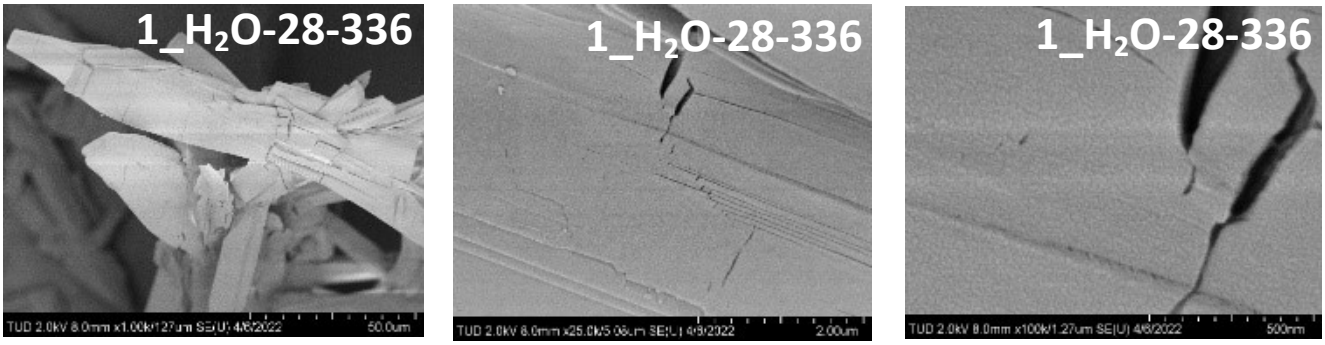
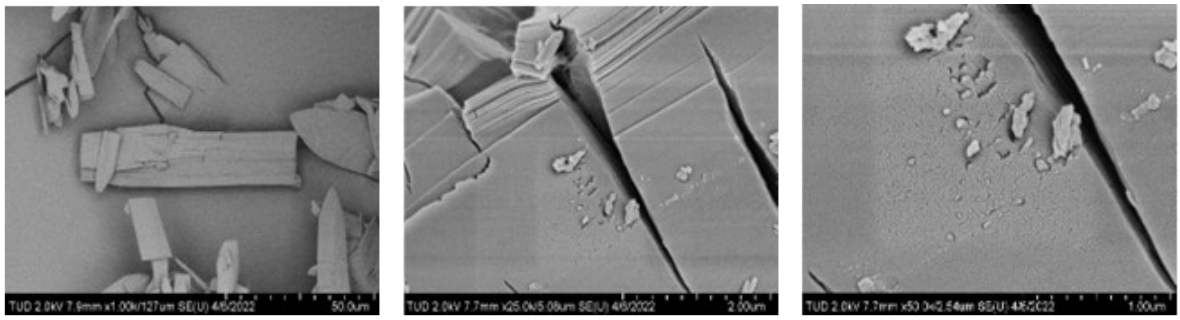
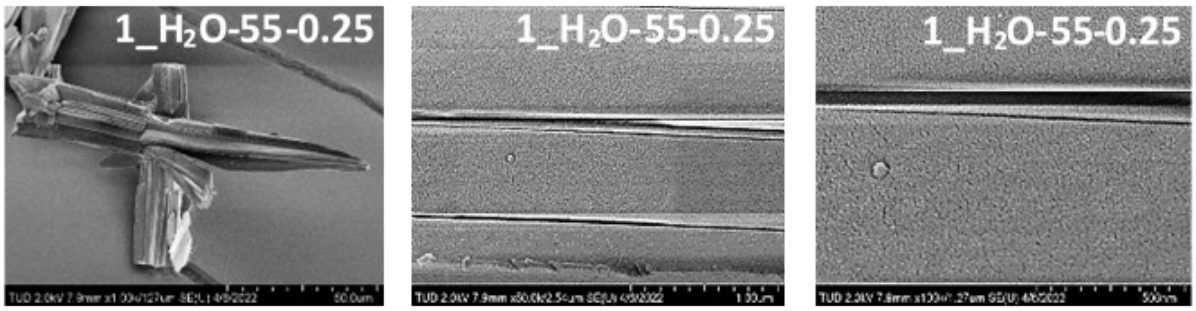


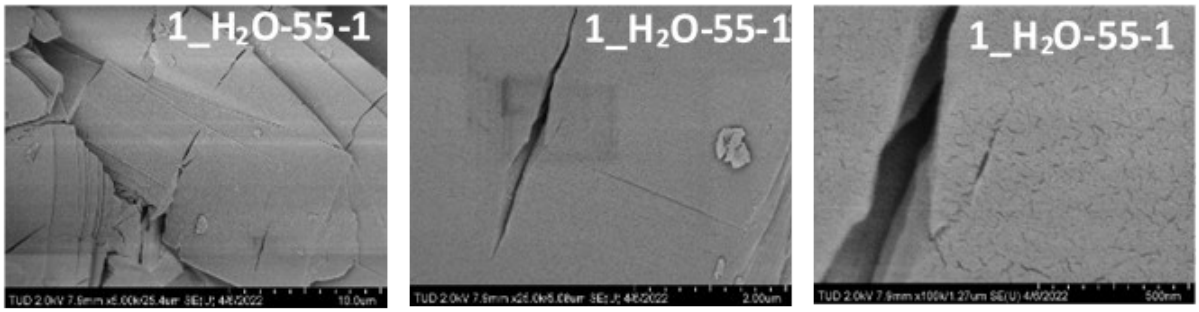
Figure S7. SEM images of a) non-treated DUT-8(Ni) and b) samples exposed to humid air (28 %) for 0.25 h, 1 h, 24 h, 336 h.

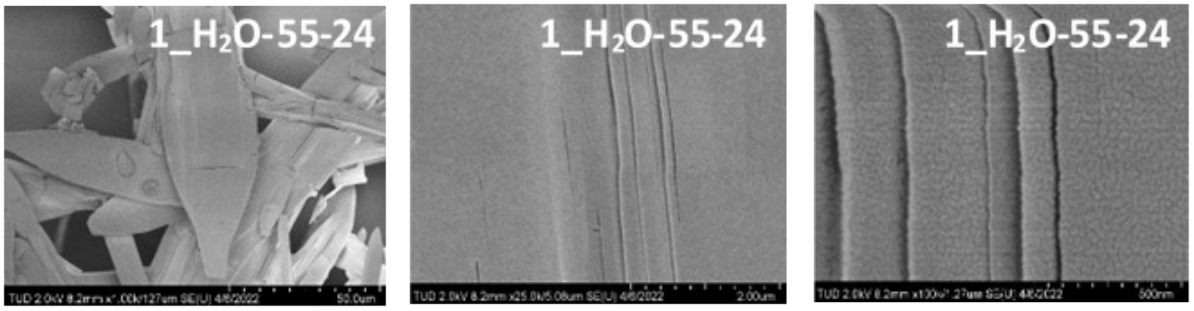
a)



b)


1_H2O-55-0.25
1_H2O-55-0.25
1_H2O-55-0.25


1_H2O-55-1
1_H2O-55-1
1_H2O-55-1


1_H2O-55-24
1_H2O-55-24
1_H2O-55-24

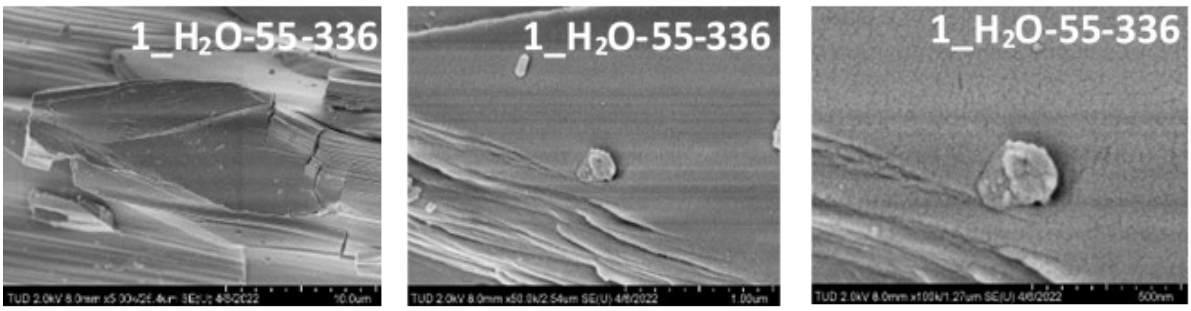

1_H2O-55-336
1_H2O-55-336
1_H2O-55-336

Figure S8. SEM images of: a) non-treated DUT-8(Ni) and b) samples exposed to humid air (55 %) for 0.25 h, 1 h, 24 h, 336 h.

5 nanoFTIR

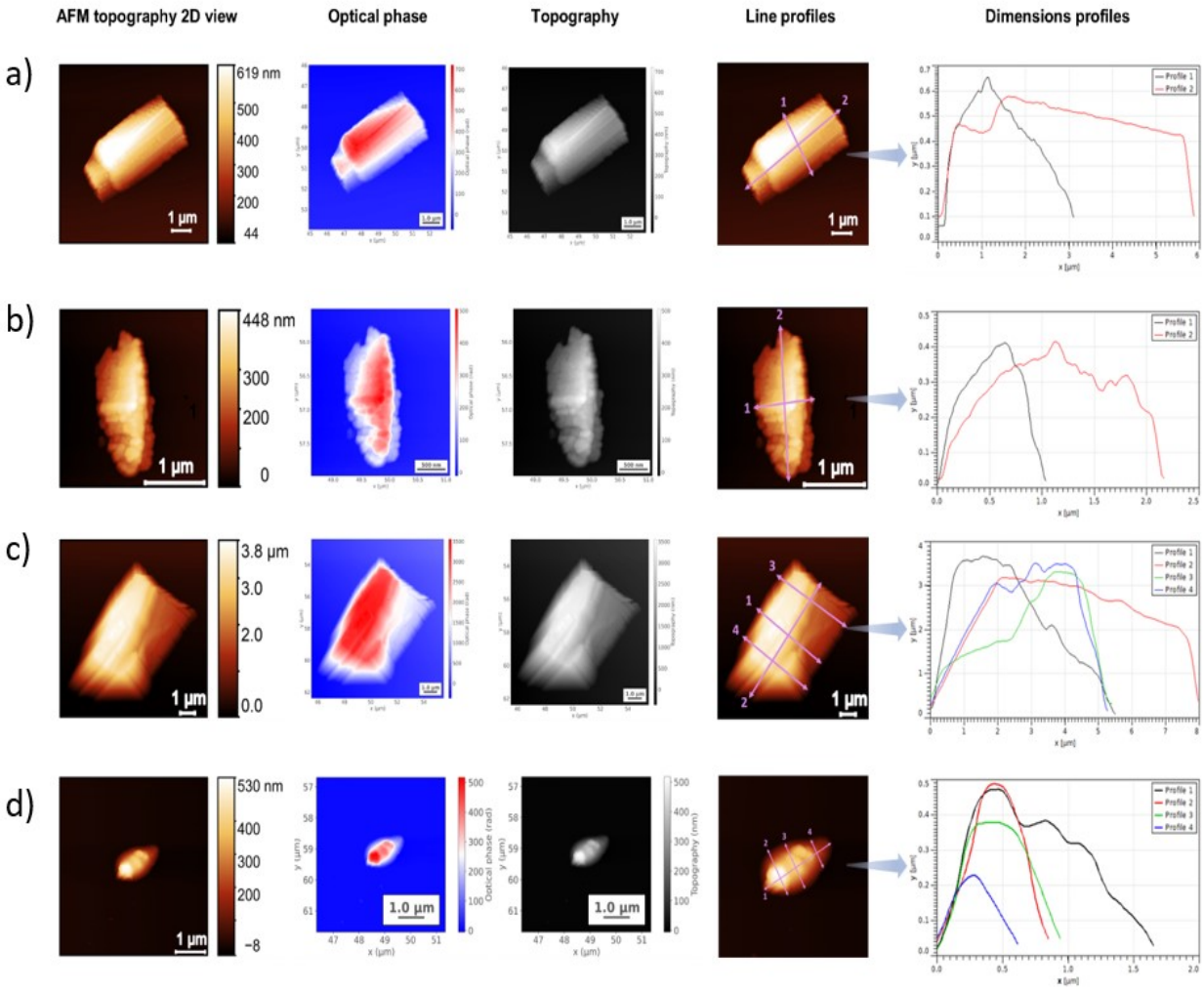


Figure S9. DUT-8(Ni) individual micro/nano-crystals subjected to localised probing through s-SNOM studies: a) Pristine DUT-8(Ni). Humity exposed samples: b) **1**_H_2O-28-336, c) **1**_H_2O-55-24, d) **1**_H_2O-70-24.

