Supporting Information

Bimetallic Metal-Organic Framework derived nanocatalyst for CO_2 fixation through benzimidazole formation and methanation of CO_2

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Section S1: Characterization of different ratios of CoNiBTC and CoNi@C

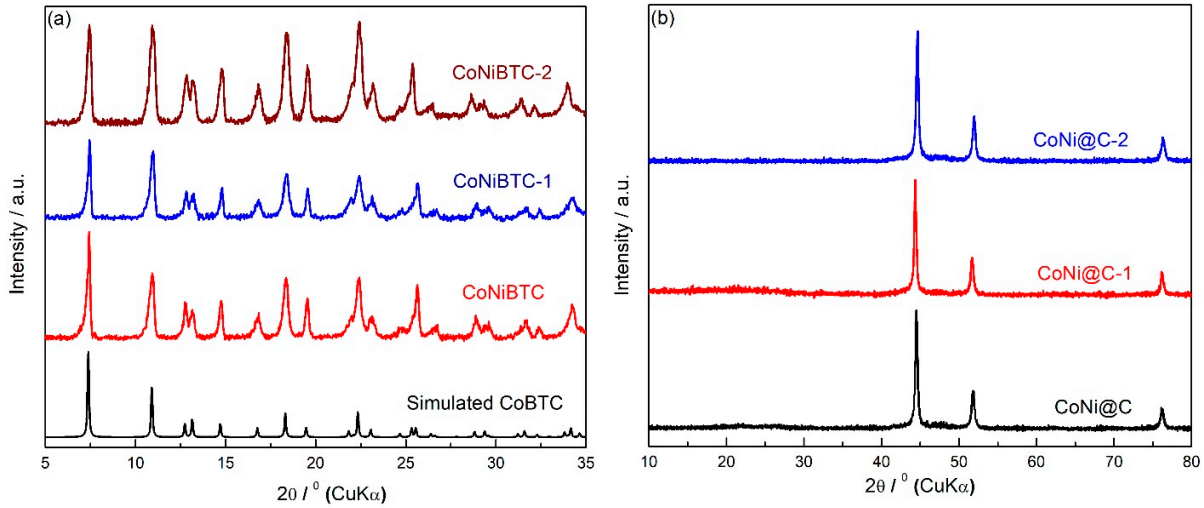


Figure S1. Pxrd of (a) CoNiBTC, CoNiBTC-1, and CoNiBTC-2; (b) CoNi@C, CoNi@C-1, CoNi@C -2.

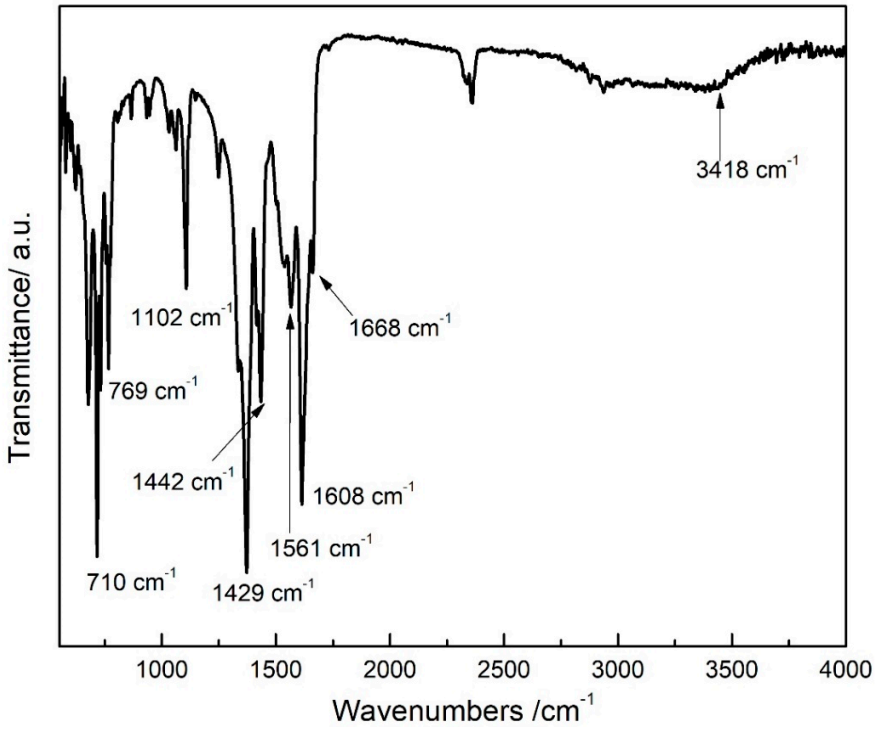


Figure S2. The FTIR spectrum of bimetallic CoNiBTC.

