

Supplementary Information:

Table S1: Rate of CO₂ conversion and the rate of CH₄ formation during CO₂ methanation over 75Ni25Co/Al₂O₃ catalyst. Reaction conditions: CO₂:H₂ = 1:24, w_{cat} = 0.1 g and reaction temperature = 523 K.

Sample	Rate of CO ₂ conversion in g-mol/g-cat/sec×10 ⁶	Rate of CH ₄ formation in g-mol/g-cat/sec×10 ⁶
75Ni25Co/Al ₂ O ₃	1.13±0.09	1.05±0.09

Table S2: Mulliken charge (e) on closed packed Ni, Fe, Co, Cu and Ni₃M (M = Fe or Co or Cu) surfaces. Charge on individual metal atoms is shown.

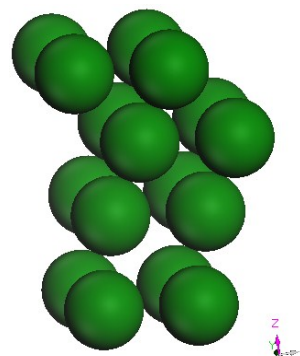
System (surface atom)		Mulliken Charge (e)
Ni ₃ Fe(111)	Ni	-0.10
	Fe	+0.09
Ni ₃ Co(111)	Ni	-0.09
	Co	+0.06
Ni ₃ Cu(111)	Ni	-0.02
	Cu	-0.22
Ni(111)		-0.05
Fe(110)		-0.04
Co(111)		-0.04
Cu(111)		-0.13

Table S3: Final electronic energy, optimized coordinates of slab models and their figures for different structures of Ni and Ni₃M (M = Fe or Co or Cu) surfaces.

System	Final Electronic energies (eV)			
	(111)	(110)	(100)	(211)
Ni	-21665.8940	-21665.9763	-21664.0887	-32498.1018
Ni ₃ Fe	-19710.3164	-19710.4746	-9854.1737	-29564.6402
Ni ₃ Co	-20420.4294E	-20420.4832E	-10209.2363	-30629.7255
Ni ₃ Cu	-22154.0936	-22154.1087	-11076.2052	-33230.4597E

Ni (111)

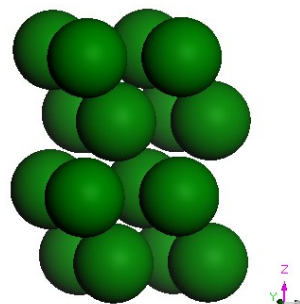
Element	Fractional coordinates of atoms		
	u	v	w
Ni	0.000000	0.000000	0.331090
Ni	-0.000013	0.000013	0.667070
Ni	0.333308	0.166692	0.555847
Ni	0.166667	0.333333	0.443697
Ni	0.500000	0.000000	0.331090
Ni	0.499987	0.000013	0.667070
Ni	0.833308	0.166692	0.555847
Ni	0.666667	0.333333	0.443697
Ni	0.000000	0.500000	0.331090
Ni	-0.000013	0.500013	0.667070
Ni	0.333308	0.666692	0.555847
Ni	0.166667	0.833333	0.443697
Ni	0.500000	0.500000	0.331090
Ni	0.499987	0.500013	0.667070
Ni	0.833308	0.666692	0.555847
Ni	0.666667	0.833333	0.443697



Cell Dimension: a = 4.99 Å
b = 4.99 Å
c = 18.12 Å

Ni (100)

Element	Fractional coordinates of atoms		
	u	v	w
Ni	0.000000	0.054527	0.448928
Ni	0.000000	0.054527	0.650824
Ni	0.250000	0.304527	0.346785
Ni	0.250000	0.304527	0.552323
Ni	0.500000	0.054527	0.448928
Ni	0.500000	0.054527	0.650824
Ni	0.750000	0.304527	0.346785
Ni	0.750000	0.304527	0.552323
Ni	0.000000	0.554527	0.448928
Ni	0.000000	0.554527	0.650824
Ni	0.250000	0.804527	0.346785
Ni	0.250000	0.804527	0.552323
Ni	0.500000	0.554527	0.448928
Ni	0.500000	0.554527	0.650824
Ni	0.750000	0.804527	0.346785
Ni	0.750000	0.804527	0.552323

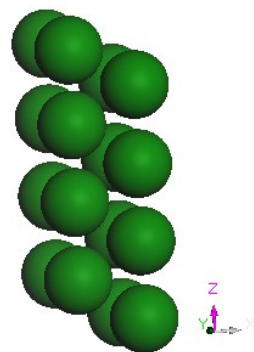


Cell Dimension: a = 4.99 Å
b = 4.99 Å
c = 17.30 Å

Ni (110)

Element Fractional coordinates of atoms

	u	v	w
Ni	0.054527	0.418210	0.349422
Ni	0.054527	0.918210	0.469884
Ni	0.054528	0.418210	0.589716
Ni	0.054528	0.918210	0.705658
Ni	0.554527	0.668210	0.289191
Ni	0.554527	0.168210	0.409653
Ni	0.554527	0.668210	0.529215
Ni	0.554528	0.168210	0.651662
Ni	0.554527	0.168210	0.289191
Ni	0.554527	0.668210	0.409653
Ni	0.554527	0.168210	0.529215
Ni	0.554528	0.668210	0.651662
Ni	0.054527	0.918210	0.349422
Ni	0.054527	0.418210	0.469884
Ni	0.054528	0.918210	0.589716
Ni	0.054529	0.418210	0.705658

