Table S1 Elementary processes included in the kMC simulation as well as corresponding kinetic parameters for Ni(111) surface

No.	Elementary process	$E_{a,f}$ (eV)	$E_{a,r}$ (eV)	$v_{0,f}$ (s^{-1})	$v_{0,r}$ (s^{-1})
1	CO(g)+* ↔ CO*	0	1.60	a	b
2	H_2(g)+2*↔H*+H*	0	0.82	c	b
3	CO*+*↔C*+O*	3.18	1.37	5.59E+12	4.31E+13
4	CO*+H*↔COH*+*	2.17	1.19	3.73E+13	4.55E+13
5	COH*+*↔C*+OH*	2.10	1.30	8.35E+12	2.08E+13
6	CO*+H*↔HCO*+*	1.68	0.40	3.23E+13	4.87E+13
7	HCO*+*↔CH*+O*	1.10	1.28	7.44E+12	3.72E+13
8	C*+H*↔CH*+*	0.98	1.55	6.03E+13	4.93E+13
9	CH*+H*↔CH_2*+*	0.75	0.42	4.89E+13	1.25E+13
10	CH_2*+H*↔CH_3*+*	0.78	0.89	6.66E+12	1.55E+13
11	CH_3*+H*↔CH_4(g)+2*	1.18	1.62	7.22E+13	d
12	O*+H*↔OH*+*	1.44	1.35	5.54E+13	2.37E+13
13	OH*+H*↔H_2O*+*	1.53	1.35	2.15E+14	1.87E+13
14	OH*+OH*↔H_2O*+O*	0.43	0.68	3.99E+12	4.69E+12
15	H_2O*→H_2O(g)+*	0.05		b	
16	CO*+O*→2*+CO_2(g)	1.65	0.51	8.26E+13	
17	CO*+*→*+CO*	0.16		3.57E+12	
18	H*+*→*+H*	0.14		1.45E+13	
19	O*+*→*+O*	0.51		9.48E+12	
20	OH*+*→*+OH*	0.29		4.28E+13	

a is calculated according to Eq. 10. **b** is calculated according to Eq. 14. **c** is calculated according to Eq. 11. **d** According to Eq. 20 and the same below.

Table S2 Elementary processes included in the kMC simulation as well as corresponding kinetic parameters for Ni(211) surface

No.	Elementary process	$E_{a,f}$ (eV)	$E_{a,r}$ (eV)	$\nu_{0,f}$ (s^{-1})	$\nu_{0,r}$ (s^{-1})
1	CO(g)+* ↔ CO*	0	1.64	a	b
2	H_2(g)+2*↔H*+H*	0	0.82	c	b
3	CO*+*↔C*+O*	2.18	1.89	1.98E+13	6.33E+13
4	CO*+H*↔COH*+*	1.31	0.87	9.65E+12	1.00E+14
5	COH*+*↔C*+OH*	1.08	1.91	3.64E+13	5.63E+13
6	CO*+H*↔HCO*+*	0.91	0.18	1.72E+13	5.09E+13
7	HCO*+*↔CH*+O*	0.97	1.14	2.06E+13	2.20E+13
8	C*+H*↔CH*+*	0.94	0.82	2.21E+13	2.85E+13
9	CH*+H*↔CH_2-1*+*	0.73	0.28	1.02E+13	2.11E+13
10	CH_2-1*+*↔*+CH_2*	0.32	0.60	1.37E+13	6.46E+12
11	CH_2*+H*↔CH_3*+*	0.42	0.76	7.30E+12	1.37E+13
12	CH_3*+H*↔CH_4(g)+2*	0.92	1.07	8.24E+12	d
13	O*+H*↔OH*+*	0.95	1.32	2.32E+14	1.14E+14
14	OH*+H*↔H_2O*+*	1.51	1.02	4.91E+14	7.09E+13
15	OH*+OH*↔H_2O*+O*	0.81	0.63	4.66E+13	1.61E+13
16	H_2O*→H_2O(g)+*	0.29		b	
17	CO*+O*→2*+CO_2(g)	1.79	1.07	3.16E+12	
18	CO*+OH*↔COOH-cis*+*	1.43	0.24	3.96E+13	6.70E+13
19	COOH-cis*↔COOH-trans*	0.40	0.71	8.68E+12	2.93E+13
20	COOH-trans*→CO_2(g)+H*	1.00	0.96	7.61E+13	
21	COOH-trans*+O*→CO_2(g)+OH*+*	0.25	0.10	1.99E+13	
22	COOH-trans*+OH*→CO_2(g)+H_2O*+*	0.41	0.34	2.13E+12	
23	CO*+*→*+CO*	0.13		2.56E+12	
24	H*+*→*+H*	0.17		2.00E+13	
25	O*+*→*+O*	0.39		1.08E+13	
26	OH*+*→*+OH*	0.70		4.72E+13	