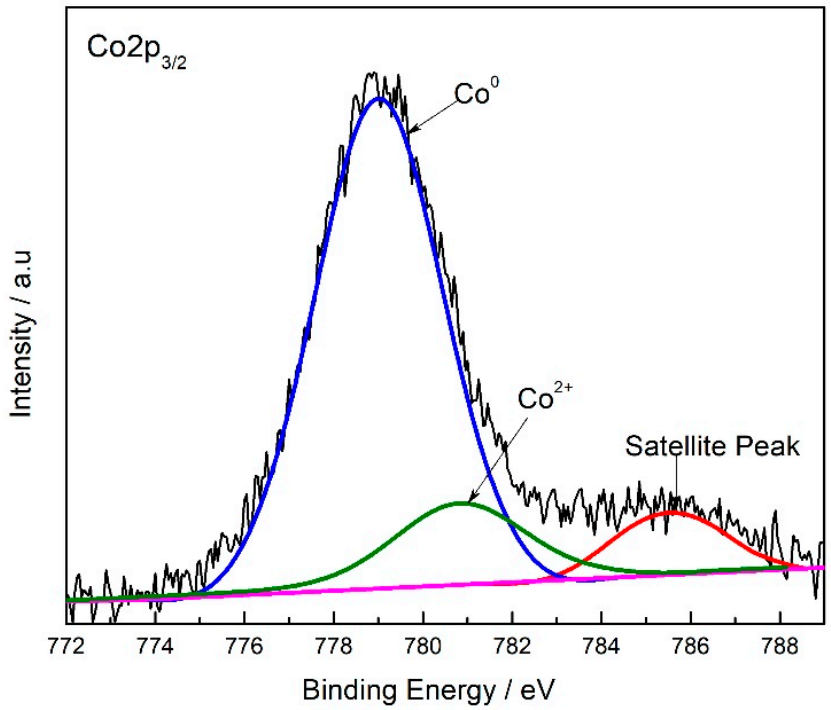


Figure S3. Deconvoluted XPS spectrum of $Co2p_{3/2}$.

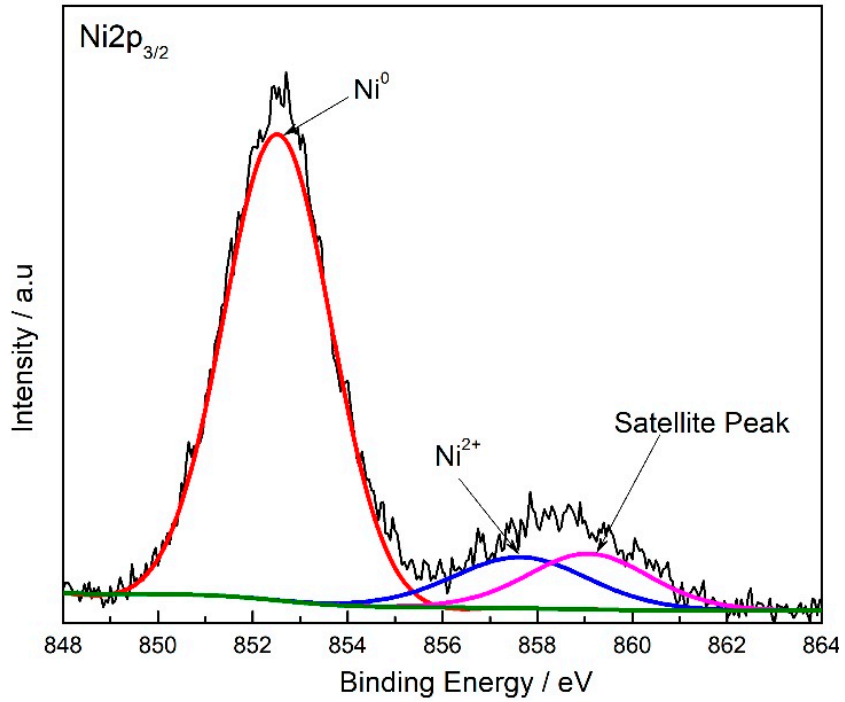


Figure S4. Deconvoluted XPS spectrum of $Ni2p_{3/2}$.

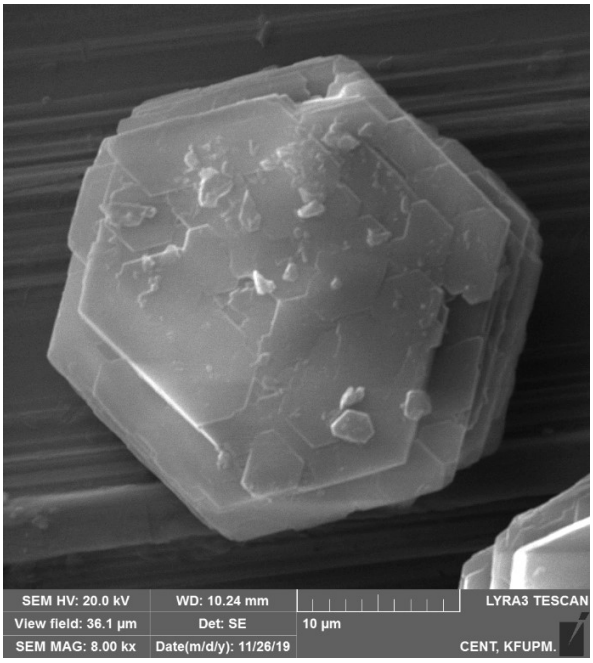


Figure S5. FESEM of bimetallic CoNiBTC.