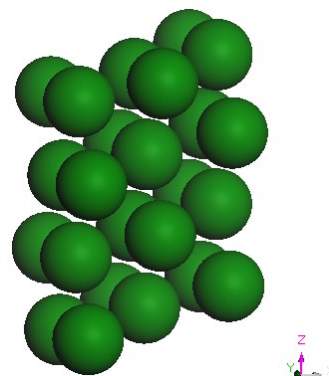


Cell Dimension: a = 3.53 Å
b = 4.99 Å
c = 20.74 Å

Ni (211)

Element Fractional coordinates of atoms

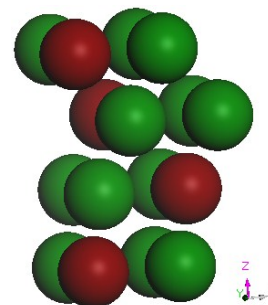
	u	v	w
Ni	0.260631	0.000000	0.300887
Ni	0.927298	0.500000	0.373292
Ni	0.593964	0.000000	0.445696
Ni	0.259160	0.500000	0.518300
Ni	0.927774	0.000000	0.589063
Ni	0.589275	0.500000	0.660055
Ni	0.260631	0.500000	0.300887
Ni	0.927298	0.000000	0.373292
Ni	0.593964	0.500000	0.445696
Ni	0.259160	0.000000	0.518300
Ni	0.927774	0.500000	0.589063
Ni	0.589275	0.000000	0.660055
Ni	0.593964	0.250000	0.337089
Ni	0.260631	0.750000	0.409494
Ni	0.927298	0.250000	0.481899
Ni	0.590050	0.750000	0.553037
Ni	0.258706	0.250000	0.628769
Ni	0.914113	0.750000	0.692433
Ni	0.593964	0.750000	0.337089
Ni	0.260631	0.250000	0.409494
Ni	0.927298	0.750000	0.481899
Ni	0.590050	0.250000	0.553037
Ni	0.258706	0.750000	0.628769
Ni	0.914113	0.250000	0.692433



Cell Dimension: a = 6.13 Å
b = 5.00 Å
c = 19.94 Å

Ni₃Fe(111)

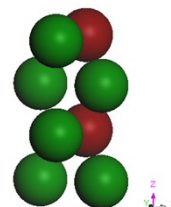
Element	Fractional coordinates of atoms		
	u	v	w
Fe	0.000000	0.000000	0.330566
Fe	0.666667	0.333333	0.443522
Fe	0.333271	0.666729	0.558770
Fe	-0.000189	0.000189	0.666756
Ni	0.500000	0.000000	0.330566
Ni	0.166667	0.333333	0.443522
Ni	0.833238	0.666745	0.556234
Ni	0.498627	-0.002280	0.667702
Ni	0.000000	0.500000	0.330566
Ni	0.666667	0.833333	0.443522
Ni	0.333255	0.166762	0.556234
Ni	0.002280	0.501372	0.667702
Ni	0.500000	0.500000	0.330566
Ni	0.166667	0.833333	0.443522
Ni	0.833203	0.166797	0.556232
Ni	0.498656	0.501344	0.667706



Cell Dimension: a = 5.02 Å
b = 5.02 Å
c = 18.15 Å

Ni₃Fe(100)

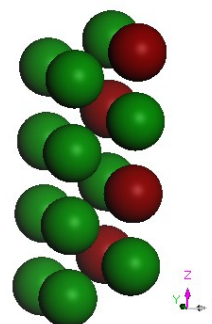
Element	Fractional coordinates of atoms		
	u	v	w
Fe	0.986111	0.986111	0.448762
Fe	0.986111	0.986111	0.652692
Ni	0.486111	0.986111	0.346287
Ni	0.486110	0.986111	0.552271
Ni	0.486111	0.486111	0.448762
Ni	0.486111	0.486111	0.650645
Ni	0.986111	0.486111	0.346287
Ni	0.986111	0.486110	0.552271



Cell Dimension: a = 3.55 Å
b = 3.55 Å
c = 17.32 Å

Ni₃Fe(110)

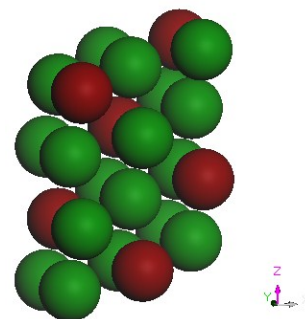
Element	Fractional coordinates of atoms		
	u	v	w
Fe	0.986111	0.506944	0.349015
Fe	0.986111	0.006944	0.469803
Fe	0.986111	0.506944	0.590800
Fe	0.986111	0.006944	0.705362
Ni	0.986111	0.006944	0.349015
Ni	0.986111	0.506944	0.469803
Ni	0.986111	0.006944	0.590291
Ni	0.986112	0.506945	0.706346
Ni	0.486111	0.756944	0.288621
Ni	0.486111	0.256944	0.409409
Ni	0.486111	0.756779	0.529798
Ni	0.486111	0.256079	0.653224
Ni	0.486111	0.256944	0.288621
Ni	0.486111	0.756944	0.409409
Ni	0.486111	0.257110	0.529798
Ni	0.486111	0.757809	0.653224