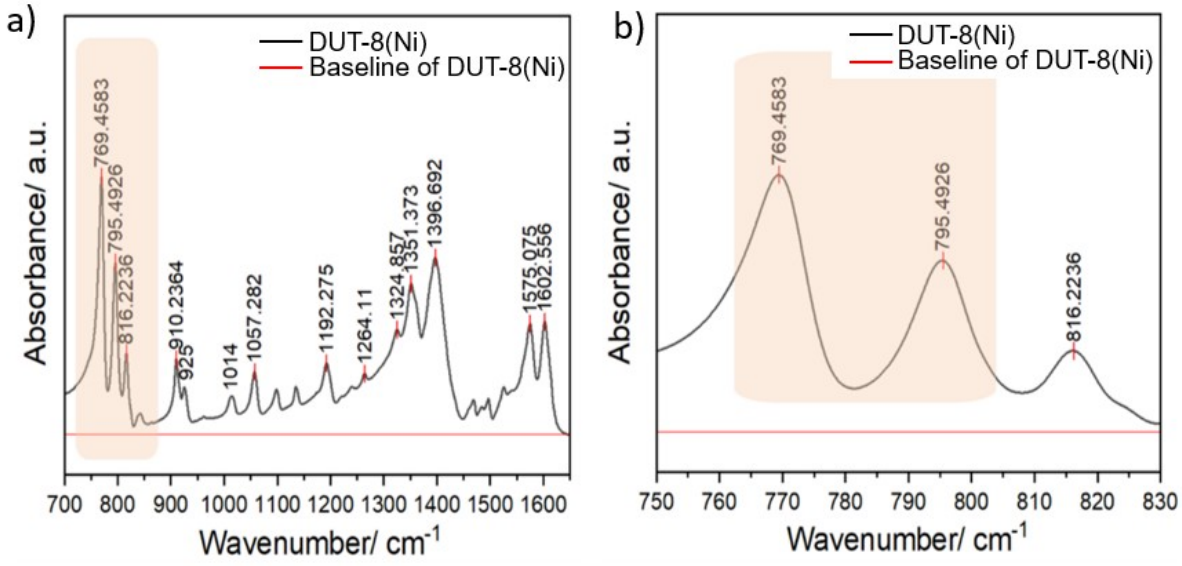


Figure S10. ATR spectrum of DUT-8(Ni): a) Mid-IR region, b) enlarged fingerprint region.

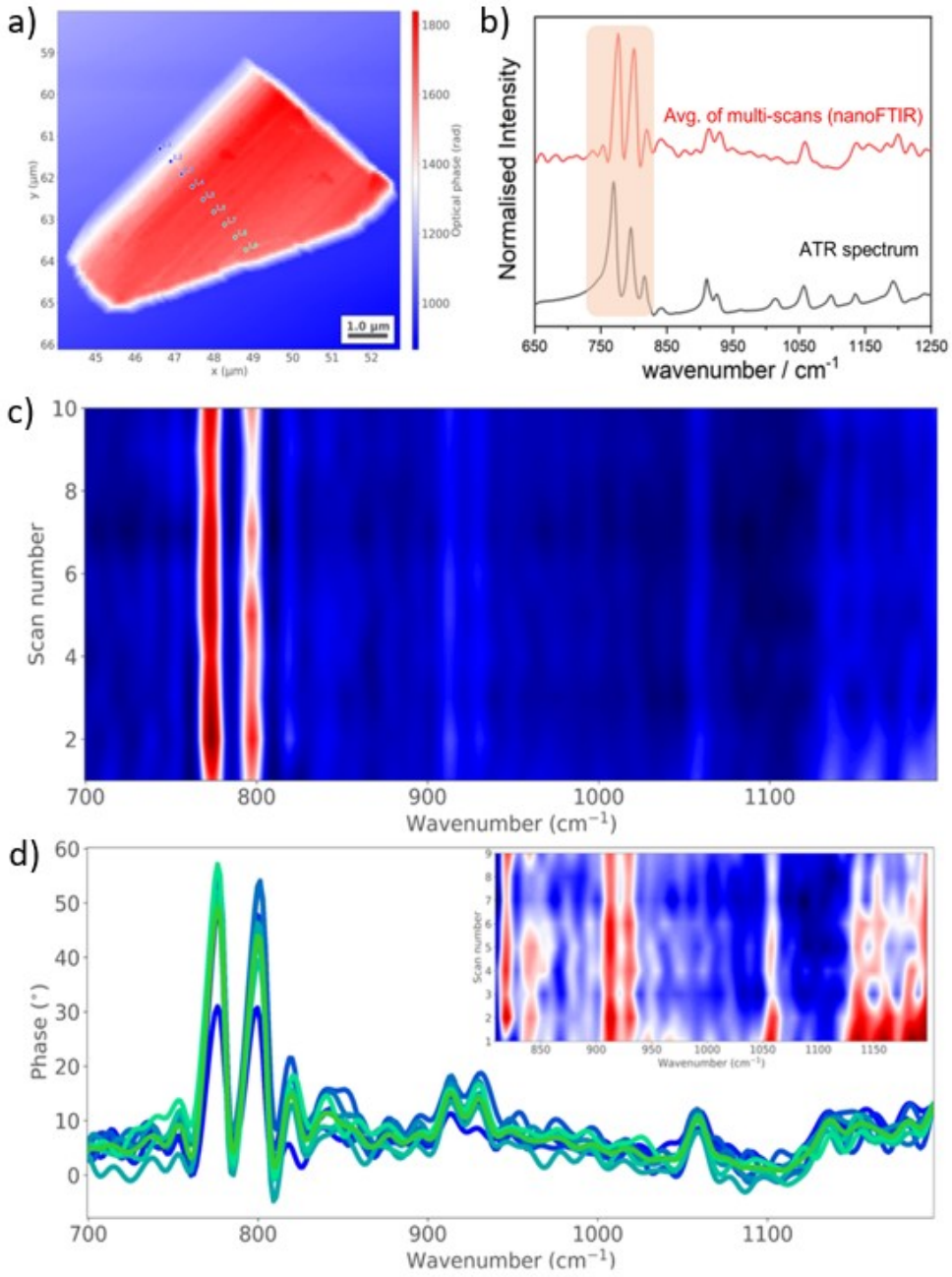


Figure S11. Crystal 1: nanoFTIR multi-scans along the indicated line. a) Optical phase image and scans, b) ATR and the average of nanoFTIR scans, c) 3D contour plot derived from s-SNOM, d) Individual scans (inset: scans rang 900 - 1200 cm^{-1}).

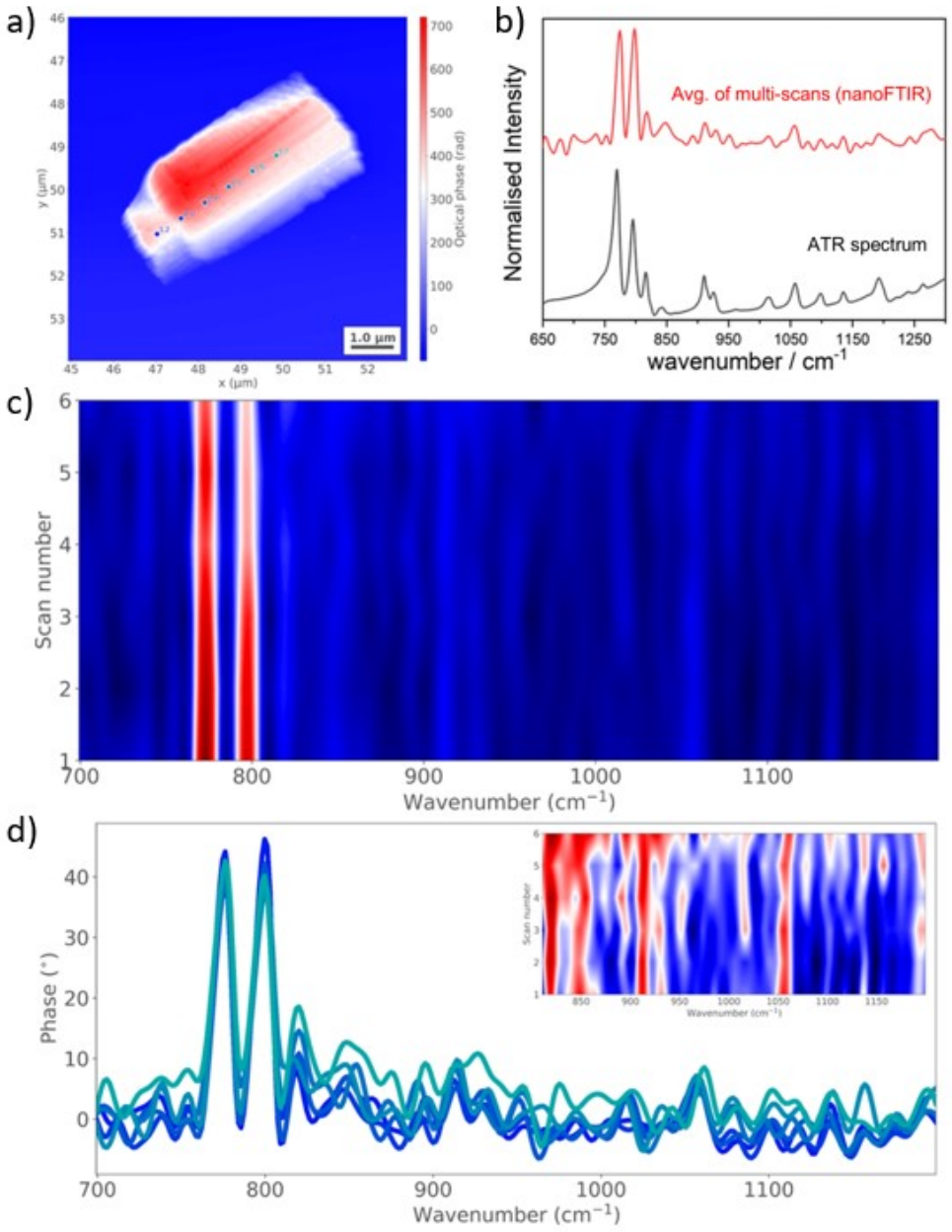


Figure S12. Crystal 2: nanoFTIR multi-scans along the indicated line. a) Optical phase image and scans, b) ATR and the average of nanoFTIR scans, c) 3D contour derived from s-SNOM, (d) Individual scans (inset: scans range 900 - 1200 cm^{-1}).

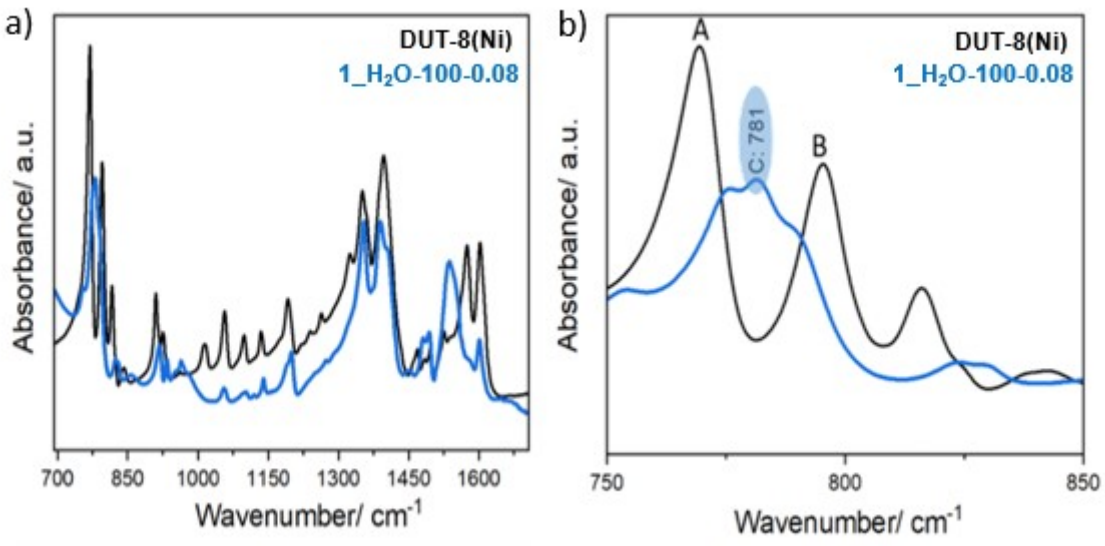


Figure S13. Bulk phase ATR analysis of pristine DUT-8(Ni) and after water treatment for 5 min (0.083 h) (**1**_H_2O-100-0.08): a) Mid-IR region, b) zoom view.

