Supporting Information

Promotional role of NiCu alloy in catalytic performance and carbon properties for CO_2-free H_2 production from thermocatalytic decomposition of methane

Mengze Xu [a,1], Juan Lopez-Ruiz [a,1], Nickolas W. Riedel [a,1], Robert S. Weber [a,1], Mark E. Bowden [b], Libor Kovarik [b], Changle Jiang [c], Jianli Hu [c,] and Robert A. Dagle [a*]

[a] *Institute for Integrated Catalysis, Pacific Northwest National Laboratory, Richland, WA 99354, USA*

[b] *Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99354, USA*

[c] *Department of Chemical & Biomedical Engineering, West Virginia University, Morgantown, WV 26506, USA*

**Correspondence to: Robert.Dagle@pnnl.gov*

Number of pages: 10

Number of Tables: 4

Number of Figures: 9

Table S1. Physiochemical properties of different support CNTs and solvothermal catalysts (which used raw CNTs as support). Fresh catalysts were reduced at 400 °C for 4 h.

Catalysts Fresh reduced (Solvothermal)	Metal loading (wt%) [a]		BET surface area ($m^2 \cdot g^{-1}$)
	Ni	Cu	
Raw CNT	-	-	161
HCNT	-	-	187
Ni/CNT	8.80	-	133
NiCu0.6/CNT	8.91	0.45	140
NiCu1/CNT	8.96	0.86	147
NiCu2/CNT	10.42	1.87	142
NiCu5/CNT	8.99	5.25	137
NiCu10/CNT	9.66	8.74	128
NiCu15/CNT	10.38	13.89	154

[a] Results derived from ICP

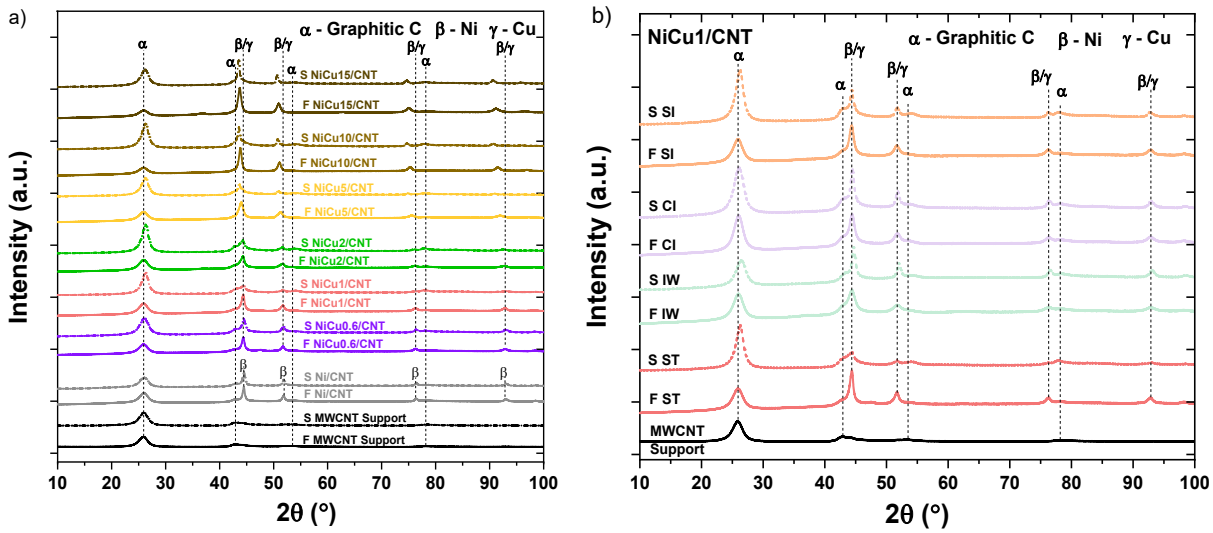


Figure S1. XRD patterns of fresh (F) reduced and spent (S) of a) solvothermal $NiCu_x$/CNT catalyst and b) $Ni1Cu_x$/CNT catalyst prepared by different synthesis method such as incipient wetness (IW), co-impregnation (CI), and sequential impregnation (SI). The fresh catalysts were reduced at 400 °C for 4 h in 5 vol% H_2 in N_2. The spent catalysts were retrieved after reaction at 600 °C under 30 cm^3/min 30 vol% CH_4 in N_2.

Table S2. Crystallite sizes and metal phases of solvothermal catalysts NiCu*x*/CNT (*x*= 0, 0.6, 1, 2, 5, 10, and 15) based on XRD analysis. Fresh catalysts were reduced at 400 °C for 4 h. Spent catalysts were retrieved after reaction at 600°C under 30 cm^3/min 30 vol% CH_4/N_2.