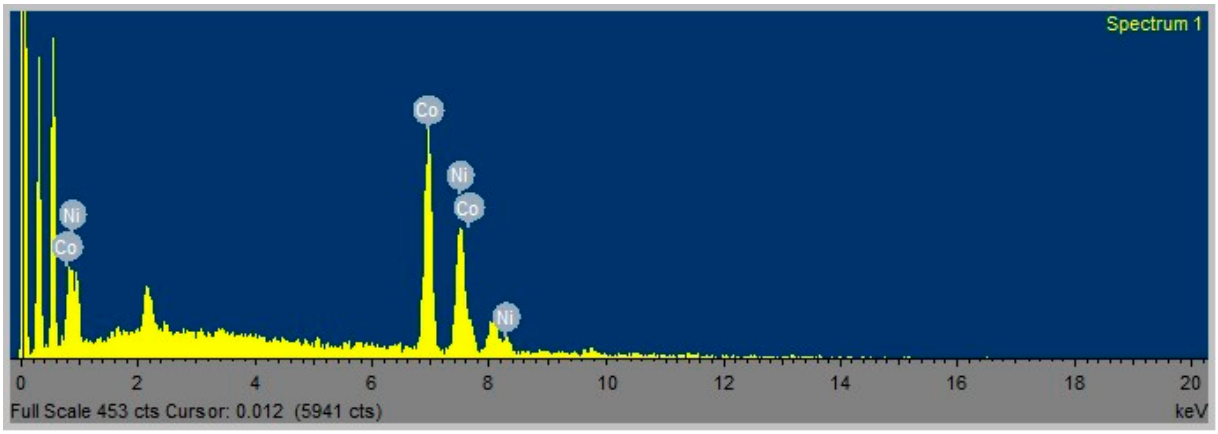


Figure S6. EDX analysis of bimetallic CoNiBTC.

Table S1: Ratio of the metals in bimetallic CoNiBTC

Element	Weight%	Atomic%
Co K	61.61	61.52
Ni K	38.39	38.48
Totals	100.00	

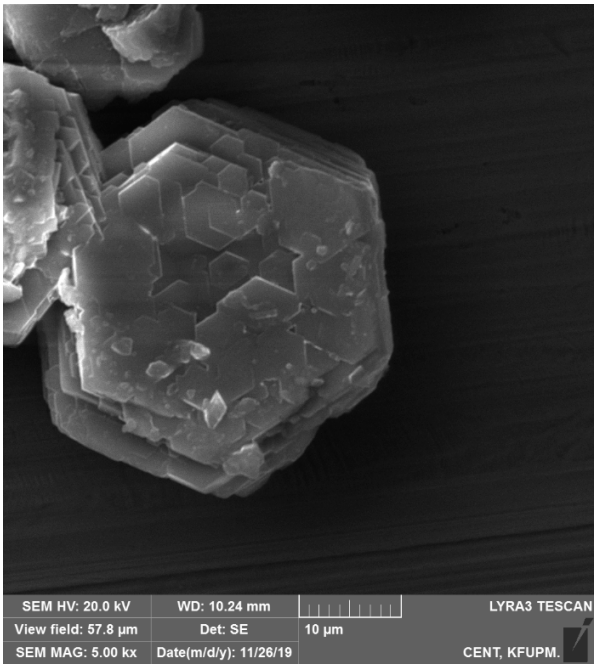


Figure S7. FESEM of bimetallic CoNiBTC-1.

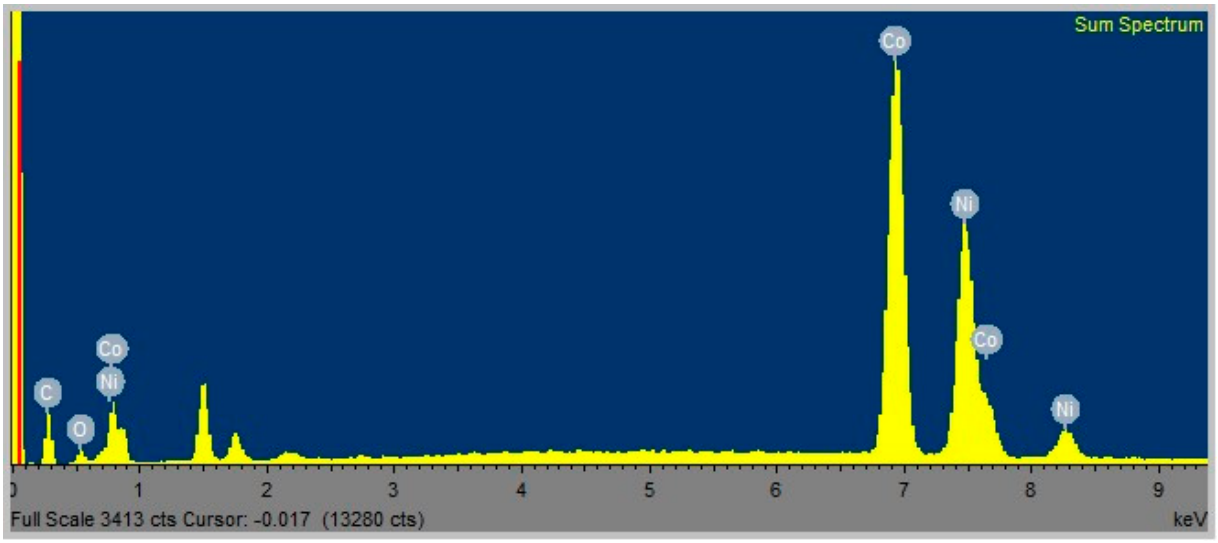


Figure S8. EDX analysis of bimetallic CoNiBTC-1.