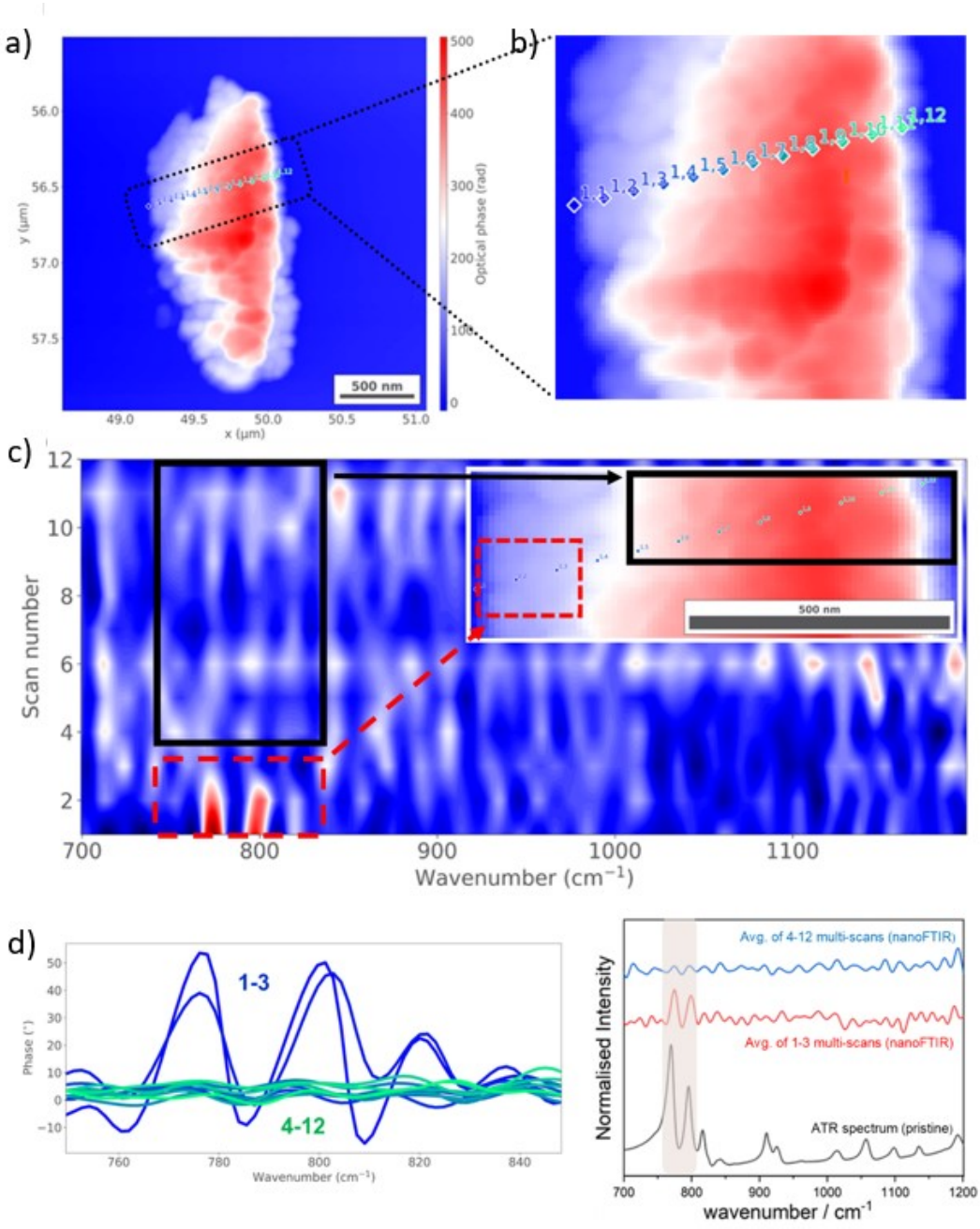


Figure S14. nanoFTIR results for DUT-8(Ni) crystal subjected to 28% humidity for 2 weeks (**1**_H_2O-28-336): a) Optical phase image indicating line scans comprising 1 - 12 points with zoom view, b) 3D contour plot derived from s-SNOM probing (indicators: red: 1 - 3, black: 4 - 12, and inset: locally probed points), c) Respective spectral features from scans (indicators: blue: 1 - 3, green: 4 - 12), d) Bulk phase (ATR) and average (nanoFTIR) of 1 - 3 and 4 - 12 point scans.

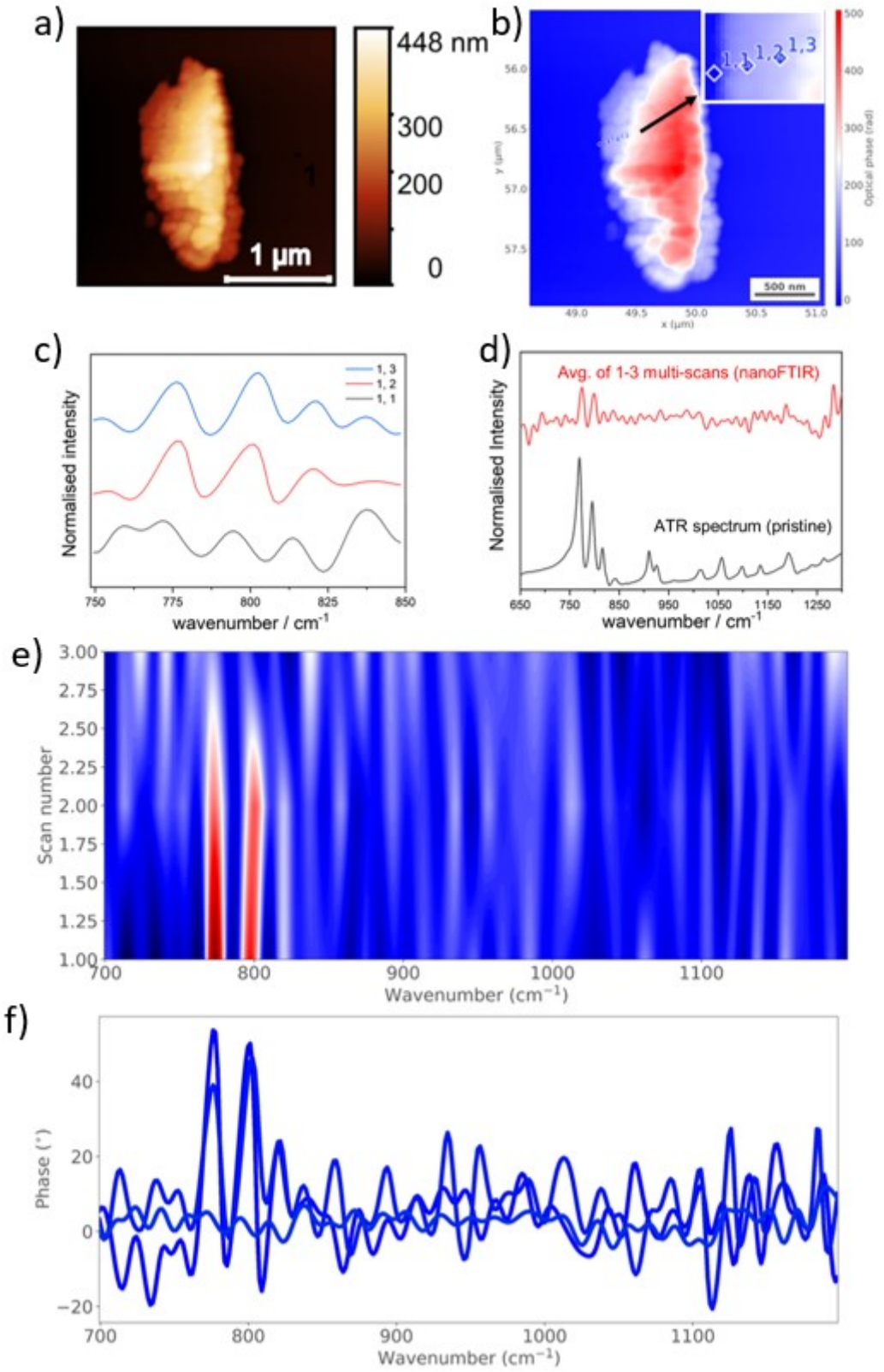


Figure S15. AFM and nanoFTIR results for DUT-8(Ni) crystal subjected to 28% humidity for 2 weeks (**1**_H_2O-28-336): a) AFM topography, b) Optical phase and local probing (inset: locally probed points), c) Respective spectral features from scans in image (b), d) Average of 1 - 3 point scans, e) 3D contour plot derived from s-SNOM, f) Phase matched individual scans.

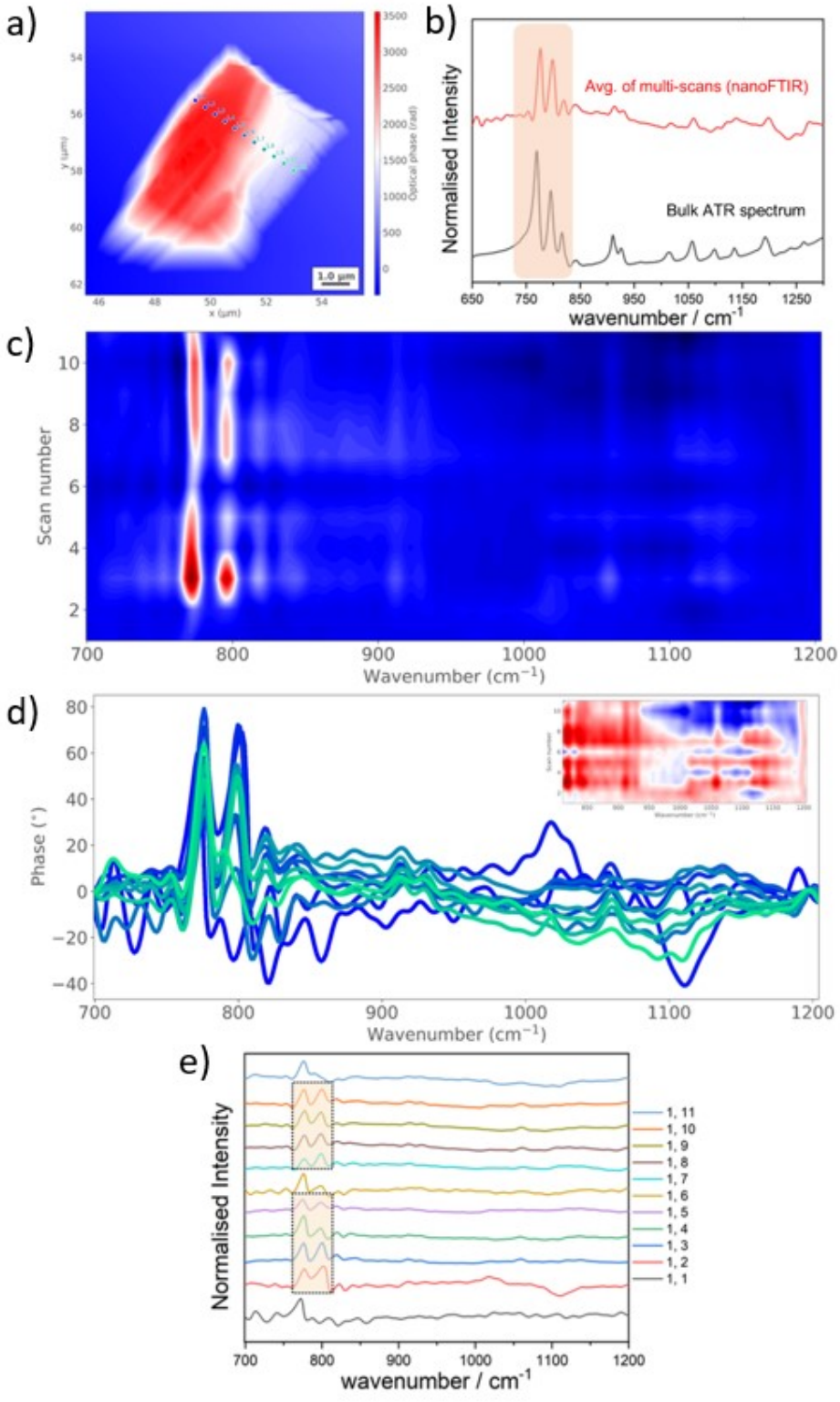


Figure S16. AFM and nanoFTIR results for DUT-8(Ni) crystal subjected to 55% humidity for 24 h (**1**_H_2O-55-24): a) Optical phase and line aligned local probing, b) Average of 1 - 11 point scans, c) 3D contour plot derived from s-SNOM, d) Respective spectral features from scans in image (inset: 800 cm^{-1} to 1200 cm^{-1} range), e) Phase matched individual scans from local probing of (a).