Table S3 Elementary processes included in the kMC simulation as well as corresponding kinetic parameters for $Ni_3Fe(111)$ surface

No.	Elementary process	$E_{a,f}$ (eV)	$E_{a,r}$ (eV)	$\nu_{0,f}$ (s^{-1})	$\nu_{0,r}$ (s^{-1})
1	CO(g)+* ↔ CO*	0	1.59	a	b
2	H_2(g)+2*↔H*+H*	0	0.90	c	b
3	CO*+*↔C*+O*	2.82	1.20	4.17E+12	3.36E+13
4	CO*+H*↔COH*+*	2.19	1.17	2.29E+13	2.55E+13
5	COH*+*↔C*+OH*	1.87	1.20	1.82E+13	2.00E+13
6	CO*+H*↔HCO*+*	1.45	0.36	7.61E+13	1.33E+14
7	HCO*+*↔CH*+O*	1.01	1.11	6.55E+12	2.54E+13
8	C*+H*↔CH*+*	0.95	1.46	4.26E+13	2.34E+13
9	CH*+H*↔CH_2*+*	0.67	0.50	1.54E+13	8.80E+12
10	CH_2*+H*↔CH_3*+*	0.74	0.91	5.77E+13	2.16E+14
11	CH_3*+H*↔CH_4(g)+2*	1.12	1.44	3.04E+14	d
12	O*+H*↔OH*+*	1.29	1.29	8.43E+13	3.59E+13
13	OH*+H*↔H_2O*+*	1.49	1.13	2.23E+14	1.77E+13
14	OH*+OH*↔H_2O*+O*	0.65	0.58	3.76E+12	8.10E+12
15	H_2O*→H_2O(g)+*	0.17		b	
16	CO*+O*→2*+CO_2(g)	1.61	0.41	2.00E+13	
17	CO*+*→*+CO*	0.20		6.05E+12	
18	H*+*→*+H*	0.11		1.23E+13	
19	O*+*→*+O*	0.35		7.96E+12	
20	OH*+*→*+OH*	0.22		4.16E+13	

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Table S4 Elementary processes included in the kMC simulation as well as corresponding kinetic parameters for $Ni_3Fe(211)$-AB surface