Cell Dimension: a = 3.55 Å
b = 5.02 Å
c = 20.78 Å

Ni₃Fe(211)

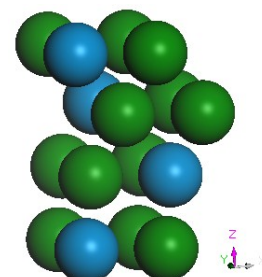
Element	Fractional u	coordinates v	of atoms w
Fe	0.342593	0.000000	0.336689
Fe	0.009259	0.500000	0.409272
Fe	0.675926	0.000000	0.481854
Fe	0.342753	0.500000	0.554912
Fe	0.005658	0.000000	0.631695
Fe	0.676408	0.500000	0.693007
Ni	0.009259	0.250000	0.300398
Ni	0.675926	0.750000	0.372980
Ni	0.342593	0.250000	0.445563
Ni	0.009691	0.750839	0.518764
Ni	0.678302	0.249851	0.589923
Ni	0.341335	0.746774	0.660652
Ni	0.342593	0.500000	0.336689
Ni	0.009259	0.000000	0.409272
Ni	0.675926	0.500000	0.481854
Ni	0.340658	0.000000	0.553732
Ni	0.009974	0.500000	0.628653
Ni	0.665064	0.000000	0.694137
Ni	0.009259	0.750000	0.300398
Ni	0.675926	0.250000	0.372980
Ni	0.342593	0.750000	0.445563
Ni	0.009691	0.249161	0.518764
Ni	0.678302	0.750149	0.589923
Ni	0.341335	0.253226	0.660652



Cell Dimension: a = 6.15 Å
b = 5.02 Å
c = 19.97 Å

Ni₃Co(111)

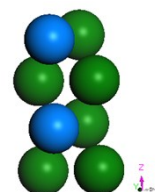
Element	Fractional u	coordinates v	of atoms w
Co	0.000000	0.000000	0.330883
Co	0.666667	0.333333	0.443628
Co	0.333148	0.666852	0.558577
Co	-0.000181	0.000181	0.668011
Ni	0.500000	0.000000	0.330883
Ni	0.166667	0.333333	0.443628
Ni	0.833146	0.666910	0.556198
Ni	0.499133	-0.001146	0.667590
Ni	0.000000	0.500000	0.330883
Ni	0.666667	0.833333	0.443628
Ni	0.333090	0.166854	0.556198
Ni	0.001146	0.500867	0.667590
Ni	0.500000	0.500000	0.330883
Ni	0.166667	0.833333	0.443628
Ni	0.833168	0.166832	0.556198
Ni	0.499124	0.500876	0.667588



Cell Dimension: a = 5.00 Å
b = 5.00 Å
c = 18.13 Å

Ni₃Co(100)

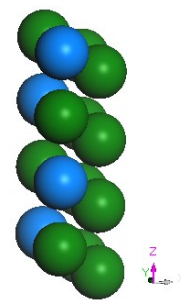
Element	Fractional u	coordinates v	of atoms w
Co	0.083333	0.083333	0.448863
Co	0.083333	0.083333	0.653234
Ni	0.583333	0.083333	0.346588
Ni	0.583333	0.083333	0.552763
Ni	0.583333	0.583333	0.448863
Ni	0.583333	0.583333	0.651066
Ni	0.083333	0.583333	0.346588
Ni	0.083333	0.583333	0.552763



Cell Dimension: a = 3.54 Å
b = 3.54 Å
c = 17.31 Å

Ni₃Co(110)

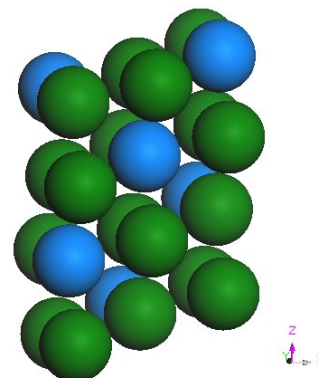
Element	Fractional coordinates of atoms		
	u	v	w
Co	0.083333	0.708333	0.349261
Co	0.083333	0.208333	0.469852
Co	0.083334	0.708333	0.590648
Co	0.083336	0.208333	0.705566
Ni	0.083333	0.208333	0.349261
Ni	0.083333	0.708333	0.469852
Ni	0.083335	0.208333	0.589449
Ni	0.083336	0.708333	0.705897
Ni	0.583333	0.958333	0.288966
Ni	0.583333	0.458333	0.409557
Ni	0.583335	0.957808	0.529245
Ni	0.583336	0.457385	0.652692
Ni	0.583333	0.458333	0.288966
Ni	0.583333	0.958333	0.409557
Ni	0.583335	0.458859	0.529245
Ni	0.583336	0.959281	0.652692



Cell Dimension: a = 3.54 Å
b = 5.00 Å
c = 20.76 Å

Ni₃Co(211)