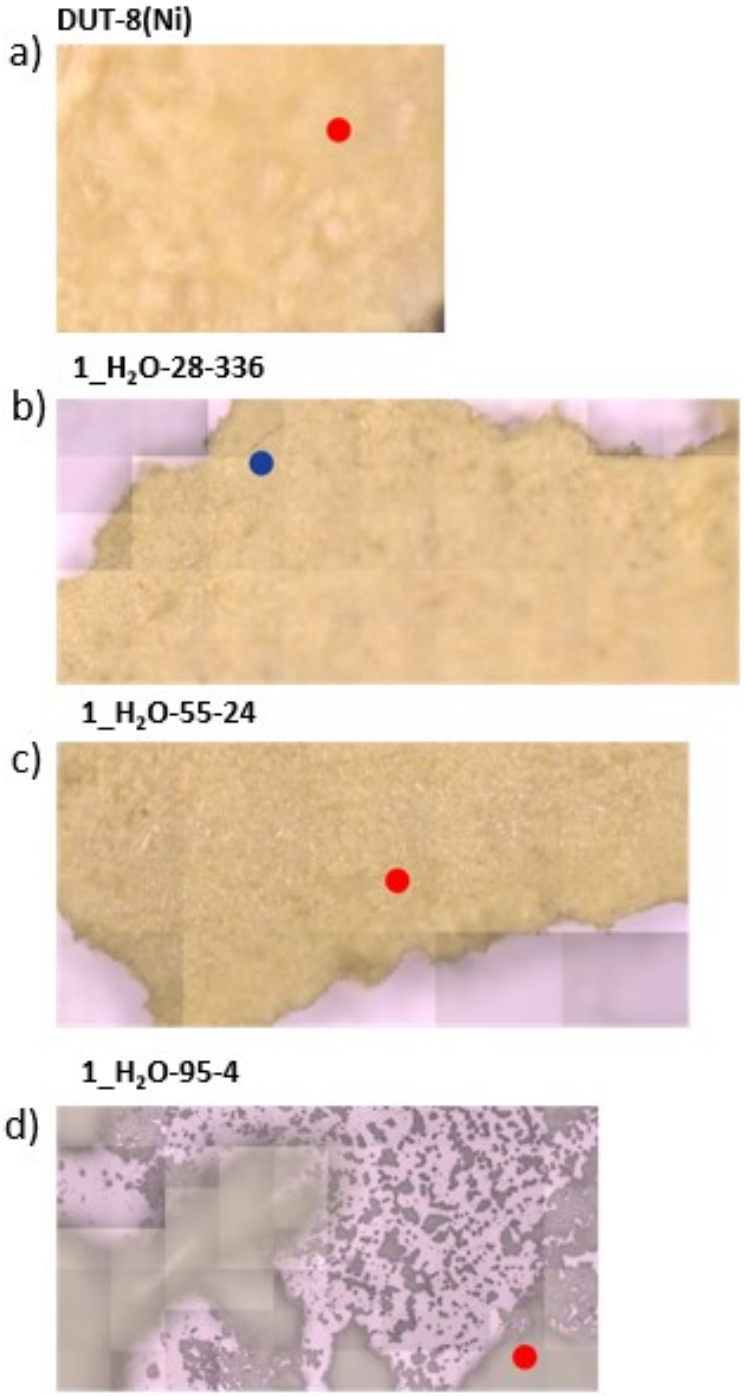
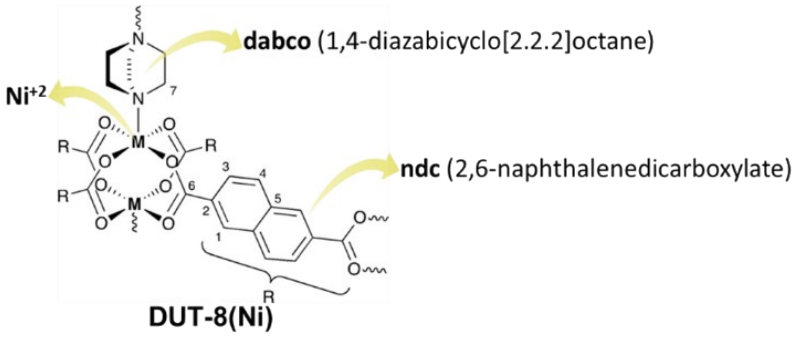


Figure S17. Micrometer thick pellets on terahertz substrate utilised for synchrotron experiments with incremental and controlled humidity conditions: a) DUT-8(Ni), b) **1**_H_2O-28-336, c) **1**_H_2O-55-24, d) **1**_H_2O-95-4.

a)


dabco (1,4-diazabicyclo[2.2.2]octane)
Ni+2
ndc (2,6-naphthalenedicarboxylate)
DUT-8(Ni)

b)

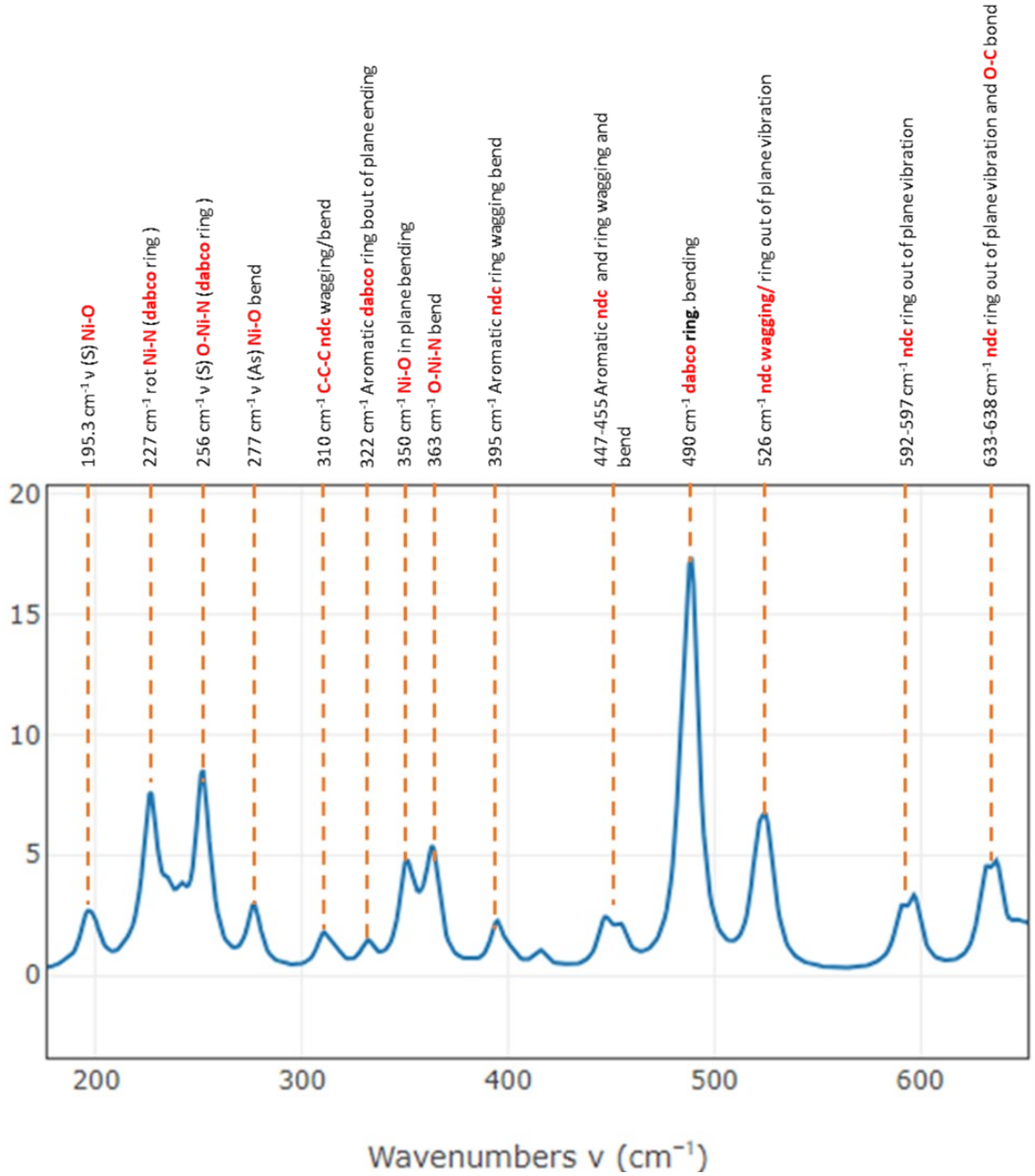
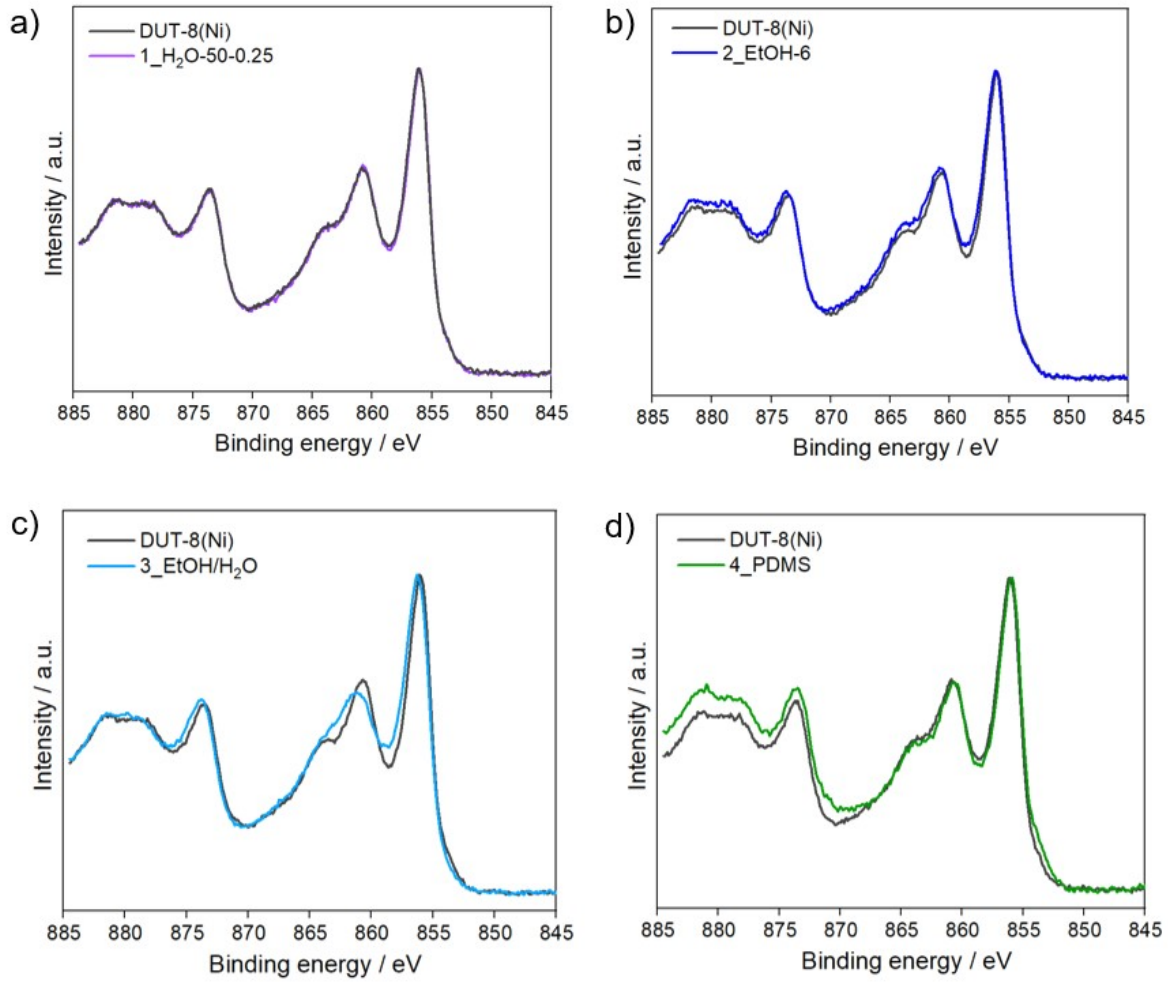

195.3 cm-1 ν (S) Ni-O
227 cm-1 rot Ni-N (dabco ring)
256 cm-1 ν (S) O-Ni-N (dabco ring)
277 cm-1 ν (As) Ni-O bend
310 cm-1 C-C-C ndc wagging/bend
322 cm-1 Aromatic dabco ring bout of plane ending
350 cm-1 Ni-O in plane bending
363 cm-1 O-Ni-N bend
395 cm-1 Aromatic ndc ring wagging bend
447-455 Aromatic ndc and ring wagging and bend
490 cm-1 dabco ring. bending
526 cm-1 ndc wagging/ ring out of plane vibration
592-597 cm-1 ndc ring out of plane vibration
633-638 cm-1 ndc ring out of plane vibration and O-C bond
20
15
10
5
0
200
300
400
500
600
Wavenumbers ν (cm-1)

Figure S18. a) Schematic of the coordination environment of DUT-8(Ni), b) Corresponding DFT calculated Far-IR (Terahertz modes) for DUT-8 (Ni) in the solvent-free model.