Table S2: Ratio of the metals in bimetallic CoNiBTC-1

Element	Weight%	Atomic%
Co K	52.18	52.23
Ni K	47.82	47.77
Totals	100.00	

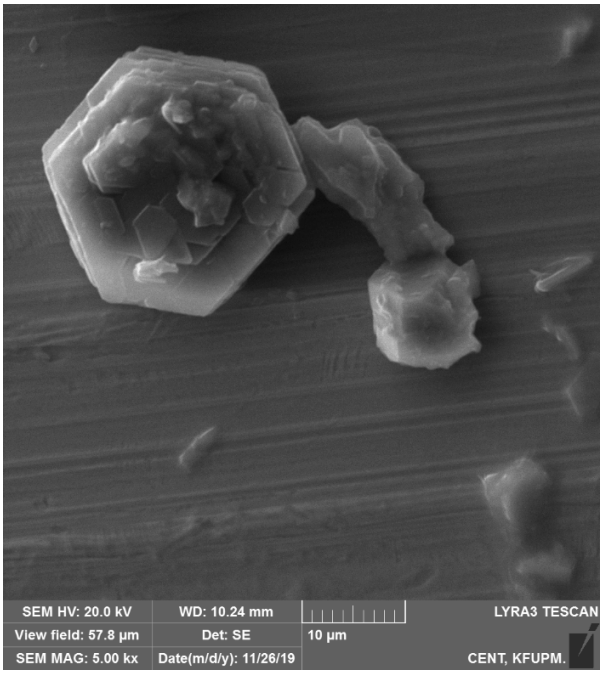


Figure S9. FESEM of bimetallic CoNiBTC-2.

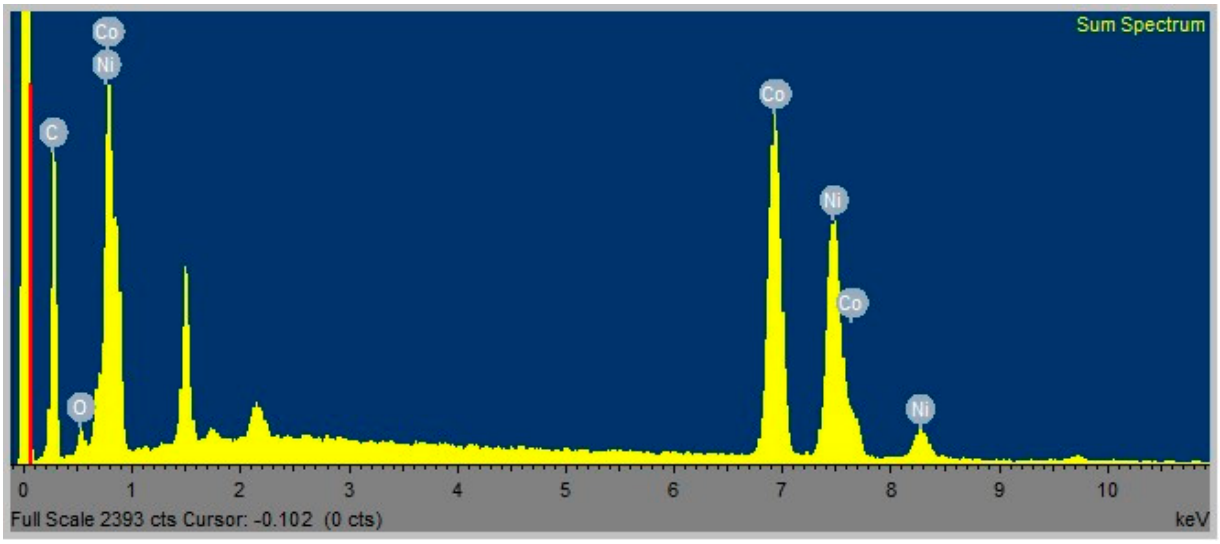
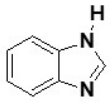


Figure S10. EDX analysis of bimetallic CoNiBTC-2.

Table S3: Ratio of the metals in bimetallic CoNiBTC-2

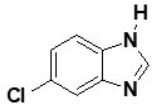
Element	Weight%	Atomic%
Co K	39.47	39.36
Ni K	60.53	60.64
Totals	100.00	

Section S2: ^{1}HNMR and ^{13}CNMR of the Benzimidazole Products



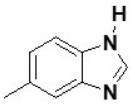
1H-benzo[d]imidazole (1)

^{1}H NMR (DMSO-*d*$_6$, 400 MHz, ppm.): δ 8.23 (s, 1H), 7.59 (d, *J* = 5.6 Hz, 2H), 7.18 (t, *J* = 2.8 Hz, 2H); ^{13}C NMR (DMSO-*d*$_6$, 400 MHz, ppm): δ 141.9, 138.1, 121.7, 115.3.



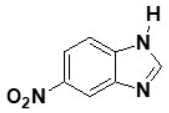
5-chloro-1H-benzo[d]imidazole (2)

^{1}H NMR (DMSO-*d*$_6$, 400 MHz, ppm.): δ 8.55 (s, 1H), 8.50 (s, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (DMSO-*d*$_6$, 400 MHz, ppm): δ 146.5, 142.4, 117.3.



5-methyl-1H-benzo[d]imidazole (3)

^{1}H NMR (DMSO-*d*$_6$, 400 MHz, ppm.): δ 8.26 (s, 1H), 7.64 (s, 1H), 7.57 (d, *J* = 5.6 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 3.39 (s, 1H); ^{13}C NMR (DMSO-*d*$_6$, 400 MHz, ppm): δ 142.1, 131.3, 123.6, 115.0, 21.7.



5-nitro-1H-benzo[d]imidazole (4)

^{1}H NMR (DMSO-*d*$_6$, 400 MHz, ppm.): δ 8.13 (s, 1H), 7.47 (s, 1H), 7.36 (s, 1H), 7.00 (s, 1H); ^{13}C NMR (DMSO-*d*$_6$, 400 MHz, ppm): δ 143.3, 142.4, 138.7, 118.7, 115.3, 111.9.

