Supplementary Information

Robust engineered catalysts for the conversion of brown grease to renewable diesel via decarboxylation/decarbonylation

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Table S1. Composition of brown grease used in this study

Compound	Composition (%)
Fatty Acid	**99.9**
Oleic acid (C18:1)	61.1
Stearic acid (C18:0)	22.5
Palmitic acid (C16:0)	15.1
Linoleic acid (C18:2)	1.3

Table S2. Surface concentration (in at. %) of elements detected via XPS

	Ni (Ni^0)*	**Cu (Cu^0)***	**Al**	**C**	**O**
E-NCA (As synthesized)	1.51 (0.25)	0.41 (0.26)	61.67	1.41	35.01
E-NCA (Reduced†)	1.81 (0.44)	0.31 (0.24)	51.87	0.82	45.19

*Ni × Ni^0 %Area
†Samples were reduced under flowing hydrogen at 350 °C for 3 hours

Table S3. Ni 2p and Cu 2p species for both as synthesized and reduced E-NCA

Ni 2p3/2 peak			
As synthesized E-NCA			
	Ni^0	$Ni(OH)_2$	$Ni(OH)_2$ Sat
% Area	16.68	40.50	42.82
Position	854.50	855.22	860.89
Reduced E-NCA			
	Ni^0	$Ni(OH)_2$	$Ni(OH)_2$ Sat
% Area	24.28	45.19	30.53
Position	854.06	855.83	861.43
Cu 2p3/2 peak			
As synthesized E-NCA			
	Cu^0	CuO	CuO Sat
% Area	63.76	24.68	11.56
Position	932.19	933.80	942.40
Reduced E-NCA			
	Cu^0	CuO	CuO Sat
% Area	80.27	14.67	5.06
Position	932.27	936.11	945.35

Table S4. Heteroatoms present in the BG feed and representative RD products

Element	Brown Grease (ppm)	Renewable Diesel (ppm)		
		t=30h	t=150h	t=300h
Calcium (Ca)	496±22.5	6.5±1.5	24.4±4.0	5.5±3.1
Sulfur (S)	324.1±20	30.3±1.7	37±19	55.5±13.2
Iron (Fe)	198.1±7.6	1.8±0.4	1.8±0.1	1.3±0.7
Aluminum (Al)	103.7±3.5	3.9±3.3	2.6±1.7	1.0±0.1
Sodium (Na)	24.3±4.3	16.9±5.2	47.4±32.6	30.1±6.4
Phosphorous (P)	8.9±0.5	3.0±0.7	9.4±5.7	0.8±0.0
Potassium (K)	4.4±0.6	1.8±0.3	1.7±0.8	2.6±1.1
Magnesium (Mg)	3.6±1.8	1.5±0.2	3.0±0.1	1.3±1.0
Silicon (Si)	2.0±0.8	7.5±4.8	6±2.7	9.2±5.6
Nitrogen (N)	1.1±0.2	1.2±0.3	1.4±0.1	0.8±0.1
Copper (Cu)	0.8±0.1	0.2±0.2	0.01±0.0	0.01±0.0
Nickel (Ni)	0.4±0.2	0.2±0.1	0.4±0.1	0.3±0.2
Lead (Pb)	0.1±0.0	0.02±0.0	0.01±0.0	0.01±0.0

Table S5. Elemental composition and heteroatoms present in fresh and spent catalyst

Element	E-NCA Catalyst	
	Fresh	**Spent***
Aluminum (Al)	36.9±1.9%	7.6±6.2%
Nickel (Ni)	19.5±0.4%	7.1±1.2%
Copper (Cu)	5.6±0.1%	2.5±0.1%
Iron (Fe)	129.0±6.1 ppm	4455.6±722.0 ppm
Calcium (Ca)	0.0±0.0 ppm	1113.3±37.5 ppm
Sodium (Na)	24.1±0.7 ppm	118.6±0.1 ppm
Potassium (K)	11.5±8.5 ppm	47.7±2.3 ppm
Phosphorous (P)	9.0±3.2 ppm	22.7±7.3 ppm
Magnesium (Mg)	0.0±0.0 ppm	14.9±10.3 ppm
Lead (Pb)	1.7±0.1 ppm	1.1±0.0 ppm
Sulfur (S)	0.0±0.0 ppm	0.4±0.0 ppm

*The spent material includes both coked E-NCA as well as the SiC diluent.