Catalysts	Fresh						Spent, reaction at 600 °C						Change, %	
	ICP	Metal oxide[a]		Ni-rich alloy			Ni-rich alloy			Cu-rich alloy			Crystallite Size	Ni/Cu Ratio
	Ni/Cu (mol/mol)	wt.% (%)	Crystallite size (nm)	wt.% (%)	Ni/Cu (mol/mol)	Crystallite size (nm)	wt.% (%)	Ni/Cu (mol/mol)	Crystallite size, (nm)	wt.% (%)	Ni/Cu (mol/mol)	Crystallite size (nm)		
Ni	-	0	-	100	-	11.8	100	-	16.9	-	-	-	43.2	-
NiCu0.6	21.4	0	-	100	52.7	13.1	100	44.6	17.8	-	-	-	35.9	-15.4
NiCu1	11.3	0	-	100	24.3	11.0	100	17.6	9.4	-	-	-	-14.6	-27.6
NiCu2	6.03	18	4.6	88	9.99	10.5	90	6.66	12.5	10	0.9	25.0	19.0	-33.3
NiCu5	1.85	0	-	100	2.11	7.30	32	5.00	10.6	68	0.4	22.0	45.2	137
NiCu10	1.20	12	6.5	84	1.17	11.9	100	0.248	12.7	-	-	-	6.7	-78.8
NiCu15	0.809	12		88	0.790	8.60	100	0.254	17.2	-	-	-	100	-67.9

[a] The presence of the metal oxide (e.g., NiO, CuO, Cu_2O) might be a result of the passivation step used after catalyst reduction and exposure to air.

Table S3. Crystallite sizes and metal phases of NiCu1 catalysts prepared by different synthesis methods based on XRD analysis. Fresh catalysts were reduced at 400 °C for 4 h. Spent catalysts were retrieved after reaction at 600 °C under 30 cm^3/min 30 vol% CH_4 in N_2.

Catalysts	Fresh									Spent		
	Metal loading[a] (%)		Ni/Cu[a] (mol/mol)	BET (m^2/g)	Metal oxide[b]		Ni-rich alloy[b]			Ni-rich alloy[b]		
	Ni	Cu			wt.%	Particle size/nm	wt.%	Ni/Cu (mol/mol)	Particle size/nm	wt. %	Ni/Cu (mol/mol)	Particle size/nm
NiCu1/CNT (ST)	8.96	0.86	11.3	147	0	-	100	24.3	11.0	100	19	9.4
NiCu1/HCNT (IW)	13.1	1.33	10.7	214	24	4.3	76	13.0	8.0	100	32	10.6
NiCu1/HCNT (CI)	10.3	0.95	11.8	217	0	-	100	19.3	7.4	100	49	9.3
Cu1Ni/HCNT (SI)	10.9	1.07	11.1	226	0	-	100	20.2	8.4	100	19	15.1

[a] Results derived from ICP
[b] Results derived from XRD analysis

Table S4. Fitting parameters for deactivation at solvothermal catalysts run at different temperatures (550, 600, 650, and 700 °C) and the carbon co-product that accumulates at the indicated time on stream, θ. The catalyst sample weighed 0.2 g so all but one of the samples (Ni/CNT (ST) accumulated an amount of carbon that exceeded the mass of the MWCNT support (i.e., <0.18 g)at the indicated, final time on stream.

Catalyst	Cu mol fraction	Temperature (°C)	X_0 (%)	k ($h^{-0.5}$)	θ (h)	Actual Carbon Yield (g_C/g_{cat})	Predicted Carbon Yield (g_C/g_{cat})
Ni/CNT (ST)	0	550	56.3	0.373	5	24.3	24.4
		600	135	3.09	0.87	0.282	0.251
		650	6094	22.1	0.67	0.268	0.228
		700	30.3	5.04	1	0.0235	0.0210
NiCu1/CNT (ST)	0.081	550	29.40	0.0787	5	3.50	1.71
		600	62.6	0.309	5	2.52	2.61
		650	225	4.50	0.53	0.266	0.187
		700	n/a	n/a	-	-	-
NiCu15/CNT (ST)	0.553	550	27.1	0.0943	5	1.88	1.55
		600	32.1	0.0561	5	1.93	1.94
		650	53.0	0.0150	5	3.11	3.39
		700	88.6	1.68	4.3	1.24	0.666