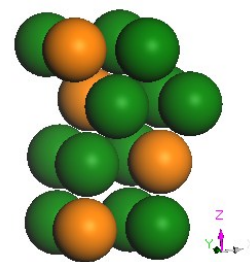
Element	Fractional coordinates of atoms		
	u	v	w
Co	0.575008	0.842379	0.336967
Co	0.241675	0.342379	0.409426
Co	0.908341	0.842379	0.481885
Co	0.571702	0.342379	0.554958
Co	0.239008	0.842379	0.631803
Co	0.898717	0.342378	0.693956
Ni	0.241675	0.092379	0.300737
Ni	0.908341	0.592379	0.373196
Ni	0.575008	0.092379	0.445656
Ni	0.241125	0.593326	0.519065
Ni	0.909281	0.092054	0.589640
Ni	0.571819	0.590643	0.660614
Ni	0.575008	0.342379	0.336967
Ni	0.241675	0.842379	0.409426
Ni	0.908341	0.342379	0.481885
Ni	0.572862	0.842379	0.553330
Ni	0.239395	0.342378	0.628538
Ni	0.899559	0.842378	0.693464
Ni	0.241675	0.592379	0.300737
Ni	0.908341	0.092379	0.373196
Ni	0.575008	0.592379	0.445656
Ni	0.241125	0.091431	0.519065
Ni	0.909281	0.592702	0.589640
Ni	0.571819	0.094114	0.660614



Cell Dimension: a = 6.13 Å
b = 5.00 Å
c = 19.95 Å

Ni₃Cu(111)

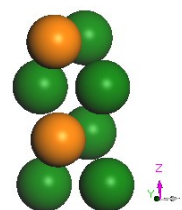
Element	Fractional coordinates of atoms		
	u	v	w
Ni	0.500000	0.000000	0.330404
Ni	0.166667	0.333333	0.443468
Ni	0.834110	0.668257	0.556338
Ni	0.500594	0.001211	0.666963
Ni	0.000000	0.500000	0.330404
Ni	0.666667	0.833333	0.443468
Ni	0.331743	0.165890	0.556338
Ni	-0.001211	0.499406	0.666963
Ni	0.500000	0.500000	0.330404
Ni	0.166667	0.833333	0.443468
Ni	0.834071	0.165929	0.556369
Ni	0.500703	0.499297	0.666932
Cu	0.000000	0.000000	0.330404
Cu	0.666667	0.333333	0.443468
Cu	0.333335	0.666665	0.555663
Cu	0.000008	-0.000008	0.672028



Cell Dimension: a = 5.03 Å
b = 5.03 Å
c = 18.16 Å

Ni₃Cu(100)

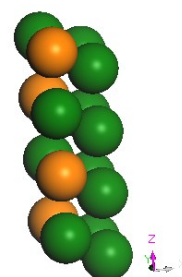
Element	Fractional coordinates of atoms		
	u	v	w
Ni	0.583333	0.083333	0.346133
Ni	0.583333	0.083333	0.552514
Ni	0.583333	0.583333	0.448711
Ni	0.583333	0.583333	0.648879
Ni	0.083333	0.583333	0.346133
Ni	0.083333	0.583333	0.552514
Cu	0.083333	0.083333	0.448711
Cu	0.083333	0.083333	0.655318



Cell Dimension: a = 3.56 Å
b = 3.56 Å
c = 17.33 Å

Ni₃Cu(110)

Element	Fractional coordinates of atoms		
	u	v	w
Ni	0.083333	0.208333	0.348889
Ni	0.083333	0.708333	0.469778
Ni	0.083338	0.208333	0.590943
Ni	0.083331	0.708333	0.706318
Ni	0.583333	0.958333	0.288444
Ni	0.583333	0.458333	0.409333
Ni	0.583324	0.958714	0.529554
Ni	0.583325	0.459565	0.652060
Ni	0.583333	0.458333	0.288444
Ni	0.583333	0.958333	0.409333
Ni	0.583324	0.457953	0.529554
Ni	0.583325	0.957102	0.652060
Cu	0.083333	0.708333	0.348889
Cu	0.083333	0.208333	0.469778
Cu	0.083325	0.708333	0.589267
Cu	0.083338	0.208333	0.710258

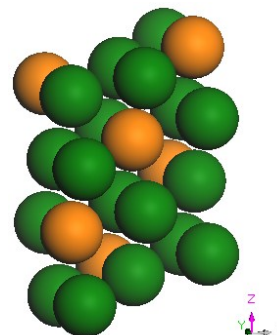


Cell Dimension: a = 3.56 Å
b = 5.03 Å
c = 20.80 Å

Ni₃Cu(211)