Table S6. Surface concentration (in at. %) of elements detected in fresh and spent catalyst via XPS

Element	Spent E-NCA	
	Top of Bed	**Bottom of Bed**
C 1s	39.30	39.67
O 1s	27.86	27.12
Al 2p	30.57	30.91
Si 2p	0.36	1.11
P 2p	0.38	0.20
S 2p	0.25	0.12
Ca 2p	0.15	0.04
Ni 2p (Ni^0)	0.90 (0.21)	0.69 (0.07)
Cu 2p (Cu^0)	0.23 (0.19)	0.16 (0.08)

Table S7. Performance comparison of E-NCA with NiMo and CoMo catalyst.

Catalyst	Reaction Conditions	Catalyst Performance	Ref.
Engineered Ni-Cu/γ-Al_2O_3 (E-NCA)	*Brown grease*; 325 °C; 580 psi; 60 sccm; WHSV = $1h^{-1}$; 300 hours; continuous reactor	Conv. = 100%; Sel. C9-C26 = ≳93%	This work
NiMo/CoMo/ Mesostructured γ-Al_2O_3	*Canola oil*; 325 °C (optimum); 450 psi; LHSV = 1-3 h^{-1}; H_2/Oil = $600mLmL^{-1}$; 6 hours; continuous reactor	Conv. = 100%; Sel. C9-C30 = ~80%	[1]
CoMo/ Powdered Al_2O_3	*Oleic acid*; 260 °C; 3MPa; LHSV = $80h^{-1}$; H_2/Oil = $500mLmL^{-1}$; 120 hours continuous reactor	Conv. = 41–57%; HDO degree = 33–53%; Sel. C18/C17 = 1.4	[2]
NiMo or CoMo/ γ-Al_2O_3 granules	*Methyl palmitate*; 300 °C; 3.5 MPa; 100 rpm; 6 hours; batch reactor	Sel. C16/C15 = 0.65 (NiMo); 2.79 (CoMo)	[3]
NiMo/ Powdered Al_2O_3	*Oleic acid*; 325 °C; 6 MPa; 1000 rpm; 330 min; batch reactor	Conv. = ~100%; Sel. C13-C18 = ~80%; Yield C18+ = 20%; Yield C17+ = 60%	[4]
NiMo/ Powdered γ-Al_2O_3	*Palm oil*; 300 °C; 40 bar; cat/oil = 0.1; 150 rpm; 3 hours; batch reactor	Max. Yield C14-C18 = 67%; Sel. = ~99%	[5]

[1] Afshar Taromi, A.; Kaliaguine, S. Green diesel production via continuous hydrotreatment of triglycerides over mesostructured γ-alumina supported NiMo/CoMo catalysts. Fuel Process. Technol. 2018, 171, 20.

[2] Nikulshin, P. A.; Salnikov, V. A.; Varakin, A. N.; Kogan, V. M. The use of CoMoS catalysts supported on carbon-coated alumina for hydrodeoxygenation of guaiacol and oleic acid. Catalysis Today 2016, 271, 45-55. DOI: https://doi.org/10.1016/j.cattod.2015.07.032.

[3] Deliy, I. V.; Vlasova, E. N.; Nuzhdin, A. L.; Gerasimov, E. Y.; Bukhtiyarova, G. A. Hydrodeoxygenation of methyl palmitate over sulfided Mo/Al2O3, CoMo/Al2O3 and NiMo/Al2O3 catalysts. RSC Advances 2014, 4 (5), 2242-2250, 10.1039/C3RA46164E. DOI: 10.1039/C3RA46164E.