6. X-ray photoelectron spectroscopy

Figure S19. Ni2*p* XPS spectra of treated samples: a) 1_H_2O-55-0.25, b) 2_EtOH-6, c) 3_EtOH/H_2O, d) 4_PDMS in comparison with non-treated DUT-8(Ni) sample.

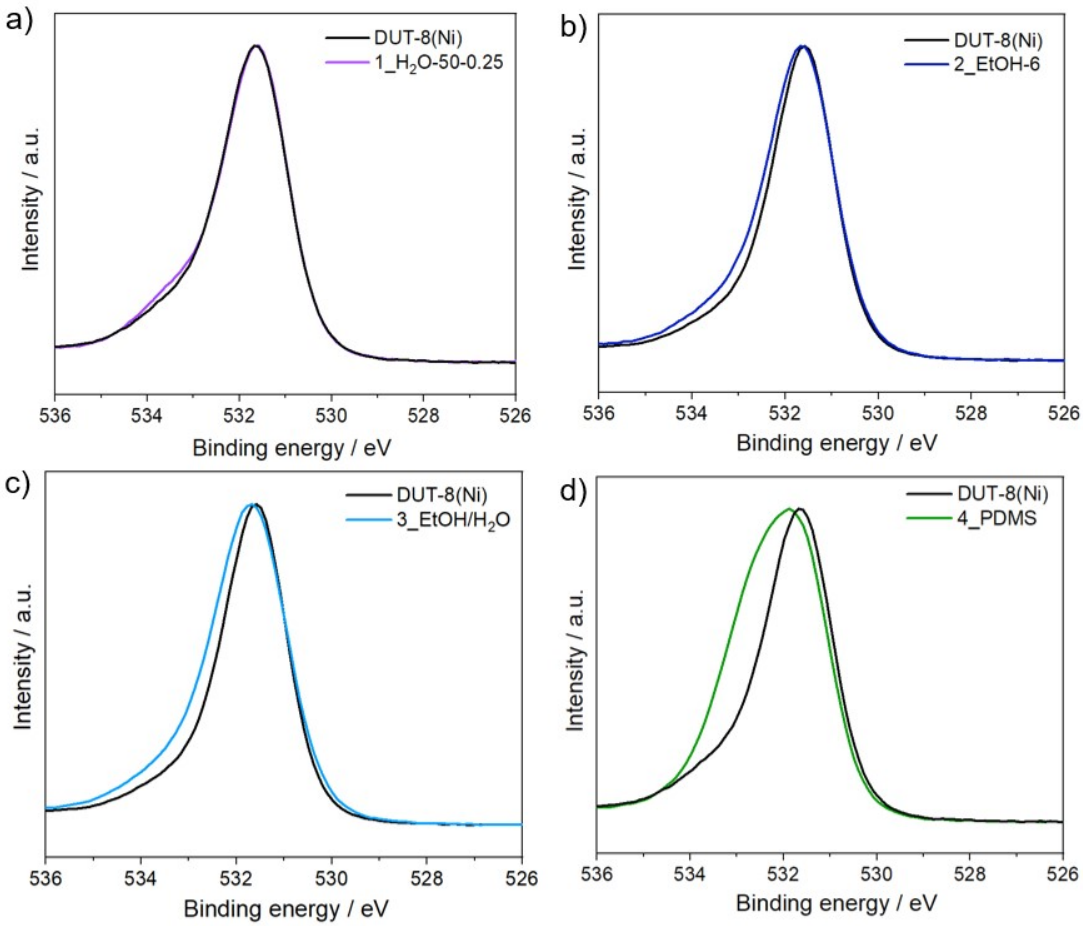


Figure S20. O1*s* XPS spectra of treated samples: a) 1_H_2O-55-0.25, b) 2_EtOH-6, c) 3_EtOH/H_2O, d) 4_PDMS in comparison with non-treated DUT-8(Ni) sample.

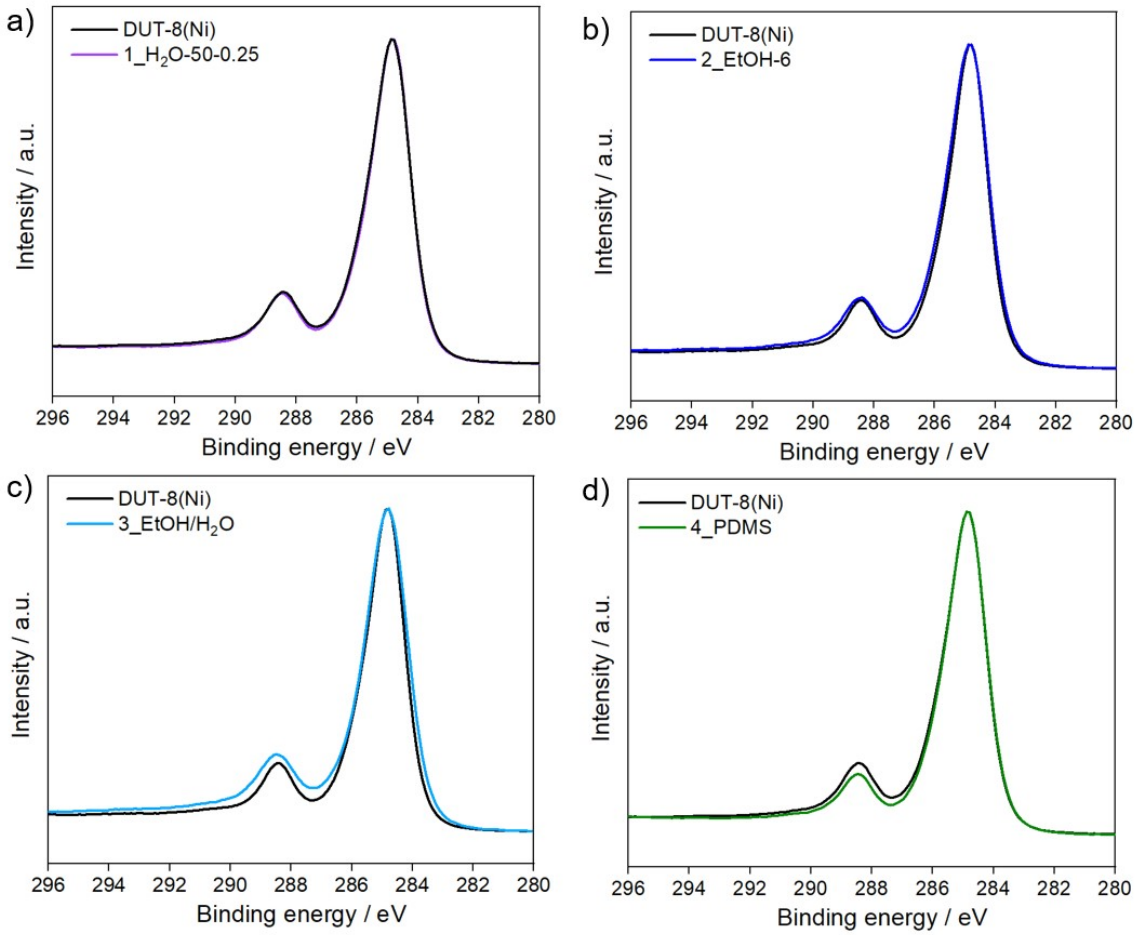


Figure S21. C1*s* XPS spectra of treated samples: a) 1_H_2O-55-0.25, b) 2_EtOH-6, c) 3_EtOH/H_2O, d) 4_PDMS in comparison with non-treated DUT-8(Ni) sample.

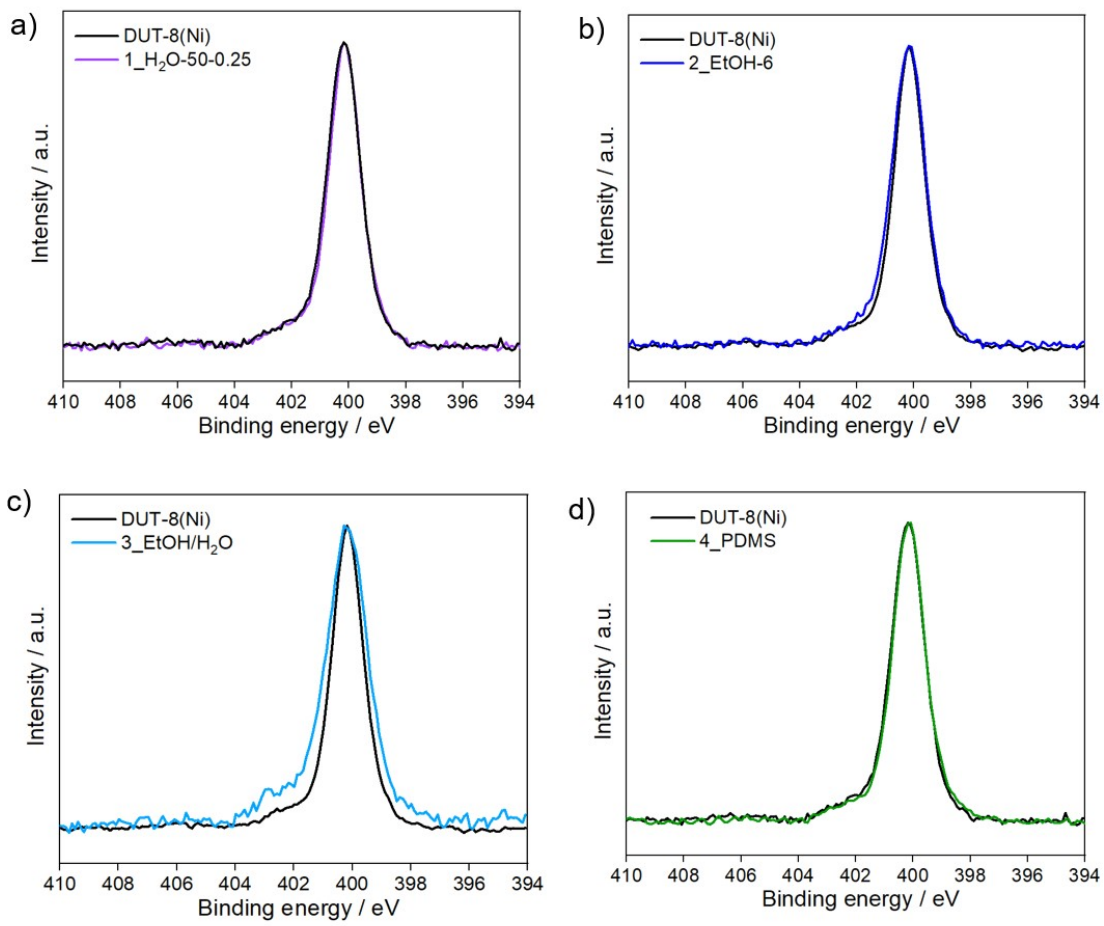


Figure S22. N1*s* XPS spectra of treated samples: a) 1_H_2O-55-0.25, b) 2_EtOH-6, c) 3_EtOH/H_2O, d) 4_PDMS in comparison with non-treated DUT-8(Ni) sample.