No.	Elementary process	$E_{a,f}$ (eV)	$E_{a,r}$ (eV)	$\nu_{0,f}$ (s^{-1})	$\nu_{0,r}$ (s^{-1})
1	CO(g)+* ↔ CO*	0	1.60	a	b
2	H_2(g)+2*↔H*+H*	0	0.92	c	b
3	CO*+*↔C*+O*	1.76	1.62	2.39E+13	5.81E+13
4	CO*+H*↔COH*+*	1.28	0.89	1.99E+13	1.50E+14
5	COH*+*↔C*+OH*	1.17	2.20	1.91E+13	3.89E+13
6	CO*+H*↔HCO*+*	0.87	0.30	1.76E+13	4.75E+13
7	HCO*+*↔CH*+O*	0.66	1.10	1.10E+13	9.25E+12
8	C*+H*↔CH*+*	0.77	1.07	4.83E+13	1.16E+14
9	CH*+H*↔CH_2-1*+*	0.63	0.37	5.18E+12	5.36E+12
10	CH_2-1*+*↔*+CH_2*	0.29	0.65	2.21E+13	1.18E+13
11	CH_2*+H*↔CH_3*+*	0.32	0.75	1.49E+12	3.67E+12
12	CH_3*+H*↔CH_4(g)+2*	0.95	0.98	1.45E+13	d
13	O*+H*↔OH*+*	0.94	1.32	1.03E+14	2.81E+13
14	OH*+H*↔H_2O*+*	1.53	0.83	9.63E+13	1.45E+13
15	OH*+OH*↔H_2O*+O*	0.74	0.44	1.87E+13	1.03E+13
16	H_2O*→H_2O(g)+*	0.40		b	
17	CO*+O*→2*+CO_2(g)	1.91	1.21	1.68E+12	
18	CO*+OH*↔COOH-cis*+*	1.49	0.11	7.93E+12	3.71E+13
19	COOH-cis*↔COOH-trans*	0.42	0.76	7.21E+12	1.55E+13
20	COOH-trans*→CO_2(g)+H*	1.13	1.13	2.92E+13	
21	COOH-trans*+O*→CO_2(g)+OH*+*	0.22	0.35	6.50E+13	
22	COOH-trans*+OH*→CO_2(g)+H_2O*+*	0.29	0.12	1.33E+12	
23	CO*+*→*+CO*	0.28		1.00E+13	
24	H*+*→*+H*	0.21		2.34E+13	
25	O*+*→*+O*	0.38		9.73E+12	
26	OH*+*→*+OH*	0.47		1.01E+13	

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Table S5 Elementary processes included in the kMC simulation as well as corresponding kinetic parameters for $Ni_3Fe(211)$-AA surface

No.	Elementary process	$E_{a,f}$ (eV)	$E_{a,r}$ (eV)	$\nu_{0,f}$ (s^{-1})	$\nu_{0,r}$ (s^{-1})
1	CO(g)+* ↔ CO*	0	1.66	a	b
2	H_2(g)+2*↔H*+H*	0	0.90	c	b
3	CO*+*↔C*+O*	2.21	1.65	6.65E+12	6.42E+13
4	CO*+H*↔COH*+*	1.37	0.92	1.60E+13	6.11E+13
5	COH*+*↔C*+OH*	1.08	1.94	1.64E+13	4.19E+13
6	CO*+H*↔HCO*+*	0.71	0.21	1.41E+13	5.31E+13
7	HCO*+*↔CH*+O*	1.10	1.59	8.24E+12	1.18E+13
8	C*+H*↔CH*+*	0.87	0.88	2.44E+13	3.70E+13
9	CH*+H*↔CH_2-1*+*	0.73	0.36	1.22E+13	2.63E+13
10	CH_2-1*+*↔*+CH_2*	0.37	0.35	2.01E+13	3.03E+12
11	CH_2*+H*↔CH_3*+*	0.33	0.83	2.77E+12	1.86E+12
12	CH_3*+H*↔CH_4(g)+2*	0.92	1.07	6.76E+13	d
13	O*+H*↔OH*+*	0.96	1.41	1.40E+14	9.43E+13
14	OH*+H*↔H_2O*+*	1.50	1.00	3.60E+14	4.26E+13
15	OH*+OH*↔H_2O*+O*	0.85	0.38	2.13E+13	1.78E+13
16	H_2O*→H_2O(g)+*	0.22		b	
17	CO*+O*→2*+CO_2(g)	2.02	1.21	2.40E+14	
18	CO*+OH*↔COOH-cis*+*	1.30	0.25	6.51E+12	2.71E+13
19	COOH-cis*↔COOH-trans*	0.57	0.68	2.17E+13	7.01E+13
20	COOH-trans*→CO_2(g)+H*	1.01	1.08	1.77E+14	
21	COOH-trans*+O*→CO_2(g)+OH*+*	0.20	0.12	1.21E+13	
22	COOH-trans*+OH*→CO_2(g)+H_2O*+*	0.31	0.37	4.51E+12	
23	CO*+*→*+CO*	0.25		2.84E+12	
24	H*+*→*+H*	0.23		1.38E+13	
25	O*+*→*+O*	0.50		8.79E+12	
26	OH*+*→*+OH*	0.70		7.42E+13	