[4] Arora, P.; Ojagh, H.; Woo, J.; Lind Grennfelt, E.; Olsson, L.; Creaser, D. Investigating the effect of Fe as a poison for catalytic HDO over sulfided NiMo alumina catalysts. Applied Catalysis B: Environmental 2018, 227, 240-251. DOI: https://doi.org/10.1016/j.apcatb.2018.01.027.

[5] Aiamsiri, P.; Tumnantong, D.; Yoosuk, B.; Ngamcharussrivichai, C.; Prasassarakich, P. Biohydrogenated Diesel from Palm Oil Deoxygenation over Unsupported and γ-Al2O3 Supported Ni–Mo Catalysts. Energy & Fuels 2021, 35 (18), 14793-14804. DOI: 10.1021/acs.energyfuels.1c02083.

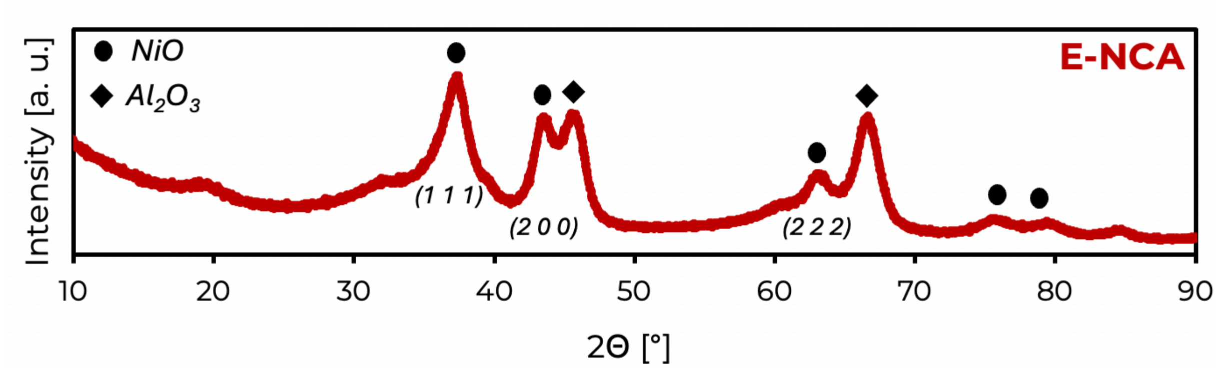

Figure S1. X-ray diffractogram of E-NCA

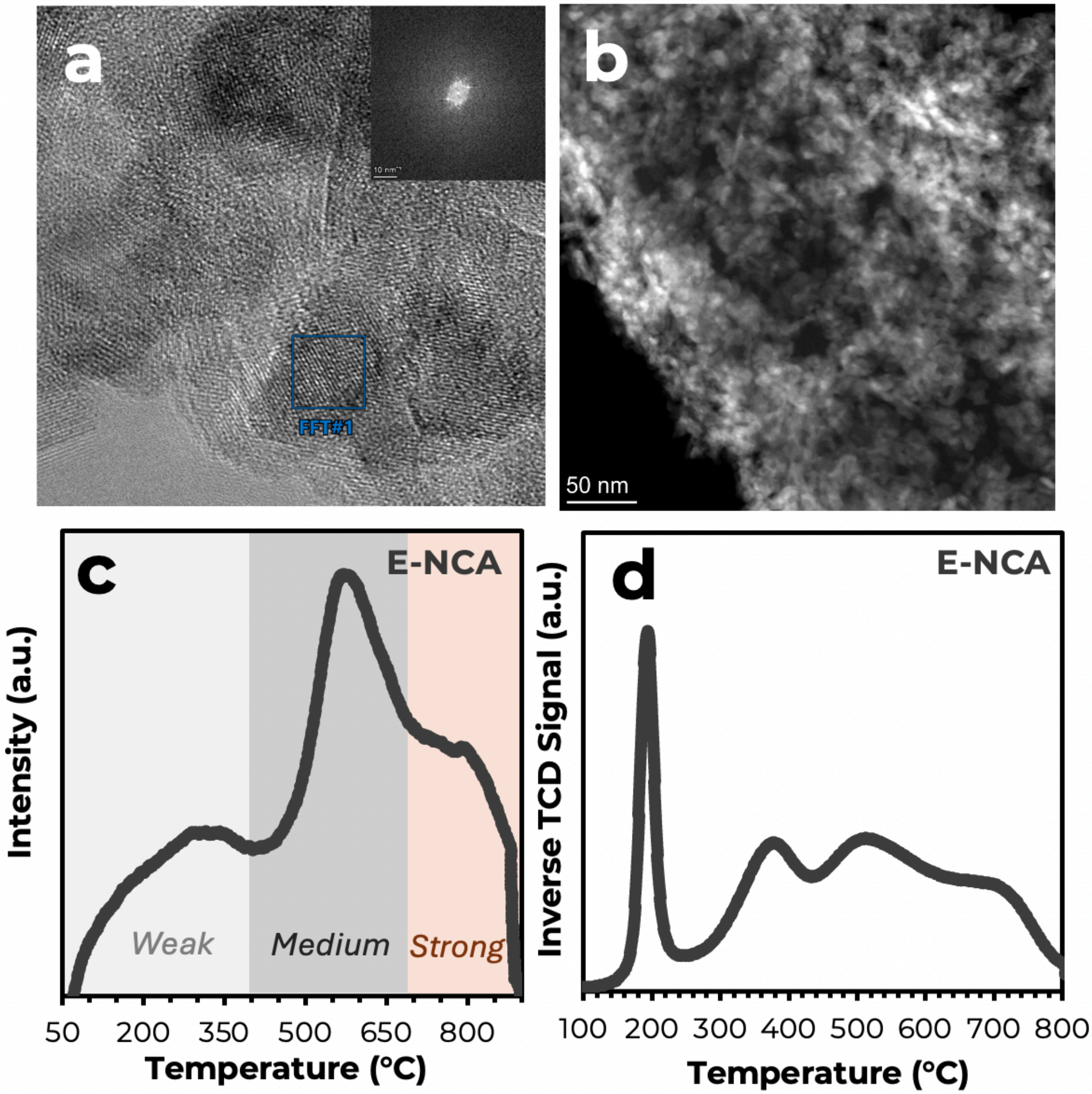

Figure S2. (a) FFT; (b) HAADF; temperature-programmed (c) desorption of NH_3; (d) reduction.