Section S3: [1]HNMR spectra of the Benzimidazole Products

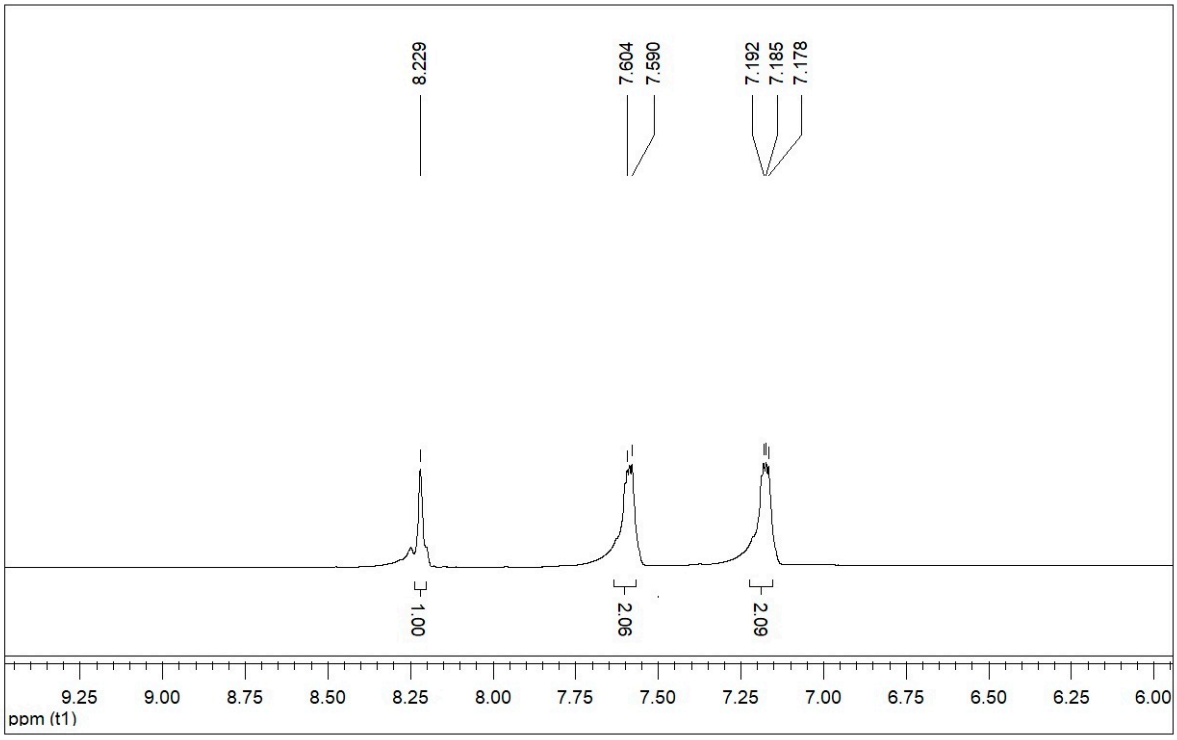


Figure S11. [1]H NMR spectrum of **1**.

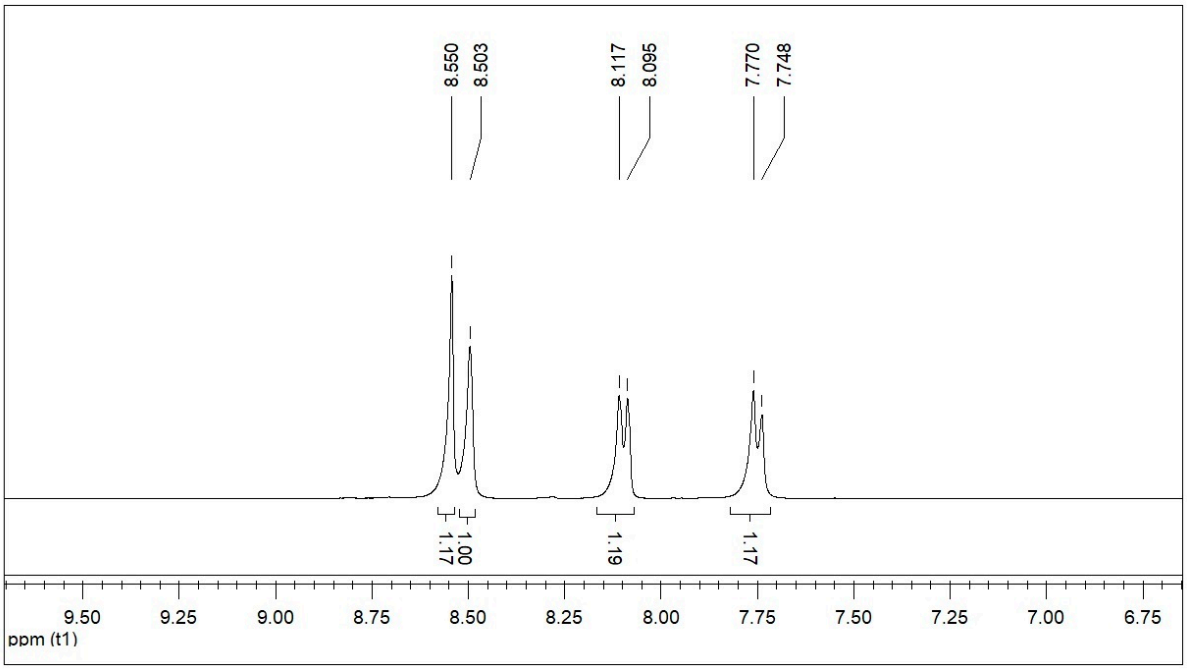


Figure S12. [1]H NMR spectrum of **2**.