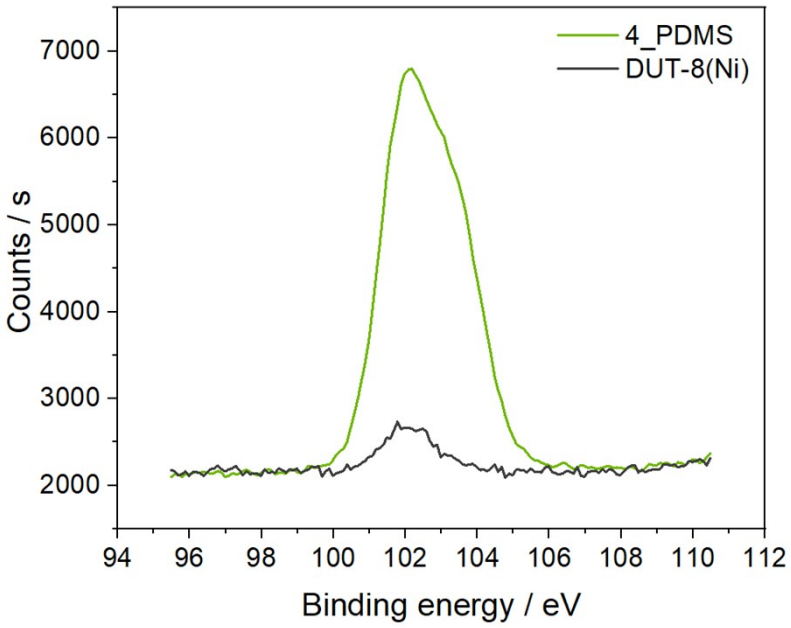


Figure S23. Si 2p XPS spectra of PDMS coated sample.

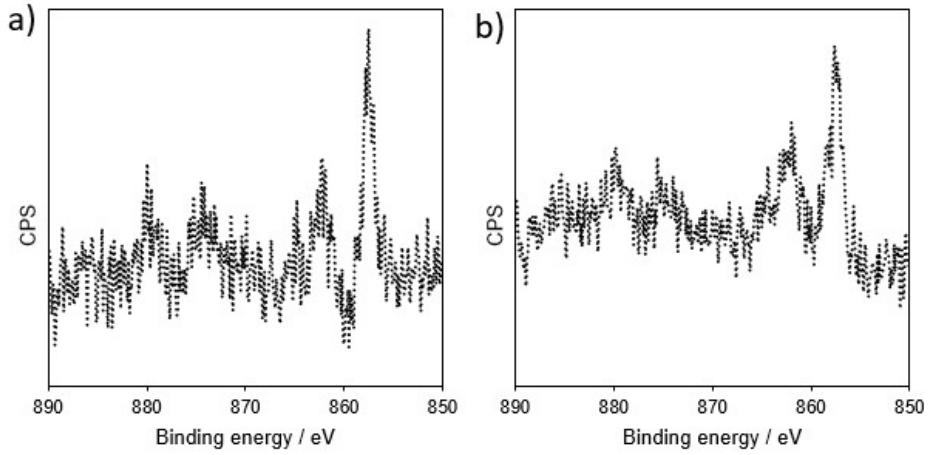


Figure S24. Computed differential spectral enveloped for Ni 2p from a) PCA analysis and b) difference spectra function.

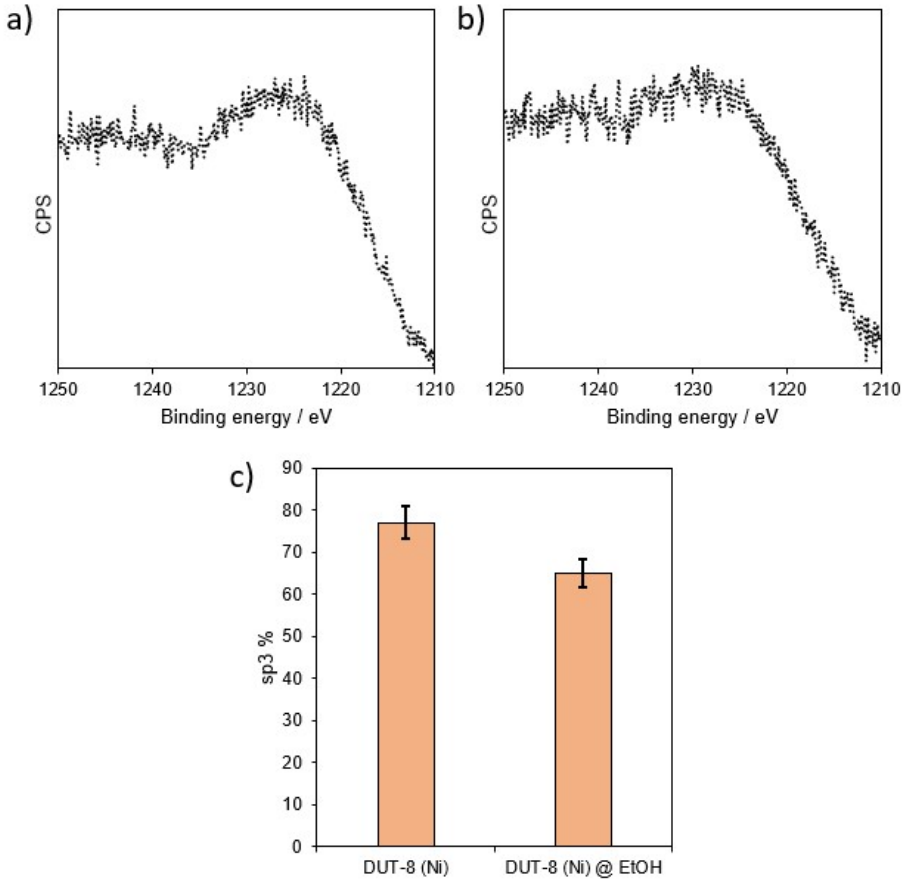


Figure S25. a) C KLL Auger spectra, b) sp2/3 ratio for DUT-8 (Ni) and DUT-8(Ni) @ EtOH and c) sp^3 content for DUT-8(Ni) and DUT-8(Ni)@EtOH.

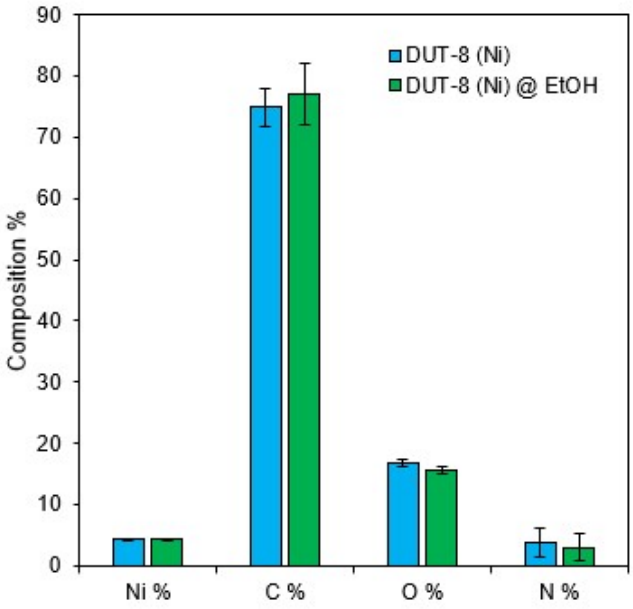
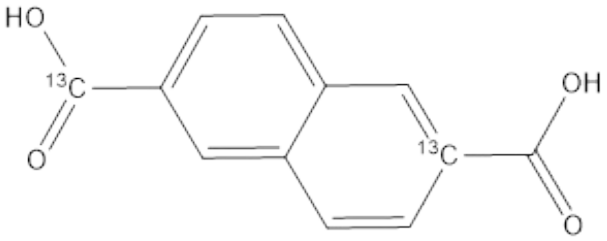


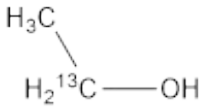
Figure S26. Quantification of XPS survey spectra of DUT-8(Ni) and DUT-8(Ni)@EtOH.

7 NMR spectroscopy

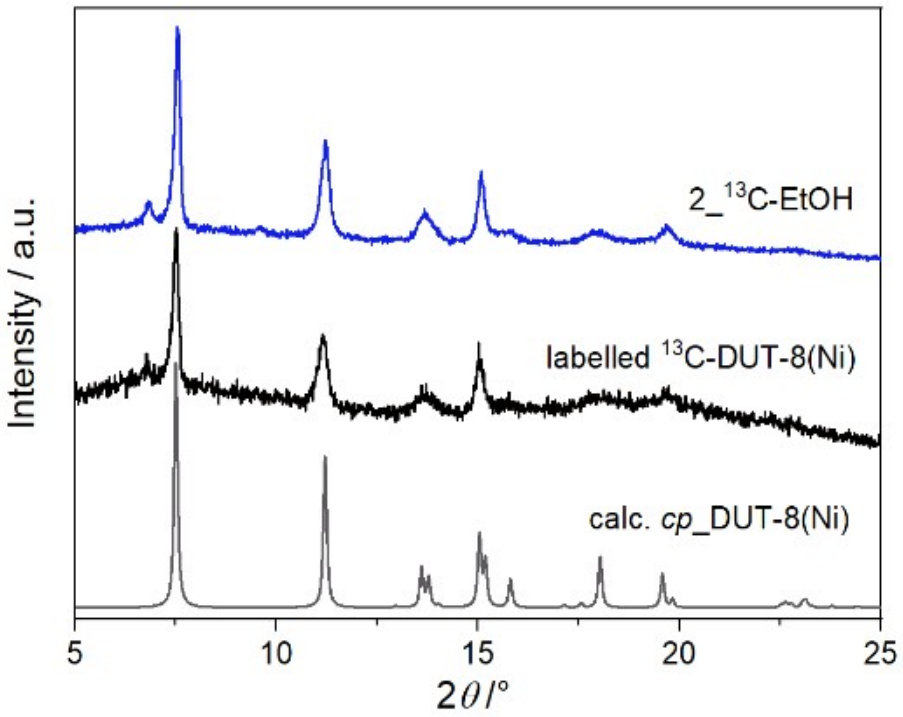
a)



b)



c)



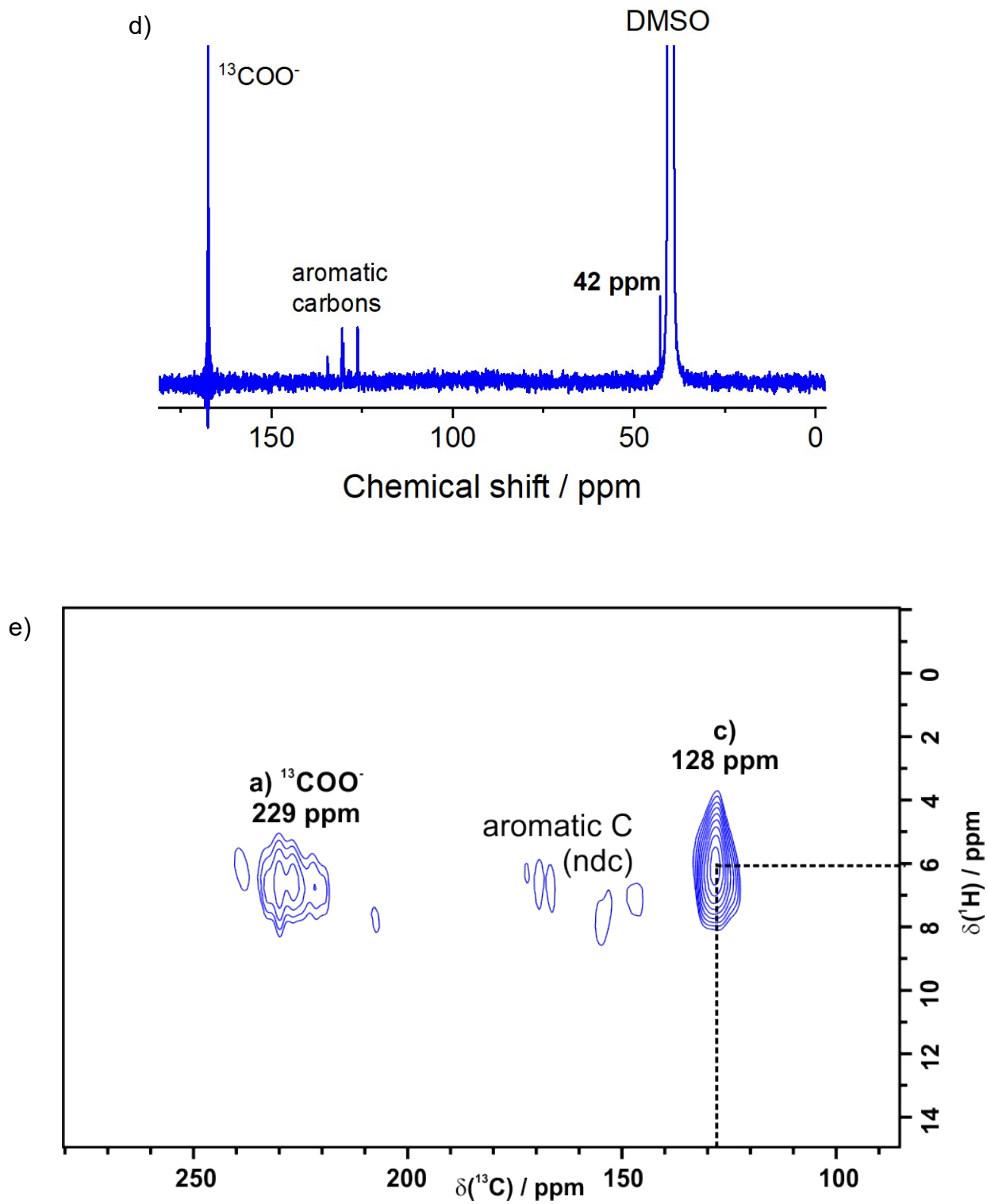


Figure S27. a-b) The ^{13}C labelled molecules used, c) PXRD pattern of samples containing ^{13}C labelled ndc linker before (black) and after (blue) treatment with ^{13}C ethanol. The calculated PXRD pattern for DUT-8(Ni)_cp is given for comparison, d) Liquid-state ^{13}C NMR spectrum of the solution of the sample treated with ^{13}C-labelled ethanol and digested by DCl in DMSO, e) ^{13}C-^{1}H HETCOR spectrum of the samples containing ^{13}C-labeled ndc linker (shown in a) after treatment with ^{13}C-ethanol (shown in b).