Element Fractional coordinates of atoms

	u	v	w
Ni	0.241675	0.092379	0.300224
Ni	0.908341	0.592379	0.372870
Ni	0.575008	0.092379	0.445516
Ni	0.240446	0.593038	0.518924
Ni	0.909239	0.092666	0.590073
Ni	0.572084	0.590704	0.659833
Ni	0.575008	0.342379	0.336547
Ni	0.241675	0.842379	0.409193
Ni	0.908341	0.342379	0.481839
Ni	0.570193	0.842378	0.553320
Ni	0.242565	0.342378	0.627809
Ni	0.885204	0.842379	0.693145
Ni	0.241675	0.592379	0.300224
Ni	0.908341	0.092379	0.372870
Ni	0.575008	0.592379	0.445516
Ni	0.240446	0.091718	0.518924
Ni	0.909239	0.592090	0.590073
Ni	0.572084	0.094053	0.659833
Cu	0.575008	0.842379	0.336547
Cu	0.241675	0.342379	0.409193
Cu	0.908341	0.842379	0.481839
Cu	0.573643	0.342378	0.552923
Cu	0.237758	0.842378	0.631928
Cu	0.901366	0.342379	0.696448



cell Dimension: a = 6.16 Å
b = 5.03 Å
c = 19.98 Å

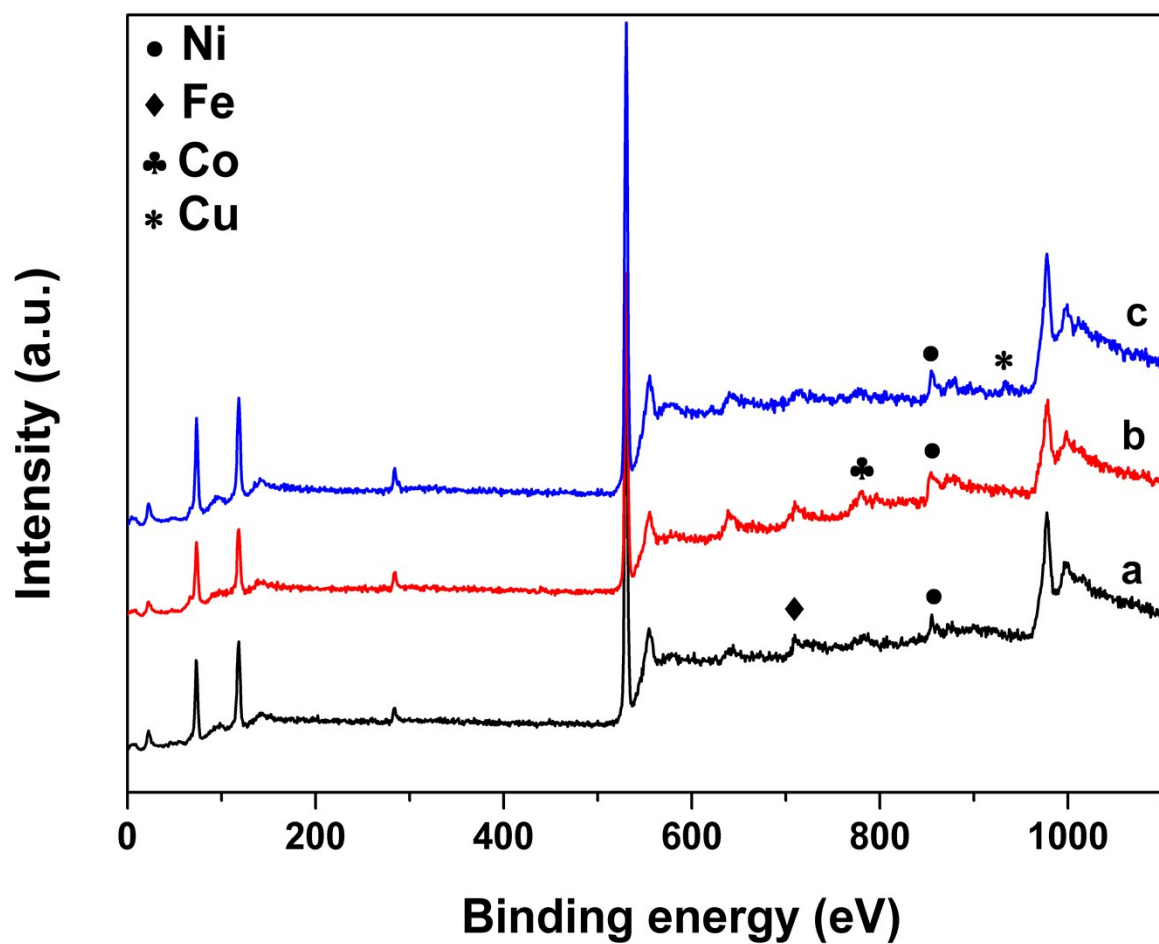


Figure S1: XPS survey spectra of the 75Ni25M (M = Fe or Co or Cu) bimetallic catalyst samples. (a) 75Ni25Fe/Al₂O₃; (b) 75Ni25Co/Al₂O₃; (c) 75Ni25Cu/Al₂O. The Ni2p_{3/2}, Fe2p_{3/2}, Co2p_{3/2} and Cu2p_{3/2} peaks were used to determine the surface Ni:M ratio (M = Fe or Co or Cu).