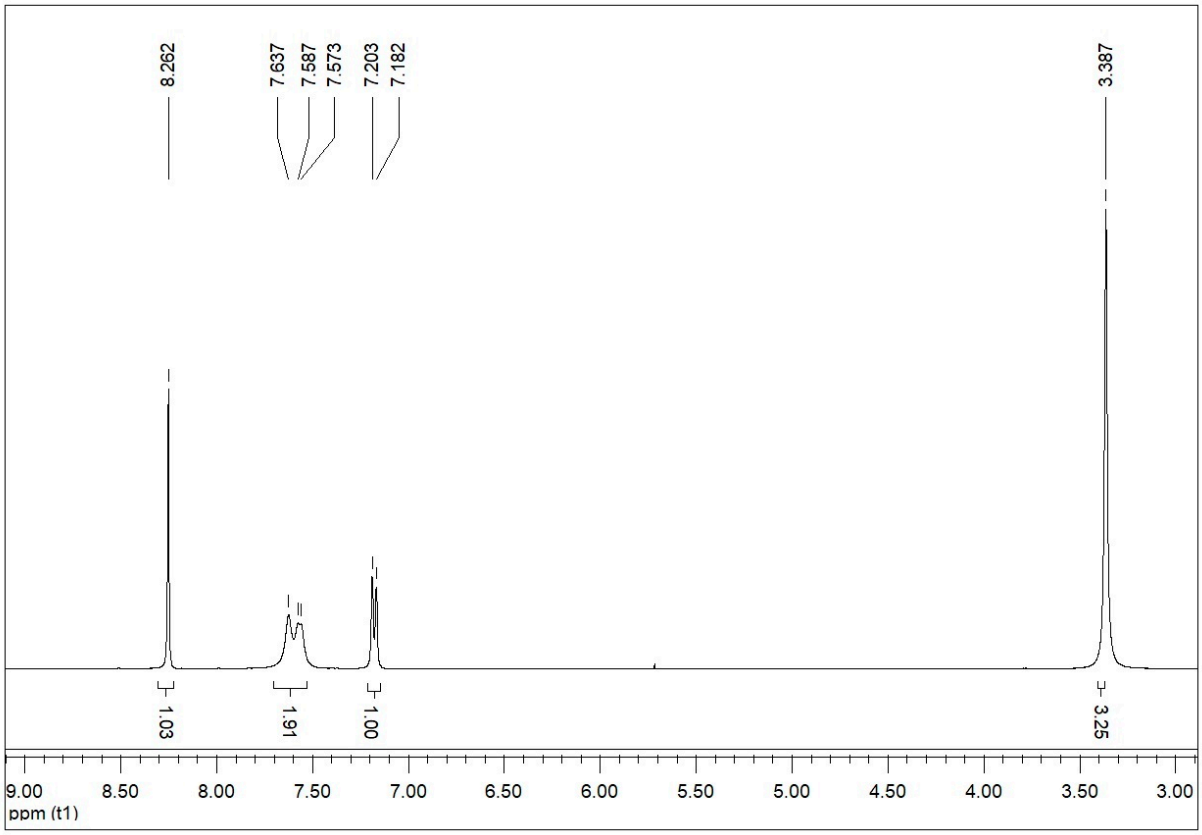


Figure S13. ^{1}H NMR spectrum of **3**.

