Supporting Information

First-principles Modeling of Ni_4M (M= Co, Fe and Mn) Alloys as Solid Oxide Fuel Cell Anode Catalyst for Methane Reforming

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Table S1. Ni_4Fe surface segregation energies (eV).

Number of Fe atoms in each layer[a]	Position of Fe atoms (see Figure 1)	Relative energy[b]
40000	1-2-3-4	2.66
00400	9-10-11-12	1.36
20002	1-2-19-20	1.64
	2-3-17-20	1.74
02020	6-7-14-15	0.62
11110	2-7-10-15	0.57
	2-7-9-13	0.76
	2-8-10-16	0.78
11101	2-7-9-18	0.90
11011	1-8-13-20	1.24
01210	6-10-11-14	0.58
	7-9-12-14	0.57
	7-9-11-14	0.29
10201	2-9-11-19	1.17
01120	6-12-13-14	0.19
	8-10-14-16	0.52
	8-10-15-16	0.20
02110	5-7-12-13	0.28
	5-6-12-13	0.00

[a]The numbers in column 1 indicate a tale of Fe atoms from the bottom layer (1st layer) to the top layer (5th layer)

[b]All energy values are relative to the 5-6-12-13 surface structure energy.

Table S2. Ni_4Co surface segregation energies (eV).

Number of Co atoms in each layer[a]	Position of Co atoms (see Figure 1)	Relative energy[b]
40000	1-2-3-4	0.73
00400	9-10-11-12	0.32
20002	1-2-19-20	0.88
	2-3-17-20	0.84
02020	6-7-14-15	0.03
11110	2-7-10-15	0.34
	2-7-9-13	0.26
	2-8-10-16	0.26
11101	2-7-9-18	0.51
11011	1-8-13-20	0.56
01210	6-10-11-14	0.14
	7-9-12-14	0.11
	7-9-11-14	0.02
10201	2-9-11-19	0.74
01120	6-12-13-14	0.02
	8-10-14-16	0.03
	8-10-15-16	0.02
02110	5-7-12-13	0.05
	5-6-12-13	0.00

[a]The numbers in column 1 indicate a tale of Co atoms from the bottom layer (1st layer) to the top layer (5th layer)

[b]All energy values are relative to the 5-6-12-13 surface structure energy.

Table S3. Ni_4Mn surface segregation energies (eV).

Number of Mn atoms in each layer[a]	Position of Mn atoms (see Figure 1)	Relative energy[b]
40000	1-2-3-4	3.88
00400	9-10-11-12	2.90
20002	1-2-19-20	1.85
	2-3-17-20	1.89
02020	6-7-14-15	0.57
01111	2-7-10-15	0.55
	2-7-9-13	0.50
	2-8-10-16	0.49
11101	2-7-9-18	0.59
11011	1-8-13-20	0.76
01210	6-10-11-14	0.90
	7-9-12-14	0.78
	7-9-11-14	0.63
10201	2-9-11-19	0.99
01120	6-12-13-14	0.33
	8-10-14-16	0.57
	8-10-15-16	0.13
02110	5-7-12-13	0.49
	5-6-12-13	0.00

[a]The numbers in column 1 indicate a tale of Mn atoms from the bottom layer (1st layer) to the top layer (5th layer)

[b]All energy values are relative to the 5-6-12-13 surface structure energy.

Table S4. CH_3 binding energies on Ni and Ni_4Fe surfaces.

Ni_4Fe					Ni				
Site	E_{bond} (kcal/mol)	Opt. spin	Ni ave. spin	Fe ave. spin	Sites	E_{bond} (kcal/mol)	Calc. spin	Opt. spin	Ni ave. spin
t_1	35.2	22.25	0.63	3.07	T	37.2	12	11.80	0.78
t_2	36.2	22.35	0.63	3.09					
t_3	35.6	22.25	0.63	3.07					
b_1	37.7	22.31	0.63	3.09	B	39.3	12	11.69	0.78
b_2	unstable, CH_3 moves to the h_1 site								
b_3	36.0	22.36	0.63	3.08					
b_4	34.5	22.34	0.63	3.06					
b_5	35.9	22.26	0.63	3.07					
b_6	37.3	22.31	0.63	3.08					
b_7	34.5	22.26	0.63	3.08					
f_1	37.3	22.29	0.63	3.06	F	42.7	12	11.54	0.79
f_2	**41.4**	22.25	0.62	3.08					
f_3	40.4	22.24	0.62	3.09					
h_1	40.5	22.32	0.63	3.08	H	42.3	12	11.60	0.80
h_2	40.0	22.34	0.63	3.08					
h_3	37.9	22.17	0.62	3.07					

Table S5. CH_2 binding energies on Ni and Ni_4Fe surfaces.

Ni_4Fe					Ni				
Site	E_{bond} (kcal/mol)	Opt. spin	Ni ave. spin	Fe ave. spin	Sites	E_{bond} (kcal/mol)	Calc. spin	Opt. spin	Ni ave. spin
t_1	62.6	22.62	0.64	3.07	T	66.0	12	11.62	0.77
t_2	64.5	22.72	0.64	3.08					
t_3	unstable, CH_2 moves to the f_2 site								
b_1	unstable, CH_2 moves to the f_3 site				B	83.9	12	11.04	0.76
b_2	unstable, CH_2 moves to the h_1 site								
b_3	82.8	21.90	0.60	3.08					
b_4	unstable, CH_2 moves to the h_2 site								
b_5	unstable, CH_2 moves to the f_2 site								
b_6	82.5	21.91	0.60	3.08					
b_7	79.5	21.90	0.60	3.07					
f_1	78.3	22.09	0.61	3.09	F	89.3	11	10.88	0.71
f_2	84.1	22.00	0.61	3.08					
f_3	**85.7**	21.99	0.60	3.09					
h_1	84.3	21.91	0.60	3.08	H	88.6	11	10.77	0.71
h_2	81.2	21.94	0.60	3.08					
h_3	79.1	21.88	0.60	3.09					

Table S6. CH binding energies on Ni and Ni_4Fe surfaces.