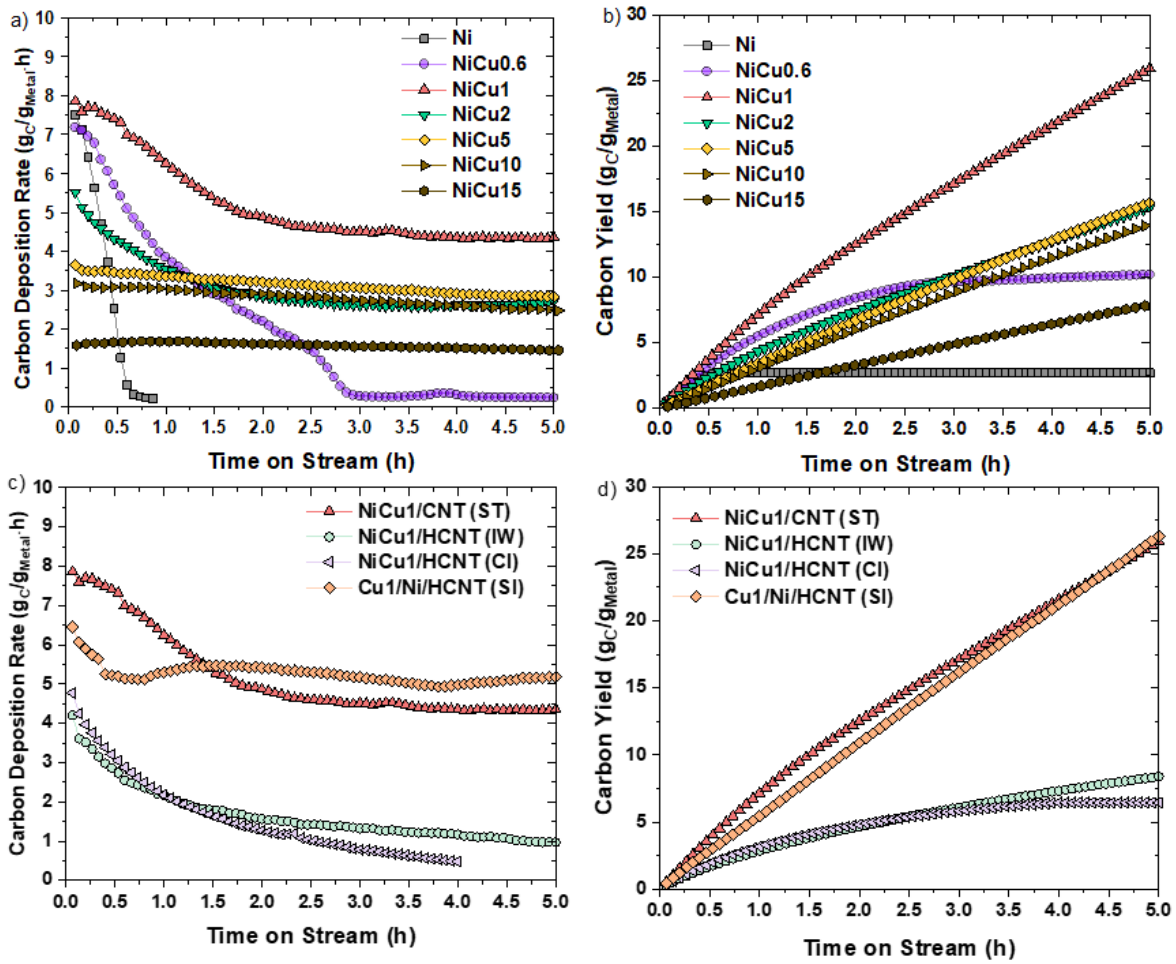


Figure S2. Activity of a-b) NiCux/CNT (x= 0, 0.6, 1, 2, 5, 10, 15) synthesized by solvothermal (ST) method and c-d) NiCu1/CNT prepared by different synthesis methods [incipient wetness (IW), co-impregnation (CI), sequential-impregnation (SI)] as a function of time on stream at reaction temperature of 600 °C under 30 cm^3/min 30 vol% CH_4 in N_2. GHSV≈ 3000 h^{-1}. The background activity of the raw CNT was <0.2% CH_4 conversion.