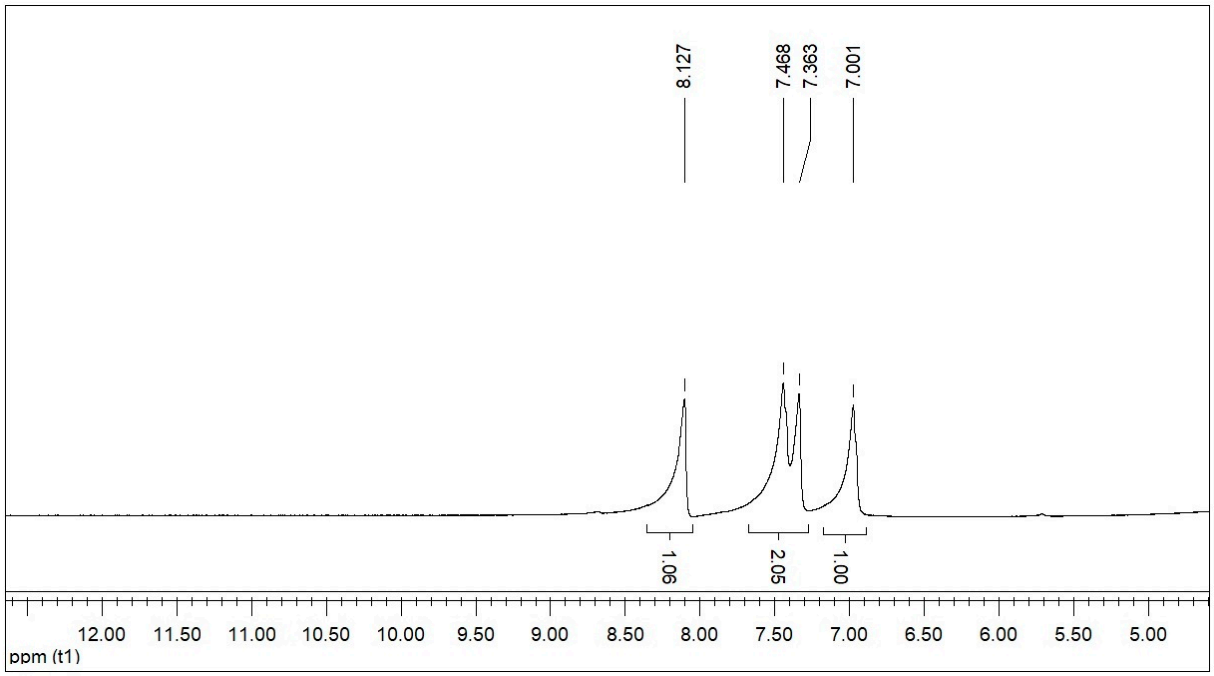


Figure S14. ^{1}H NMR spectrum of **4**.

Section S4: Regeneration of Catalyst after Reaction

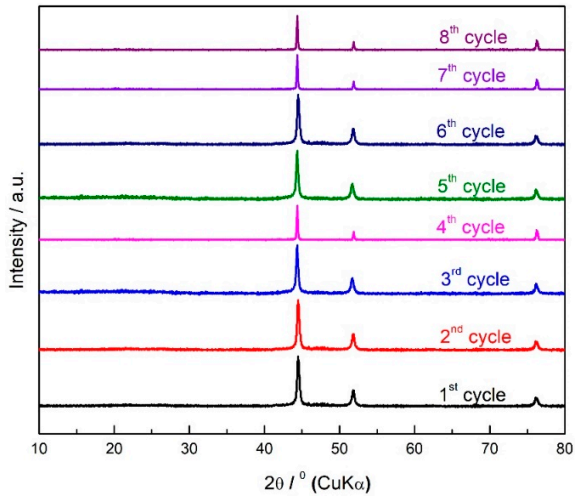


Figure S15. Powdered XRD of the catalyst CoNi@C after each cycle of catalysis.

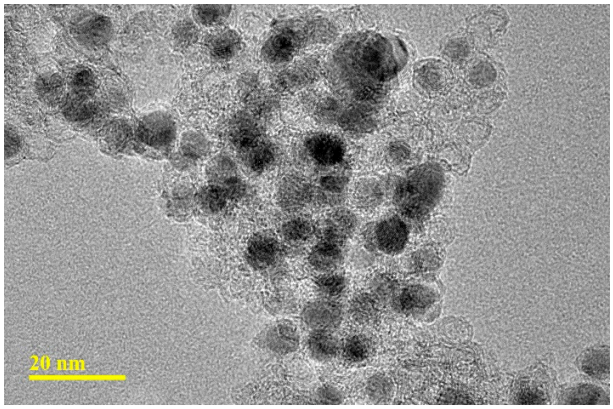


Figure S16. TEM of the catalyst CoNi@C 8 cycles of catalysis.

Table S4

S.N	Catalysts	Condition (temperature/pressure/time)	Yield (%)	Ref.
1.	CH_3COOK, Phenylsilane	40°C/1 bar CO_2/24 h	90	37
2.	Cu-NPs@COF[a]	60°C/1 bar CO_2/12 h	95	19
3.	$RuCl_2(dppe)_2$	120°C/150 bar CO_2 +H_2/40 h	92	23
4.	Au/TiO_2	100°C/80 bar CO_2 +H_2/12 h	95	38
5.	[PS-Zn(II)-SALTETA,[a]	100°C/1 bar CO_2 /24 h	93	39
6.	CoF_2, Ph_3P, CsF	140°C/60 bar CO_2 +H_2/24 h	94	40
7.	Cu@U-g-C_3N_4[a]	100°C/25 bar CO_2 /24 h	92	41
8.	$CuFe_2O_4$	180°C/1 bar CO_2 /12 h	96	42
9.	CoNi@C	115°C/30 bar CO_2 +H_2/18 h	81	This work

[a]DMAB- dimethylamine borane

Section S5: Methanation Reaction

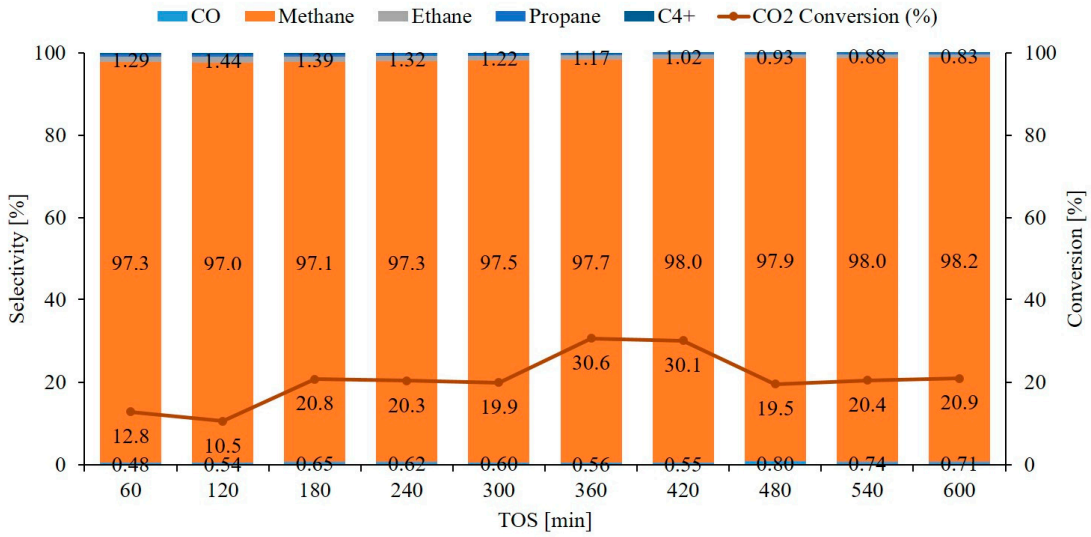


Figure S17. CoNi@C 0.2g, Flow of Mixture=15 ml, mixture (H_2: CO_2) =3:1, T=375˚C, 10 bar