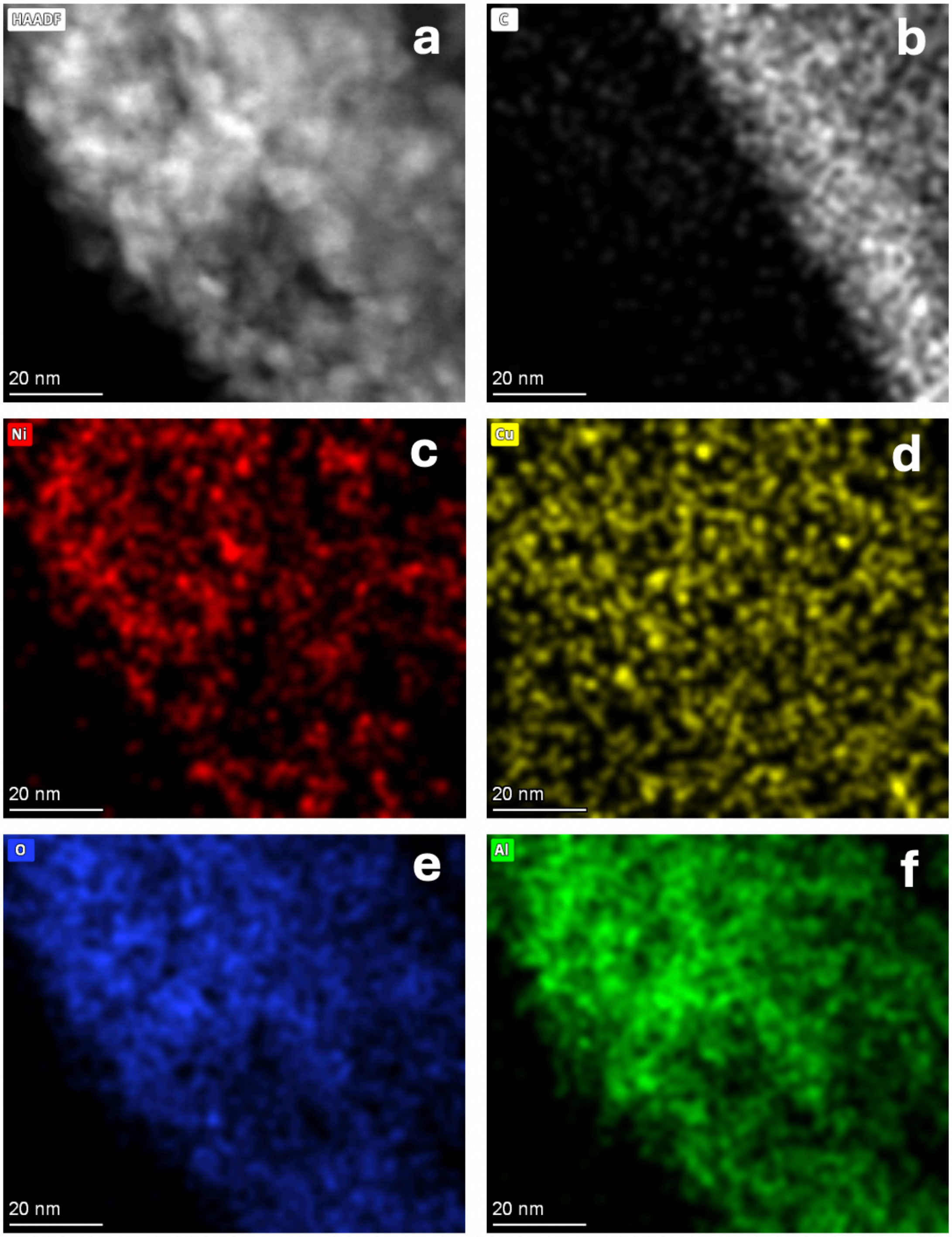

Figure S3. (a) High-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) and **(b-f)** elemental maps of C, Ni, Cu, O, and Al for fresh E-NCA