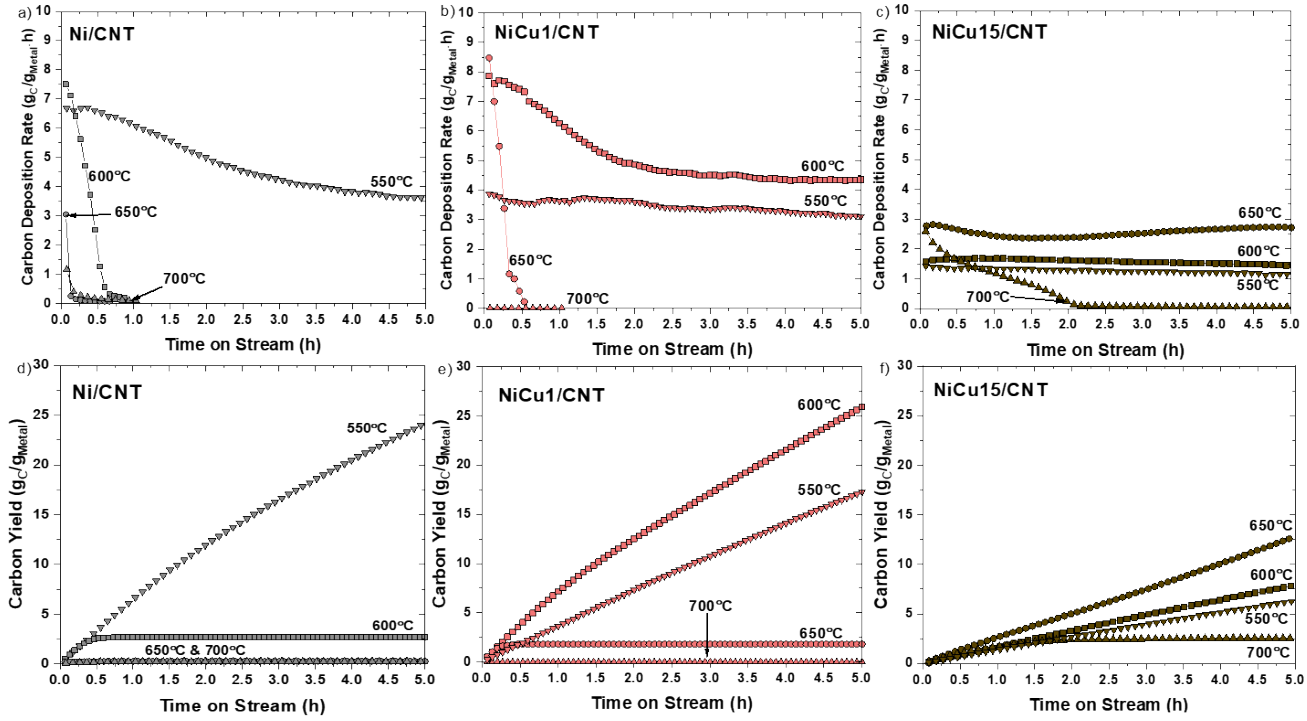


Figure S3. a-c) carbon deposition rate and d-e) carbon yield for Ni/CNT, NiCu1/CNT, and NiCu15/CNT at different reaction temperature (550 to 700°C) as a function of time on stream (SOT) under 30 cm^3/min 30 vol.% CH_4 in N_2.

Table S5. Crystallite sizes and composition of spent solvothermal Ni/CNT, NiCu1/CNT, and NiCu15/CNT catalysts based on XRD analysis. The spent catalysts were retrieved after reaction at different temperatures (550, 600, 650, and 700°C) under 30 cm^3/min 30 vol.% CH_4 in N_2.

Spent catalysts	550°C			600°C			650 °C						700 °C		
	Ni-rich alloy			Ni-rich alloy			Ni-rich alloy			Cu-rich alloy			Ni-rich alloy		
	wt.% (%)	Ni/Cu (mol/mol)	Crysta-llite size (nm)	wt.% (%)	Ni/Cu (mol/mol)	Crysta-llite size (nm)	wt% (%)	Ni/Cu (mol/mol)	Crysta-llite size (nm)	wt.% (%)	Ni/Cu (mol/mol)	Crysta-llite size (nm)	wt.% (%)	Ni/Cu (mol/mol)	Crysta-llite size (nm)
Ni/CNCT (ST)	100	-	9.20	100	-	16.9	100	-	18.3	-	-		100	-	14.6
NiCu1/CNT (ST)	BDL[a]	BDL[a]	BDL[a]	100	17.6	9.40	87	∞	19.4	13.	2.80	27.0	100	19.7	14.6
NiCu15/CNT (ST)	100	0.133	21.4	100	0.254	17.2	100	0.418	21.5	-	-	-	100	0.676	10.4

[a] Below Detection Limit: The features of the metal were too dilute due to carbon formation and potential metal fragmentation and crystallite properties could not be determined.