8 EPR spectroscopy

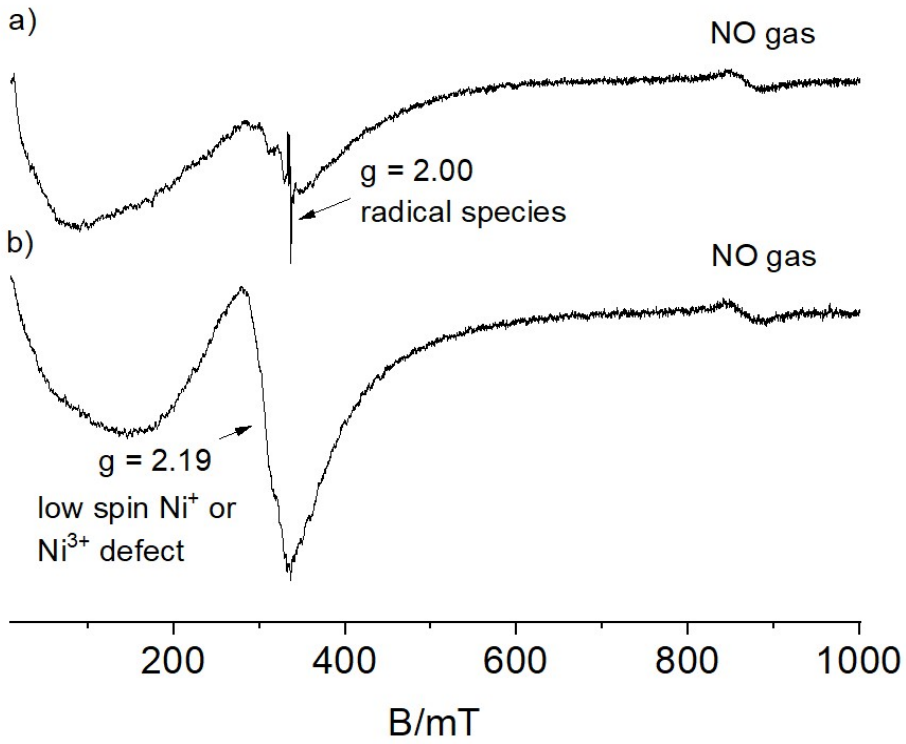


Figure S28. Experimental EPR spectra of a) DUT-8(Ni) and b) sample treated by ethanol 2_EtOH-6 at room temperature.

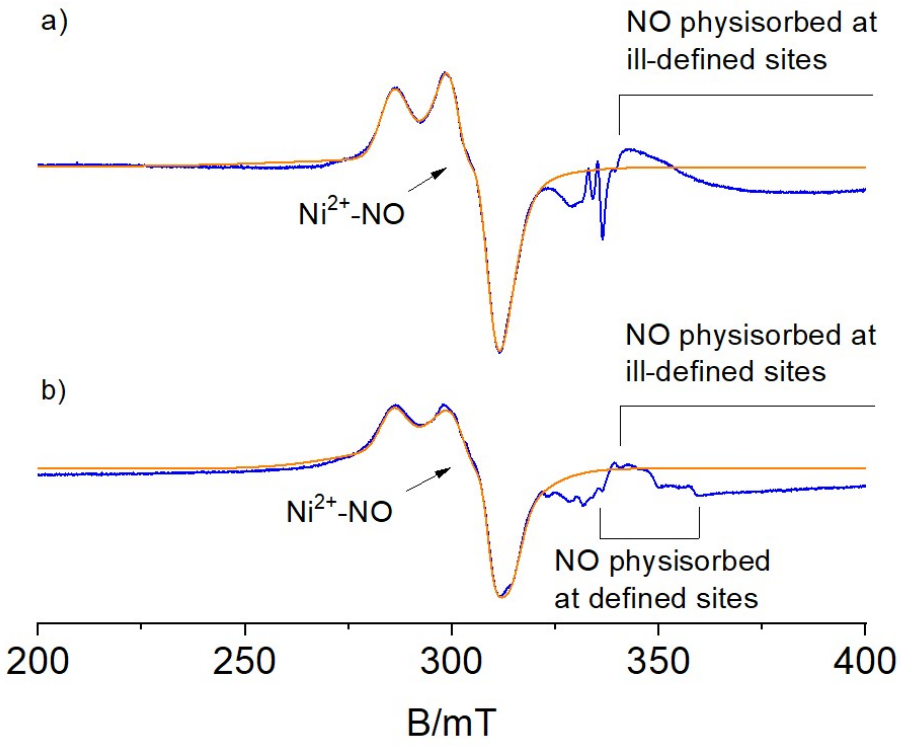


Figure S29. Experimental (blue) and simulated (orange) EPR spectra of a) DUT-8(Ni) and b) sample treated by ethanol 2_EtOH-6 at T = 14 K showing NO species binding axially to open metal sites of a Ni^{2+} defect site (Ni^{2+}-NO).

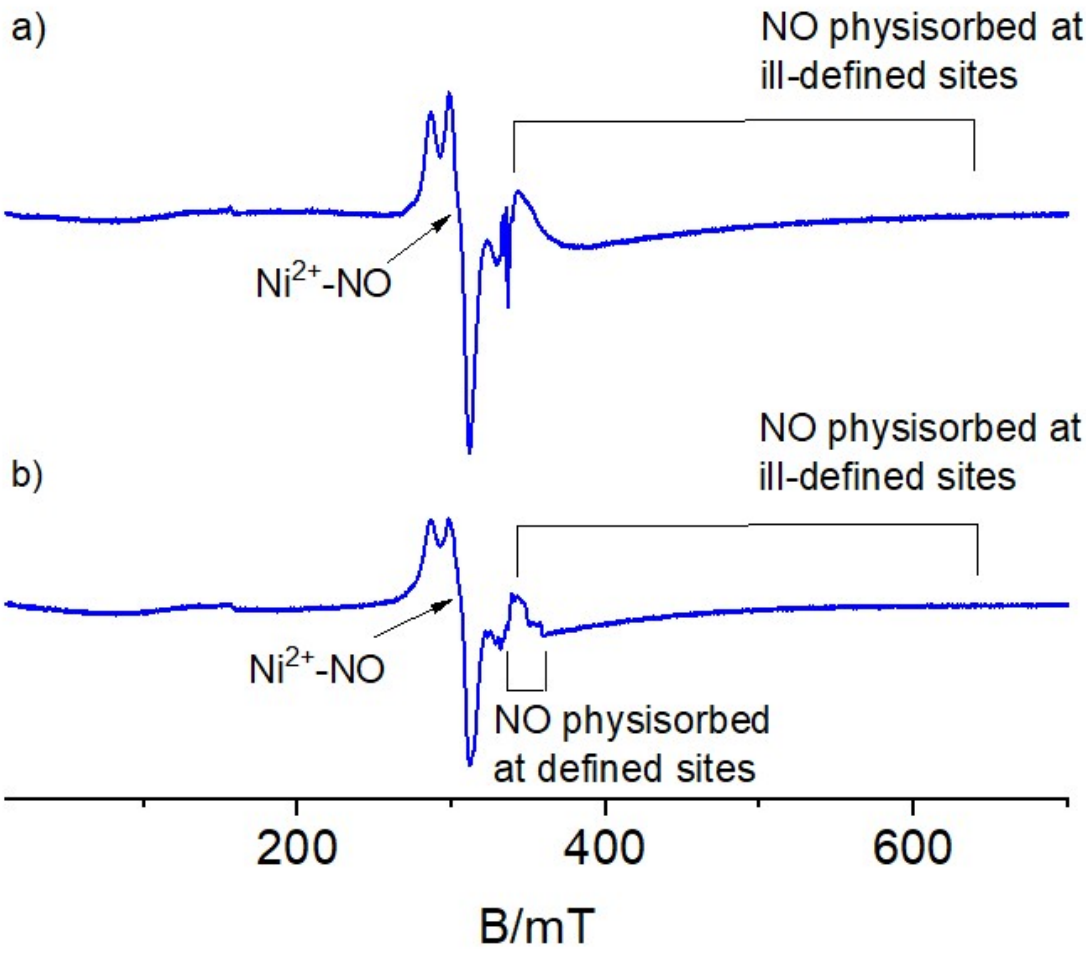


Figure S30. Extended experimental (blue) and simulated (orange) EPR spectra of a) DUT-8(Ni) and b) sample treated by ethanol 2_EtOH-6 at T = 14 K showing the full spectrum of the physisorbed NO species.

9 Raman spectroscopy

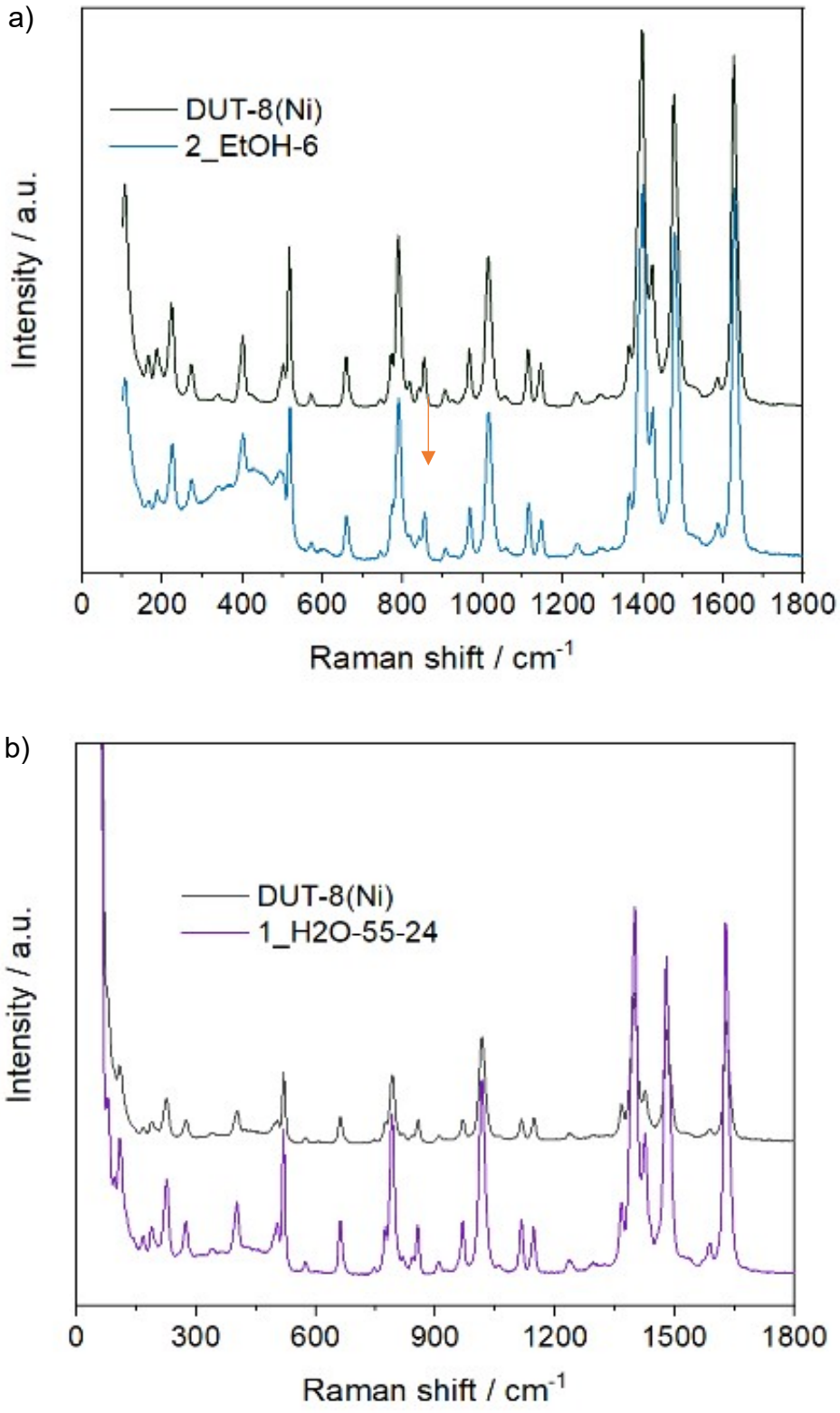


Figure S31. Raman spectra of samples exposed to ethanol a) 2_EtOH-6 and to humid air, b) 1_H_2O-55-24 in comparison with non-treated DUT-8(Ni).