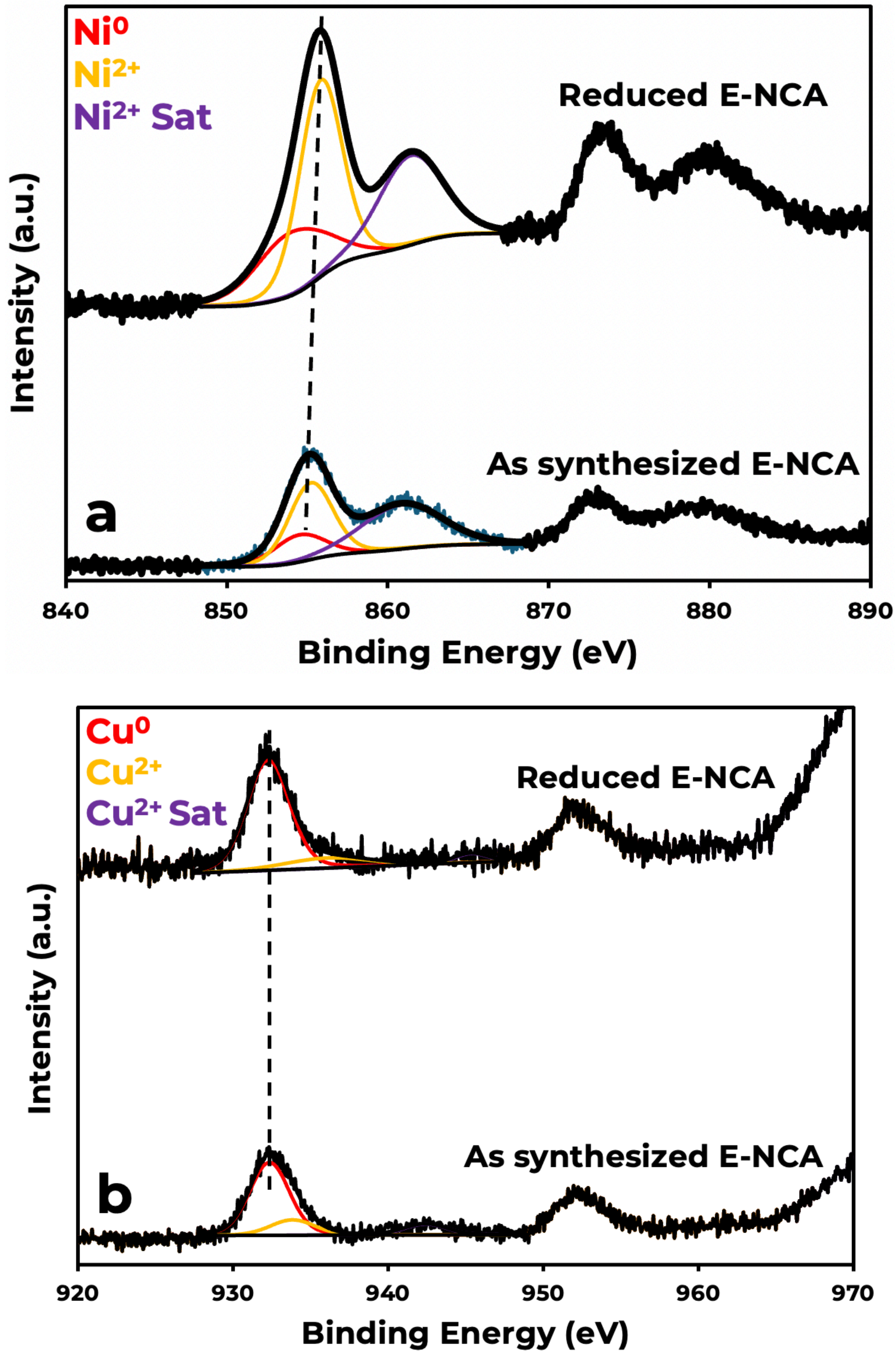

Figure S4. (a) Ni and (b) Cu 2p x-ray photoelectron spectra.