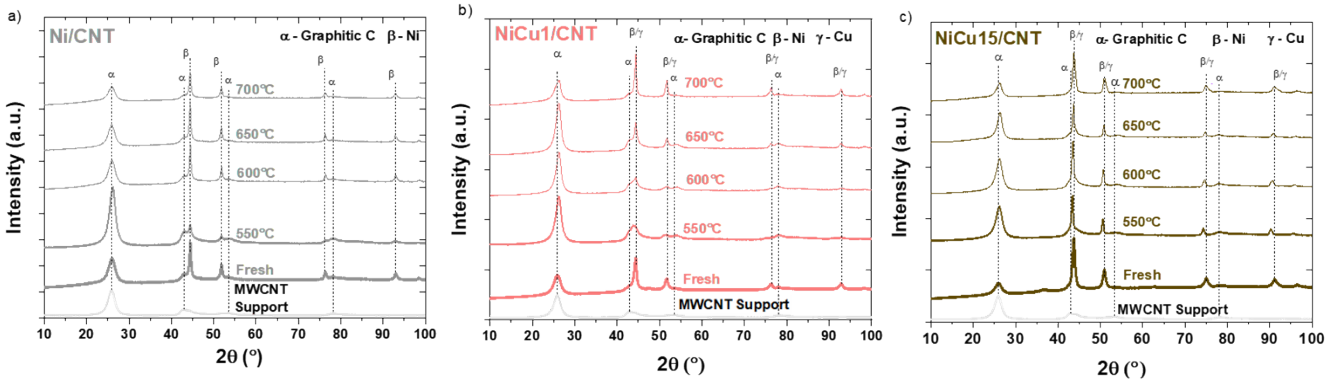


Figure S4. XRD patterns of a) Ni/CNT, b) NiCu1/CNT, and c) NiCu15 prepared by solvothermal synthesis at different reaction temperature under 30 cm^3/min 30 vol.% CH_4 in N_2.

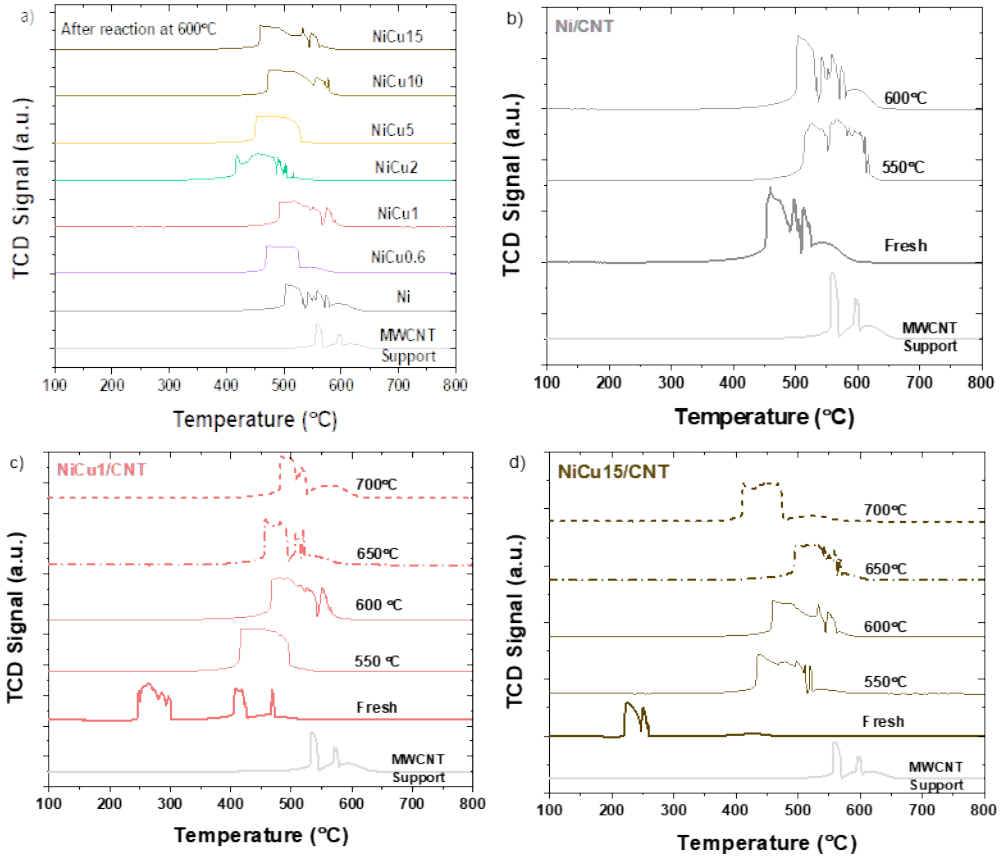


Figure S5. TPO plots of spent solvothermal catalysts retrieved after reaction. a) NiCu*x*/CNT (ST) (*x*=0, 0.6, 1, 2, 5, 10, and 15) at reaction of 600 °C; b) NiCu1/CNT (ST); c) NiCu15/CNT (ST) at different reaction temperatures (600 °C, 650 °C and 700 °C) respectively.