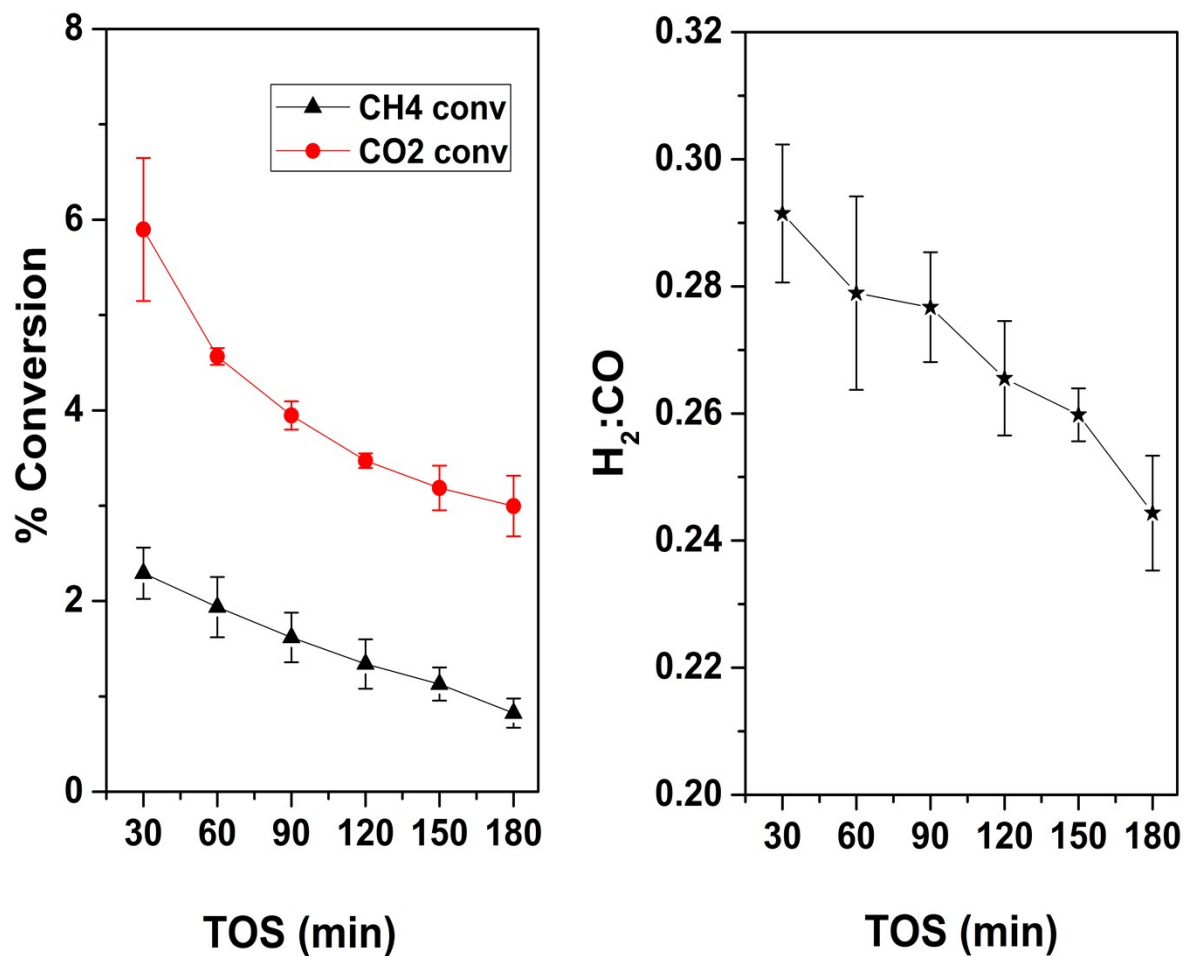


Figure S2: CH₄ and CO₂ conversions and H₂:CO ratio during DRM versus time-on-stream (TOS) over 75Ni25Cu/Al₂O₃ catalyst: CH₄:CO₂:N₂ = 1:1:3 (vol. ratio), W/F_{A0,CH4} = 0.14 kgcat.h/kgCH₄ and reaction temperature = 873 K.