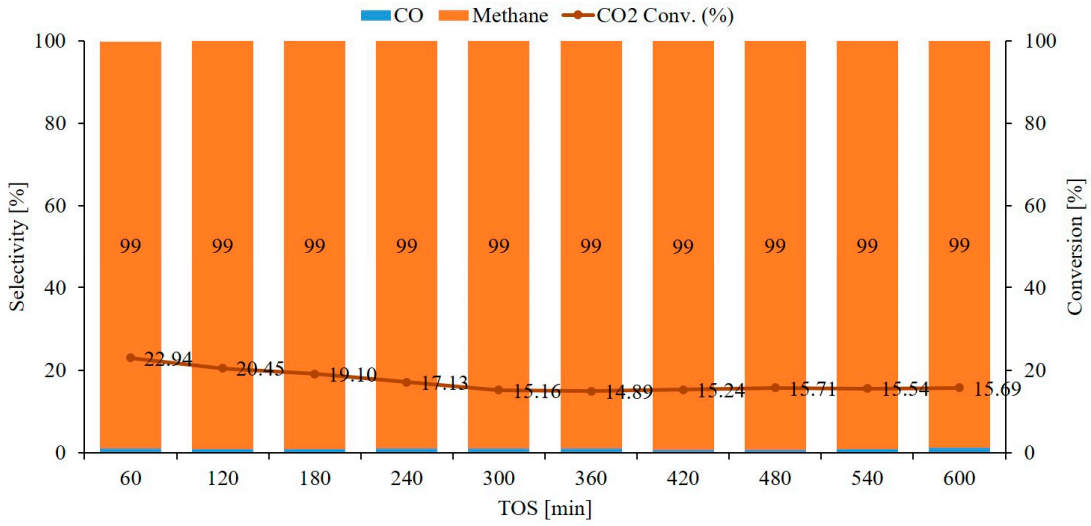


Figure S18. CoNi@C-1 0.2g, Flow of Mixture=15 ml, mixture (H_2: CO_2) =3:1, T=375˚C, 10 bar

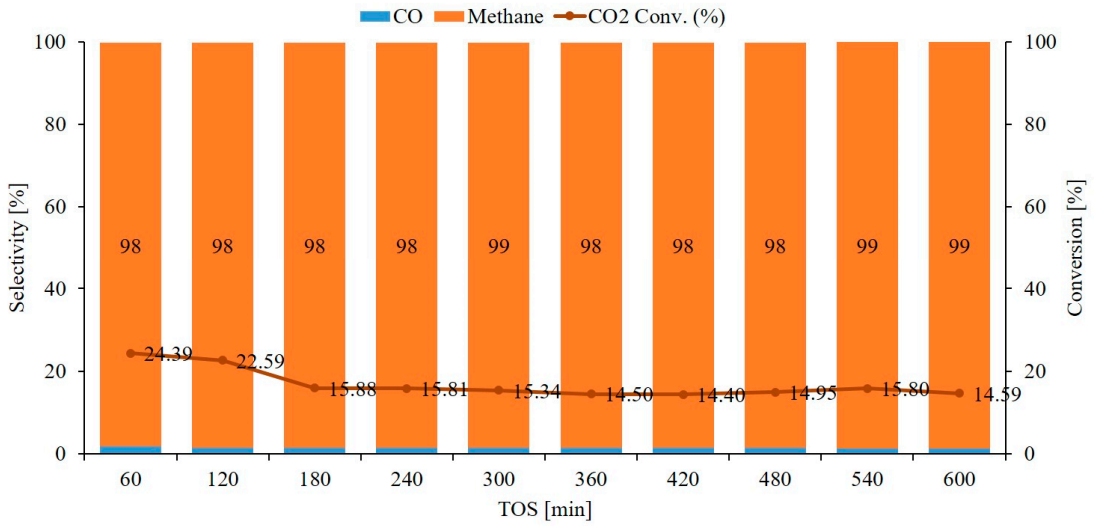


Figure S19. CoNi@C-2 0.2g, Flow of Mixture=15 ml, mixture (H_2: CO_2) =3:1, T=375˚C, 10 bar

Table S5

S.N	Catalysts	Condition (temperature/pressure)	Selectivity (%)	Ref.
1.	Ni@C	350 ºC	98	29
2.	Ni/SiO_2	250 ºC/1 bar	98	43
3.	Co/SiO_2	360 ºC/1 bar	86.5	44
4.	Co/KIT-6	360 ºC	94.5	45
5.	NiWP	327 ºC	80	46
6.	Ni/CeO2-NR	300 ºC	99	47
7	$CoMn_xAl_{2-x}O_4$	400 ºC	97	48
8	Ru-TiO_x	259.3 ºC	99.9	49
9.	CoNi@C	375ºC/30 bar	99.8	This work