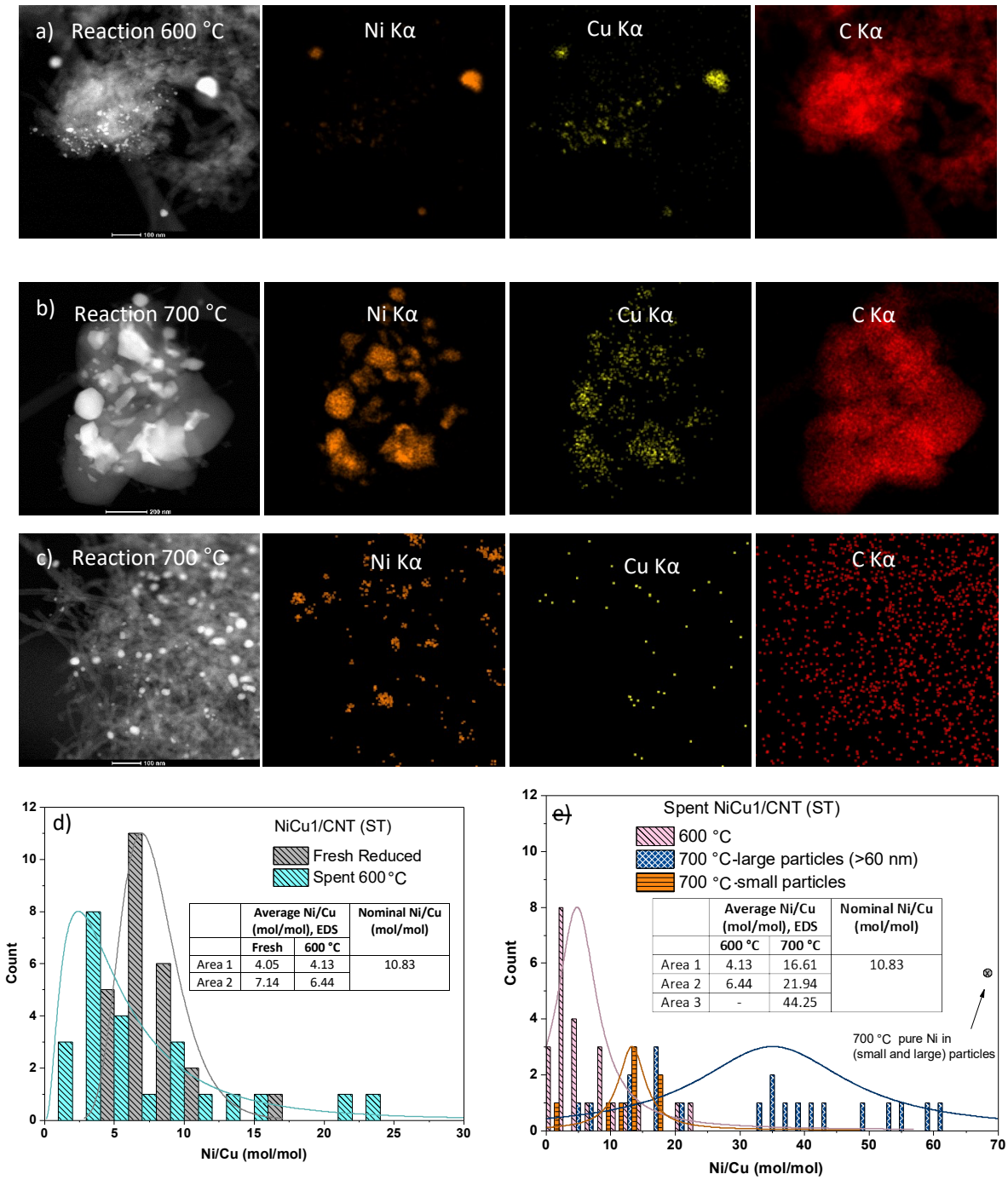
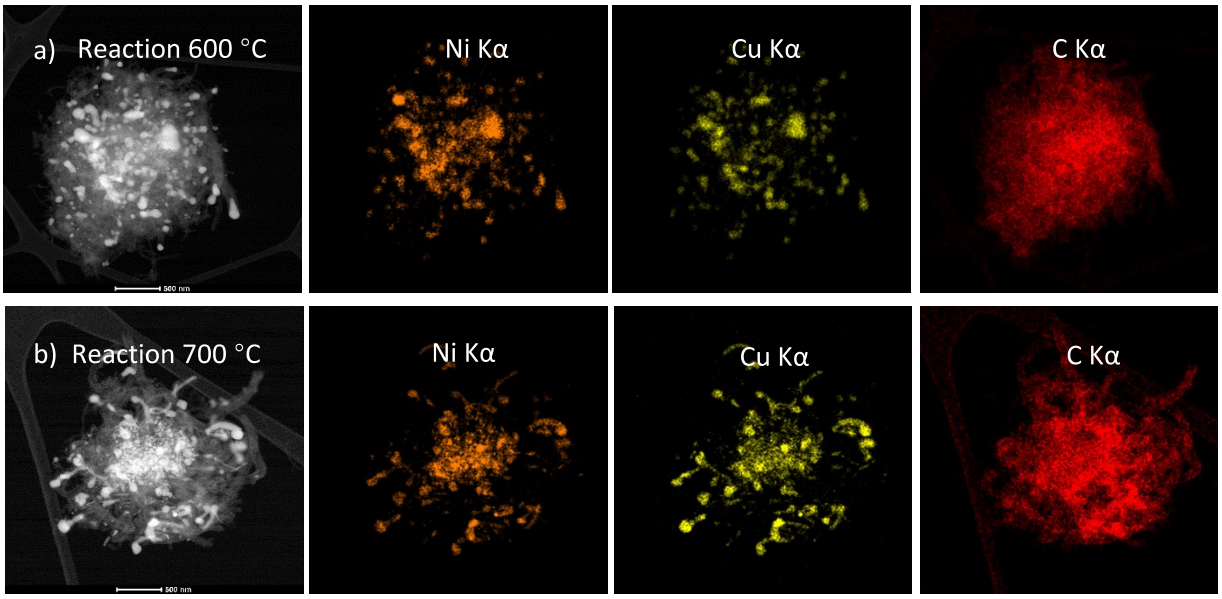
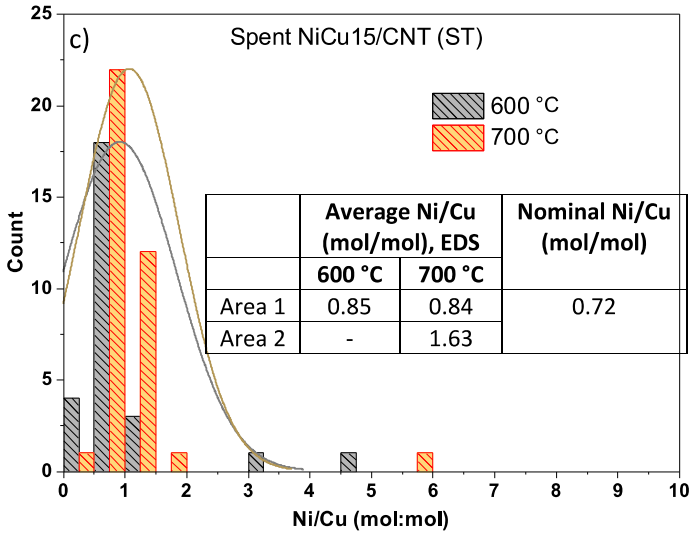