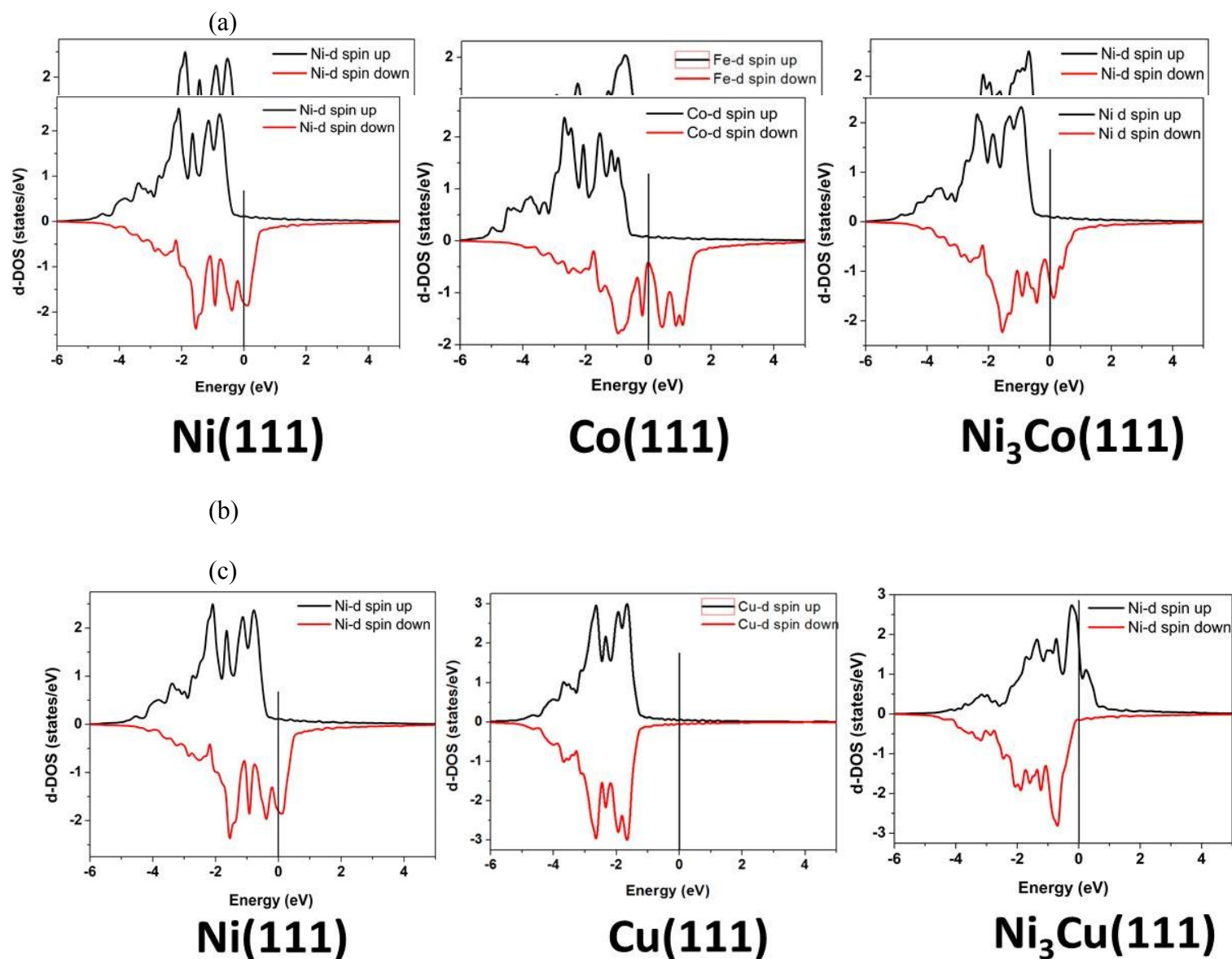


Figure S3: Spin resolved Ni d density of states in Ni(111), Ni₃Fe(111), Ni₃Co(111) and Ni₃Cu(111) are shown. Spin resolved d-DOS of second metals (Fe or Co or Cu) in their closed packed metallic phases are also shown.