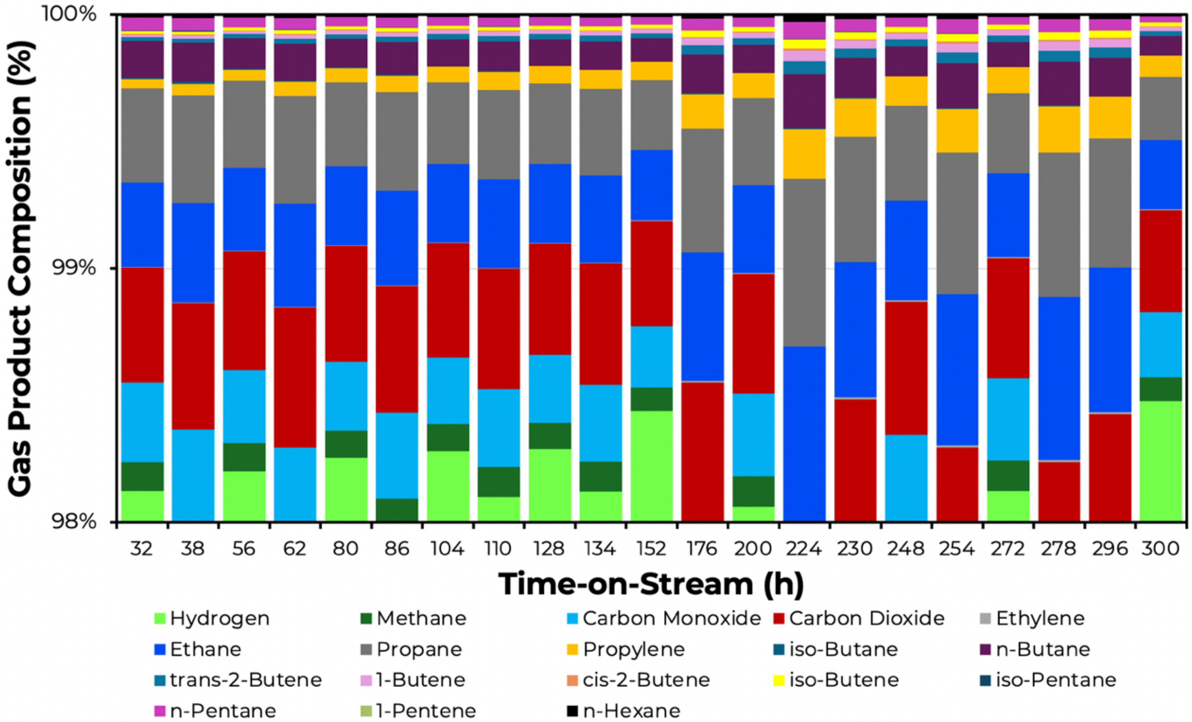

Figure S5. Detailed composition of gaseous products

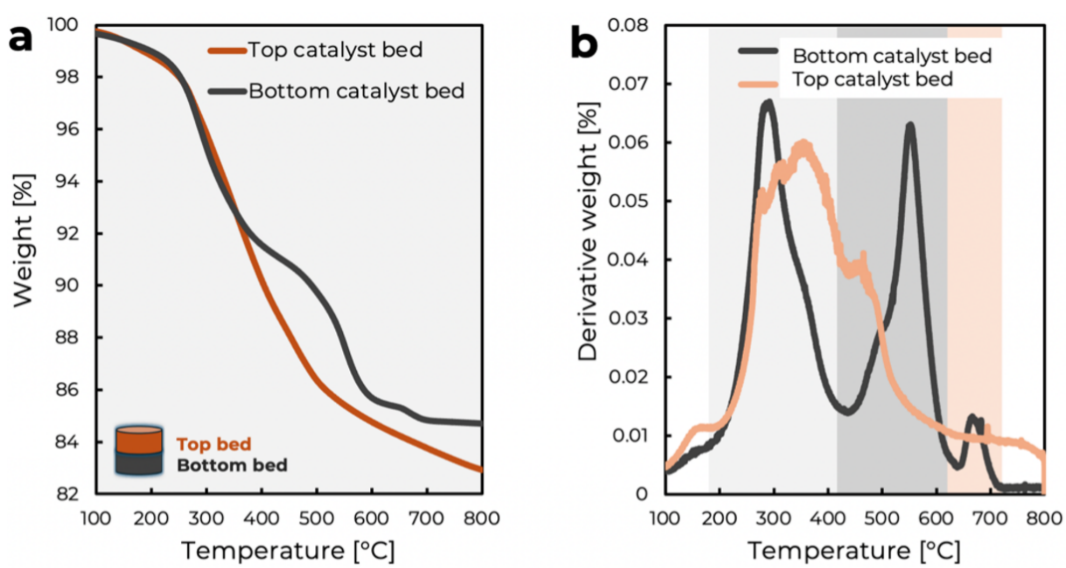

Figure S6. (a) Thermogravimetric analysis under air of spent E-NCA; **(b)** Derivative weight loss curve of spent E-NCA