Figure S6. Elemental analysis of spent NiCu1/CNT (ST) after reaction at a) 600°C and b-c) 700°C under 30 cm^3/min 30 vol.% CH_4 in N_2. d) is the histogram representing the change in elemental distribution between fresh and spent at 600°C. e) is the histogram representing the change in elemental distribution between spent at 600°C and 700°C.





	Average Ni/Cu (mol/mol), EDS		Nominal Ni/Cu (mol/mol)
	600 °C	700 °C	
Area 1	0.85	0.84	0.72
Area 2	-	1.63	

Figure S7. Elemental analysis of spent NiCu15/CNT (ST) after reaction at a) 600°C and b) 700°C under 30 cm^3/min 30 vol.% CH_4 in N_2. c) histogram representing the change in elemental distribution between spent at 600°C and 700°C.

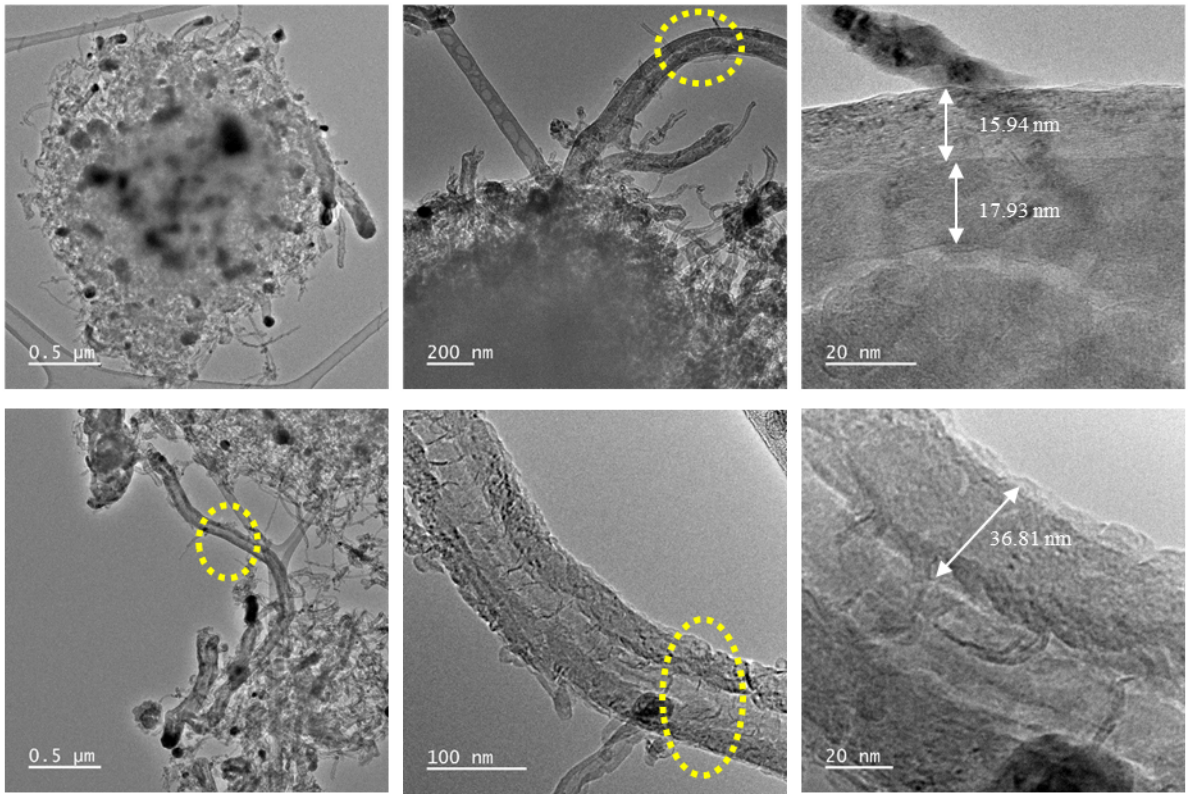


Figure S8. STEM images of spent NiCu15/CNT (ST) at 600°C under 30 cm^3/min 30 vol.% CH_4 in N_2.

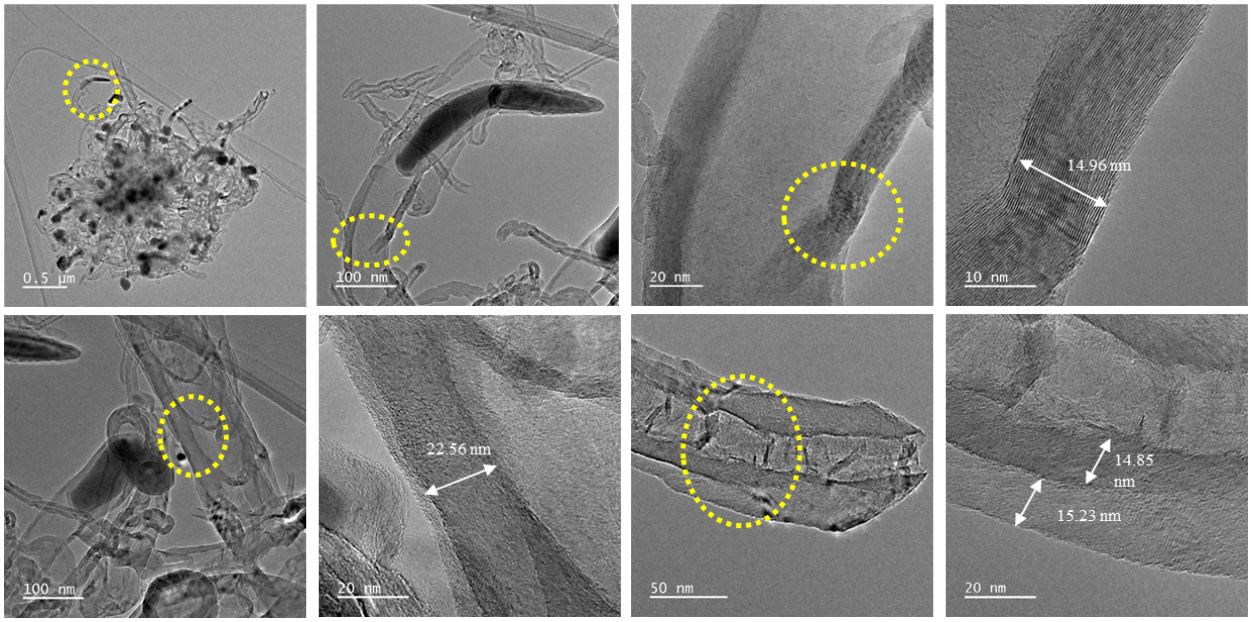


Figure S9. STEM images of spent NiCu15/CNT (ST) at 700°C under 30 cm^3/min 30 vol.% CH_4 in N_2.