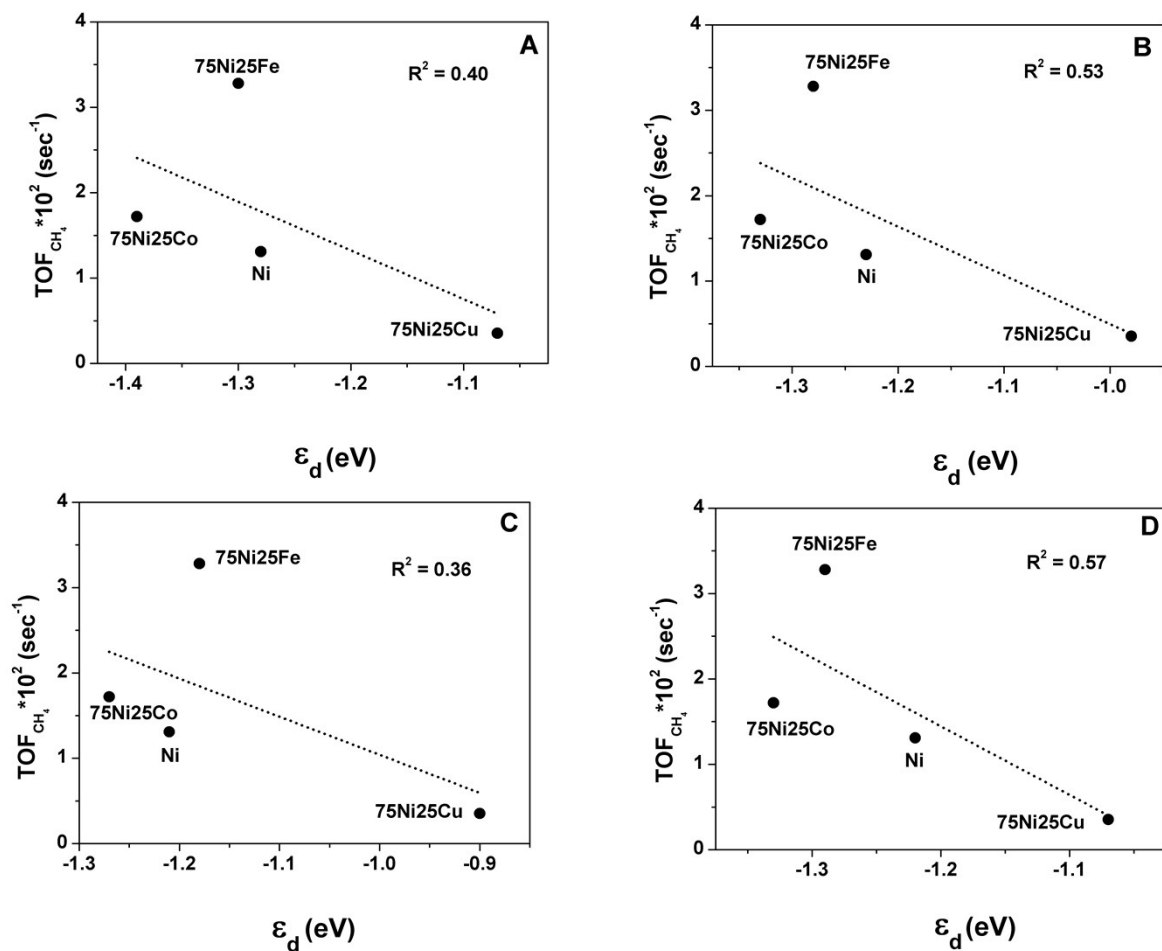


Figure S4: Correlation between TOF_{CH_4} during CO_2 methanation and the Ni d-band center of different surfaces (A) (111), (B) (110), (C) (100), (D) (211) for Ni and 75Ni25M alloy catalysts (M = Fe or Co or Cu).

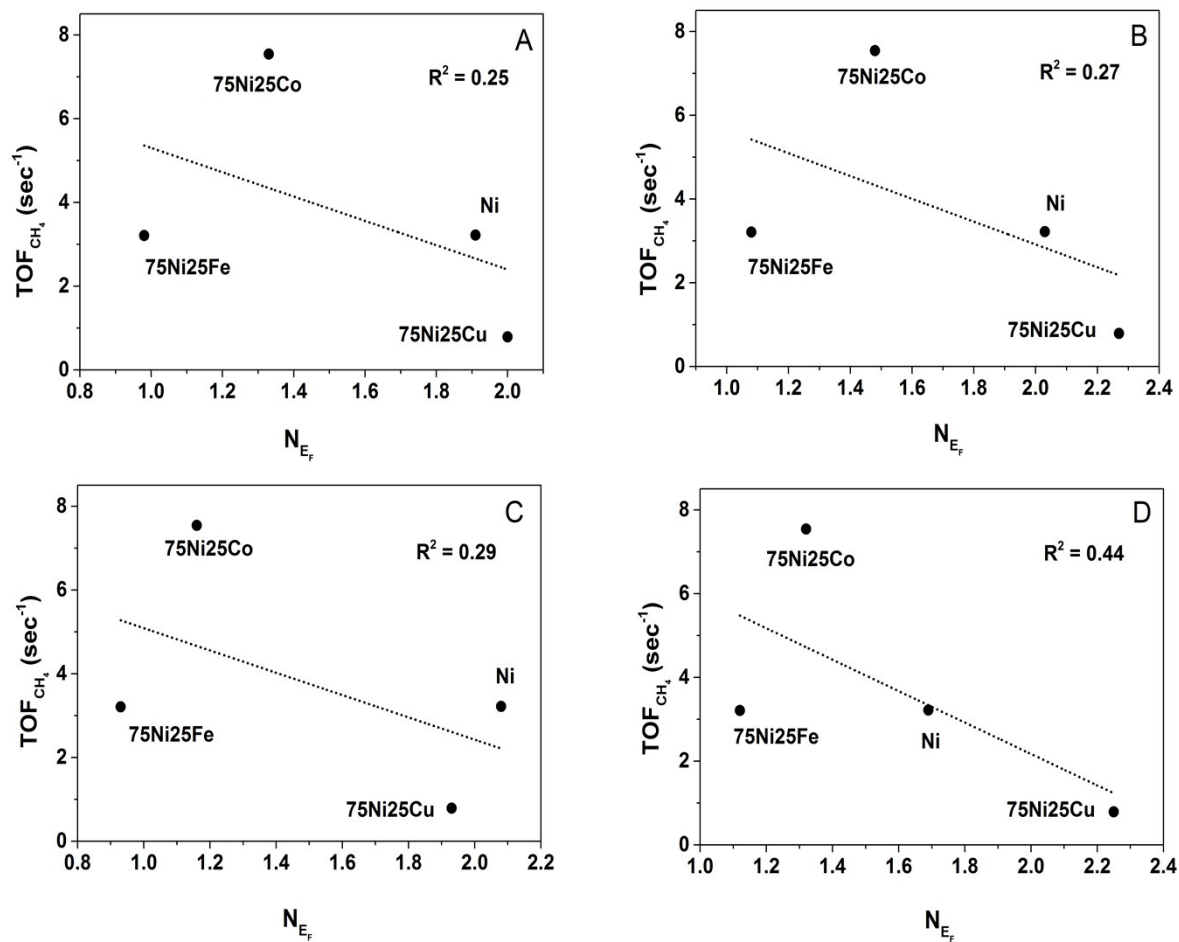


Figure S5: Correlation between TOF_{DRM} during DRM reaction and the number of Ni d-density of states at Fermi Level of different surfaces (A) (111), (B) (110), (C) (100), (D) (211) for Ni and 75Ni25M alloy catalysts (M = Fe or Co or Cu).