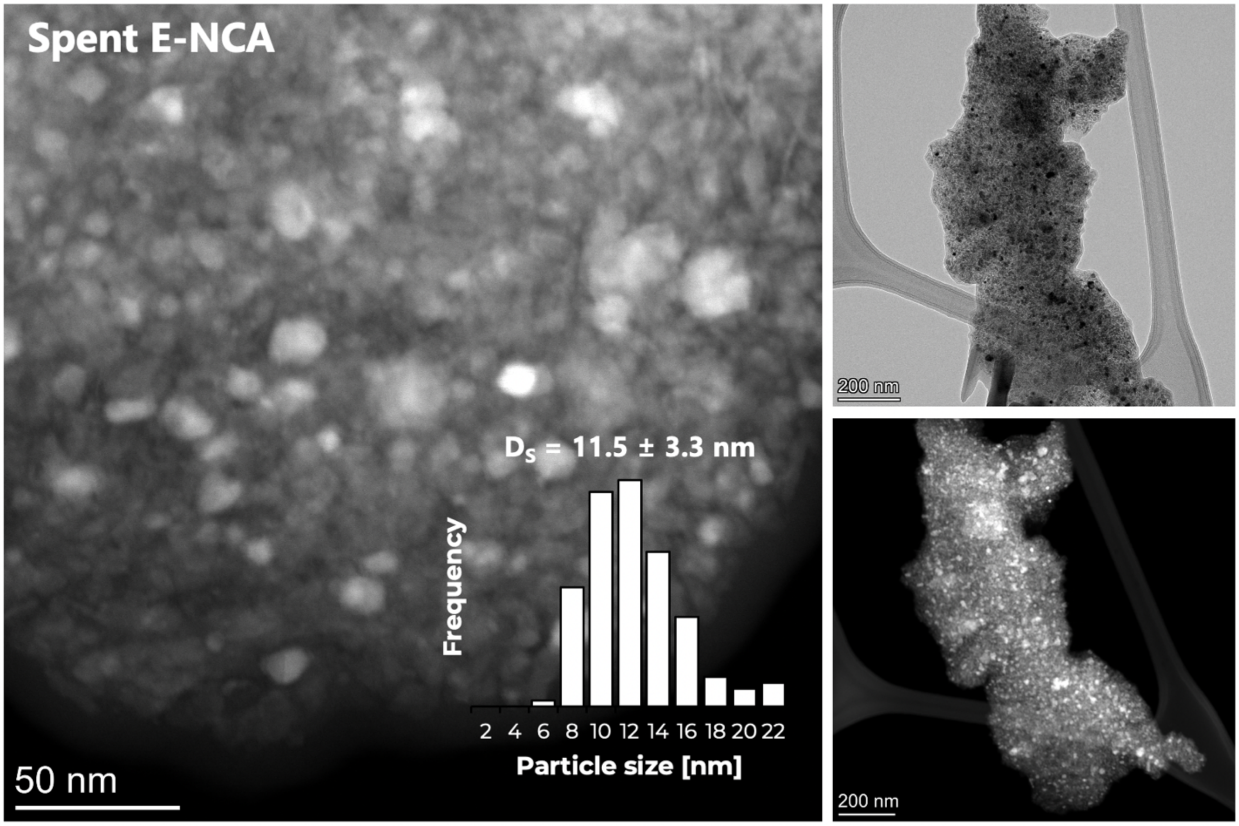

Figure S7. Particle size distribution and TEM images of spent E-NCA catalyst