10 The influence of pressing on crystal structure and adsorption properties

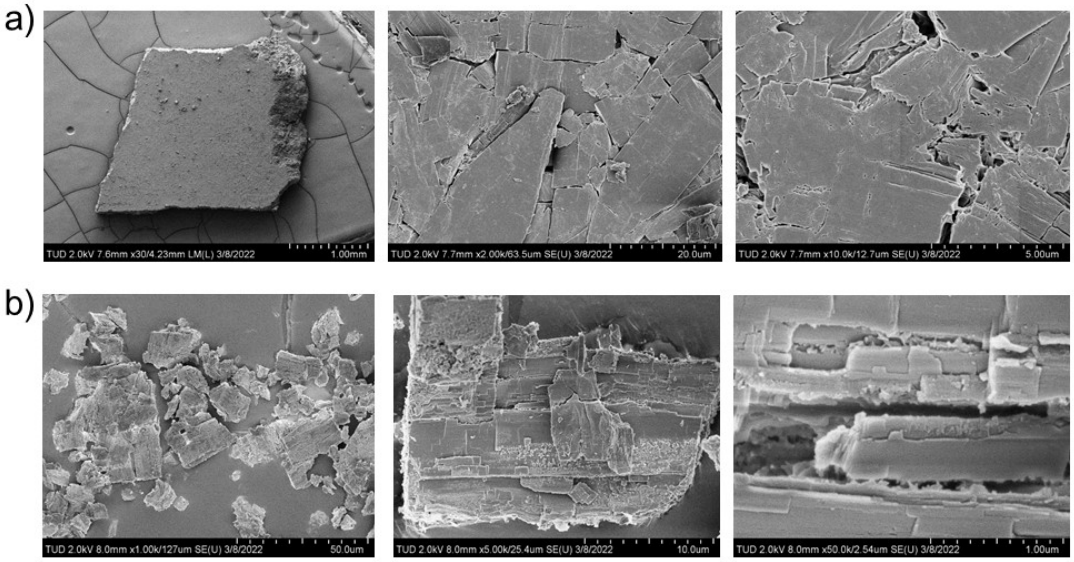


Figure S32. SEM images of pellet DUT-8(Ni) a) before and b) after N_2 physisorption (77 K).

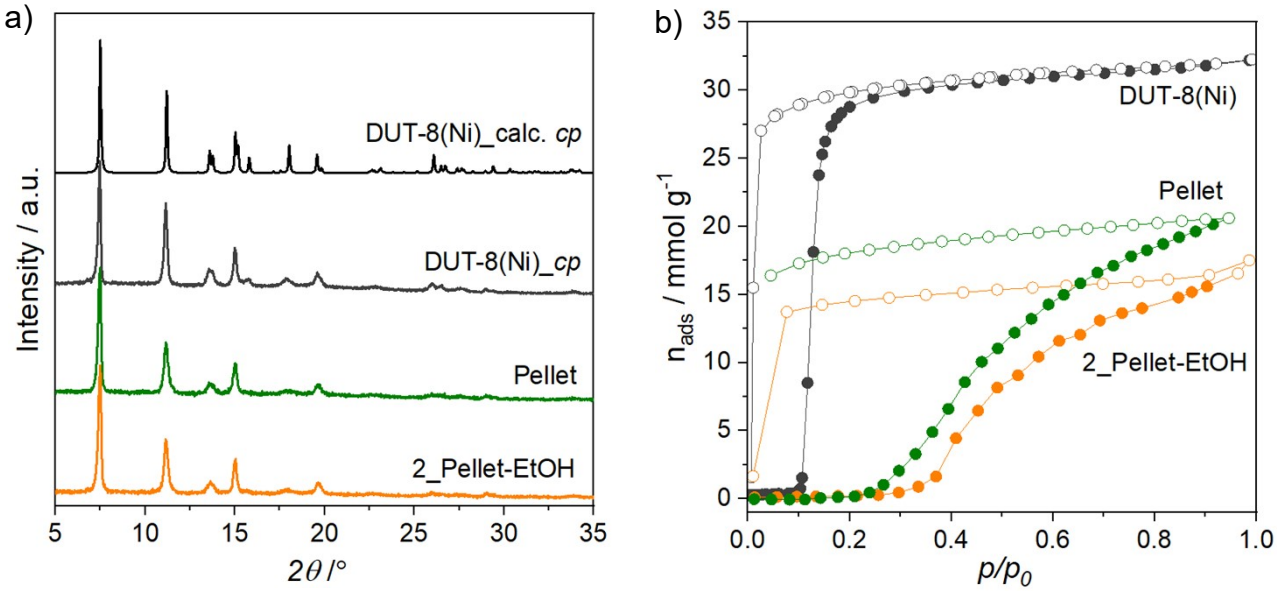


Figure S33. a) PXRD patterns for reference DUT-8(Ni), pellet and pellet treated with ethanol, b) Nitrogen physisorption isotherms at 77 K.

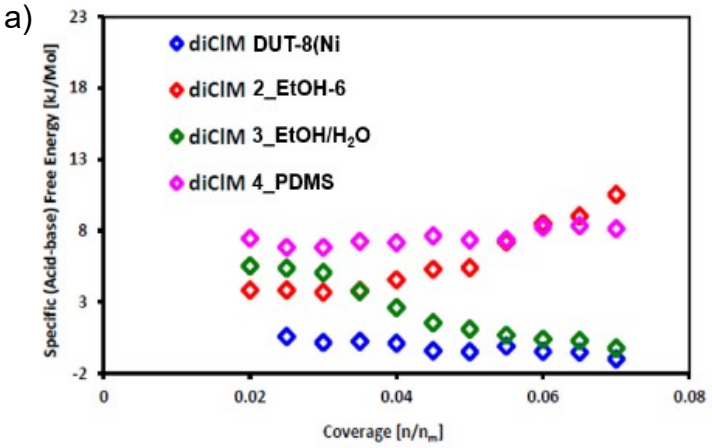
11 Contact angle measurement

Table S1. Contact angle data (°).

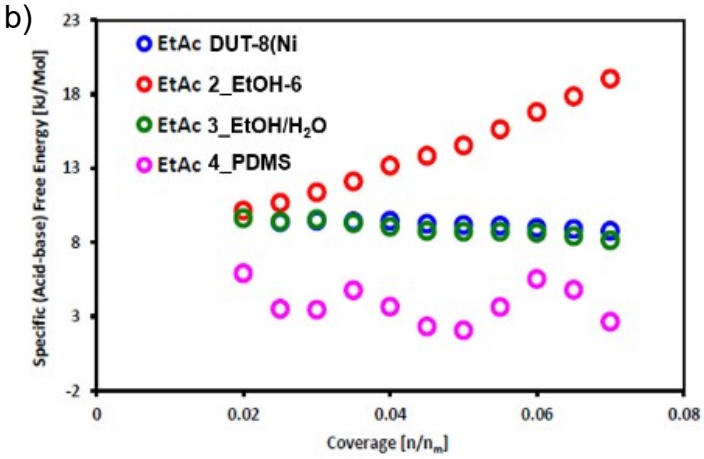
Sample	Static contact angle	Receding contact angle	Advancing contact angle
	Diiodomethane, γL= 50.8 [mN/m]		
Pellet	23	12	34
2_EtOH	9	5	18
4_PDMS	57	27	63
	Water, γL= 72.0 [mN/m]		
Pellet	64	16	72
2_Pellet-EtOH	36	7	54
4_Pellet-PDMS	106	7	118

12 Surface energy analysis

a)



b)



c)

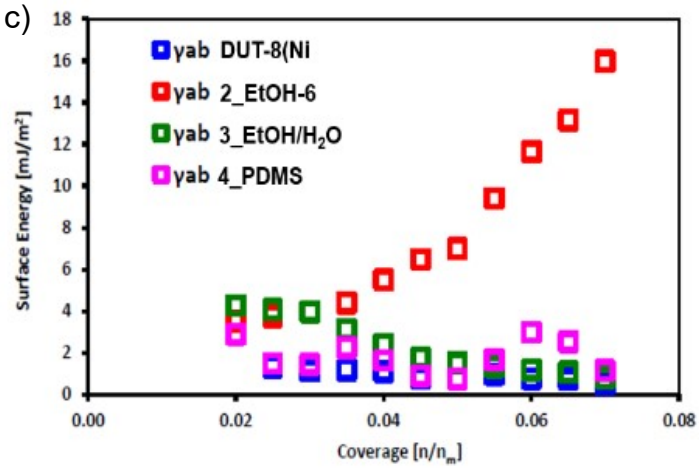


Figure S34. a), b) Specific (acid-base) and c) total surface free energy profiles of untreated DUT-8(Ni) (blue) and DUT-8(Ni) treated with EtOH (red), EtOH/water (green), and PDMS (pink).

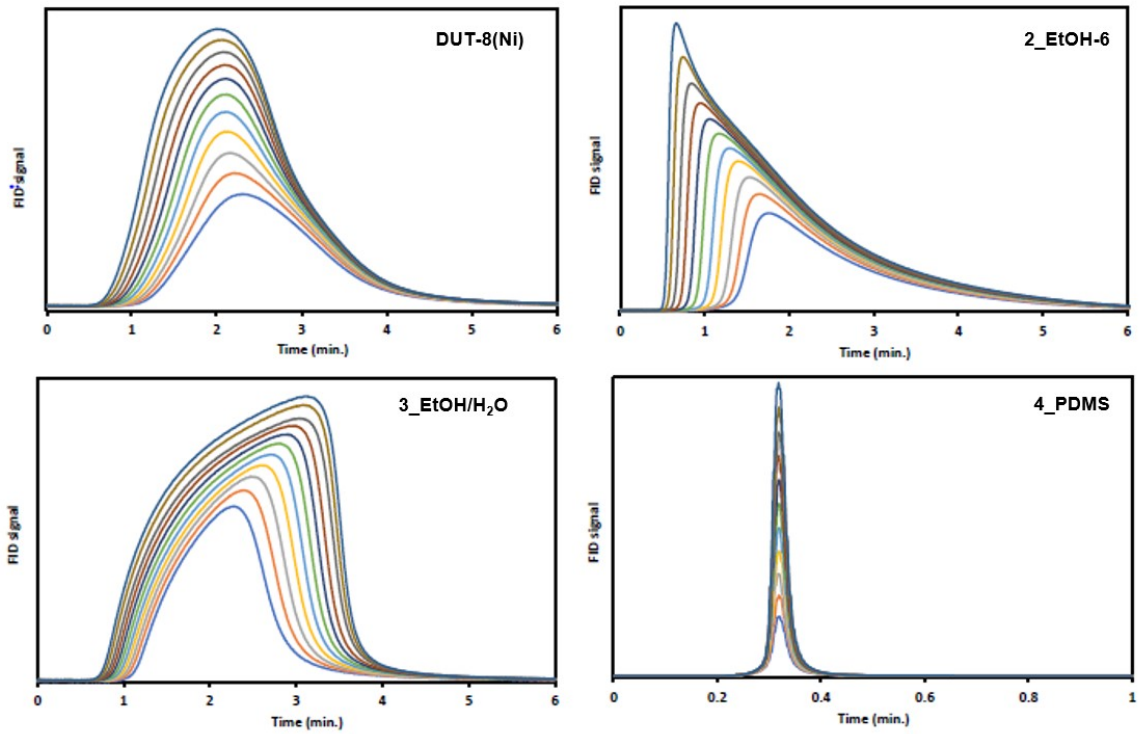


Figure S35. Chromatograms of hexane (at surface coverages ranging from 2 to 7% of monolayer) of all probed samples.