Ni_4Fe					Ni				
Site	E_{bond} (kcal/mol)	Opt. spin	Ni ave. spin	Fe ave. spin	Sites	E_{bond} (kcal/mol)	Calc. spin	Opt. spin	Ni ave. spin
t_1	unstable, CH moves to the h_3 site				T	99.5	11	10.92	0.72
t_2	unstable, CH moves to the f_3 site								
t_3	unstable, CH moves to the h_1 site								
b_1	unstable, CH moves to the h_1 site				B	139.4	10	10.42	0.65
b_2	unstable, CH moves to the h_1 site								
b_3	unstable, CH moves to the h_1 site								
b_4	unstable, CH moves to the h_2 site								
b_5	unstable, CH moves to the f_2 site								
b_6	unstable, CH moves to the h_2 site								
b_7	unstable, CH moves to the h_3 site								
f_1	129.9	21.79	0.58	3.11	F	148.0	10	10.24	0.63
f_2	138.9	21.34	0.57	3.09					
f_3	139.0	21.43	0.57	3.09					
h_1	**139.3**	21.22	0.56	3.09	H	148.9	10	10.06	0.65
h_2	138.8	21.25	0.56	3.08					
h_3	133.6	21.16	0.55	3.10					

Table S7. C binding energies on Ni and Ni_4Fe surfaces.

Ni_4Fe					Ni				
Site	E_{bond} (kcal/mol)	Opt. spin	Ni ave. spin	Fe ave. spin	Sites	E_{bond} (kcal/mol)	Calc. spin	Opt. spin	Ni ave. spin
t_1	unstable, C moves to the h_3 site				T	103.6	11	10.96	0.71
t_2	unstable, C moves to the f_3 site								
t_3	unstable, C moves to the h_3 site								
b_1	unstable, C moves to the h_1 site				B	143.1	10	10.04	0.64
b_2	unstable, C moves to the h_1 site								
b_3	unstable, C moves to the h_1 site								
b_4	unstable, C moves to the h_2 site								
b_5	unstable, C moves to the f_2 site								
b_6	unstable, C moves to the h_2 site								
b_7	unstable, C moves to the f_3 site								
f_1	137.0	20.59	0.52	3.08	F	153.2	10	9.87	0.64
f_2	141.7	20.50	0.51	3.08					
f_3	141.5	20.51	0.51	3.08					
h_1	**142.9**	20.35	0.51	3.06	H	154.8	10	9.82	0.63
h_2	141.8	20.32	0.51	3.06					
h_3	140.0	20.34	0.50	3.10					

Table S8. H binding energies on Ni and Ni_4Fe surfaces.

Ni_4Fe					Ni				
Site	E_{bond} (kcal/mol)	Opt. spin	Ni ave. spin	Fe ave. spin	Sites	E_{bond} (kcal/mol)	Calc. spin	Opt. spin	Ni ave. spin
t_1	unstable, H moves to the h_3 site				T	52.7	12	11.93	0.79
t_2	53.9	22.52	0.64	3.09					
t_3	51.9	22.42	0.64	3.06					
b_1	unstable, H moves to the f_3 site				B	62.6	12	11.79	0.79
b_2	unstable, H moves to the h_1 site								
b_3	58.0	22.30	0.63	3.08					
b_4	unstable, H moves to the h_2 site								
b_5	unstable, H moves to the f_2 site								
b_6	unstable, H moves to the f_3 site								
b_7	unstable, H moves to the f_3 site								
f_1	58.1	22.40	0.64	3.07	F	65.7	12	11.77	0.79
f_2	**60.4**	22.33	0.63	3.08					
f_3	59.2	22.24	0.63	3.07					
h_1	60.2	22.35	0.63	3.08	H	65.4	12	11.78	0.79
h_2	59.6	22.35	0.63	3.08					
h_3	58.1	22.27	0.63	3.08					

Table S9. Binding energies (kcal/mol) of the reaction intermediates at f and h sites of Ni_4M alloys.

Ni_4M alloy	Site	CH_3	CH_2	CH	C	H
Ni_4Fe	f_1	37.3	78.3	129.9	137.0	58.1
	f_2	**41.4**	84.1	138.9	141.7	**60.4**
	f_3	40.4	**85.7**	139.0	141.5	59.2
	h_1	40.5	84.3	**139.3**	**142.9**	60.2
	h_2	40.0	81.2	138.8	141.8	59.6
	h_3	37.9	79.1	133.6	140.0	58.1
Ni_4Co	f_1	39.5	81.1	135.3	135.7	59.8
	f_2	**42.9**	**86.3**	143.1	140.3	**61.9**
	f_3	40.5	86.1	**143.4**	140.2	61.1
	h_1	41.1	84.2	141.1	142.7	60.0
	h_2	40.1	81.2	140.4	**143.0**	60.3
	h_3	41.1	81.3	137.8	137.8	59.6
Ni_4Mn	f_1	39.2	79.4	133.6	138.4	60.6
	f_2	42.9	81.4	136.4	138.5	61.8
	f_3	42.3	**84.0**	138.2	138.0	61.9
	h_1	**43.5**	82.8	**140.8**	**144.1**	**62.1**
	h_2	42.2	79.3	136.2	143.4	62.0
	h_3	35.9	76.0	133.9	140.2	58.5