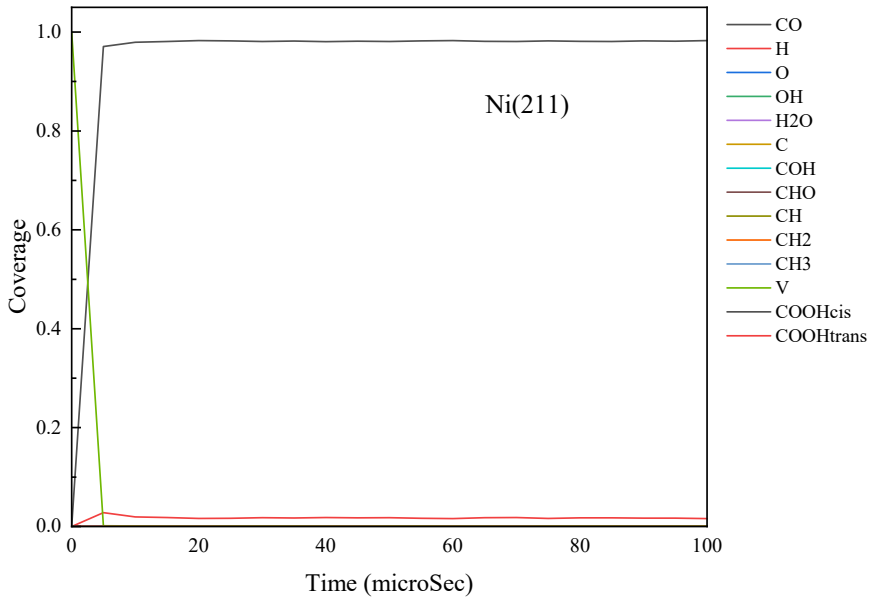

Figure S1 The variation of coverage in simulation time at 100 microSec on Ni(211) at 673 K

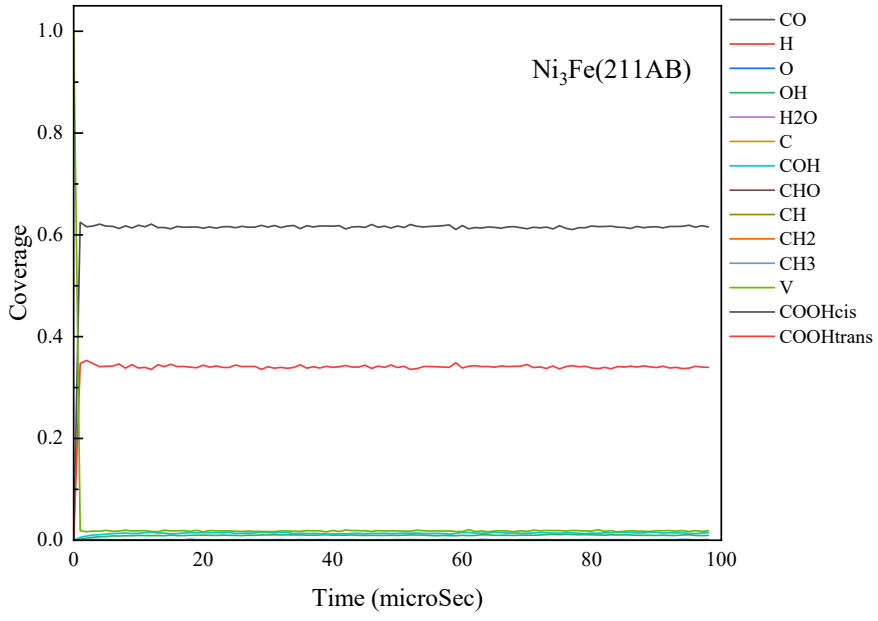

Figure S2 The variation of coverage in simulation time at 100 microSec on Ni_3Fe(211AB) at 673K

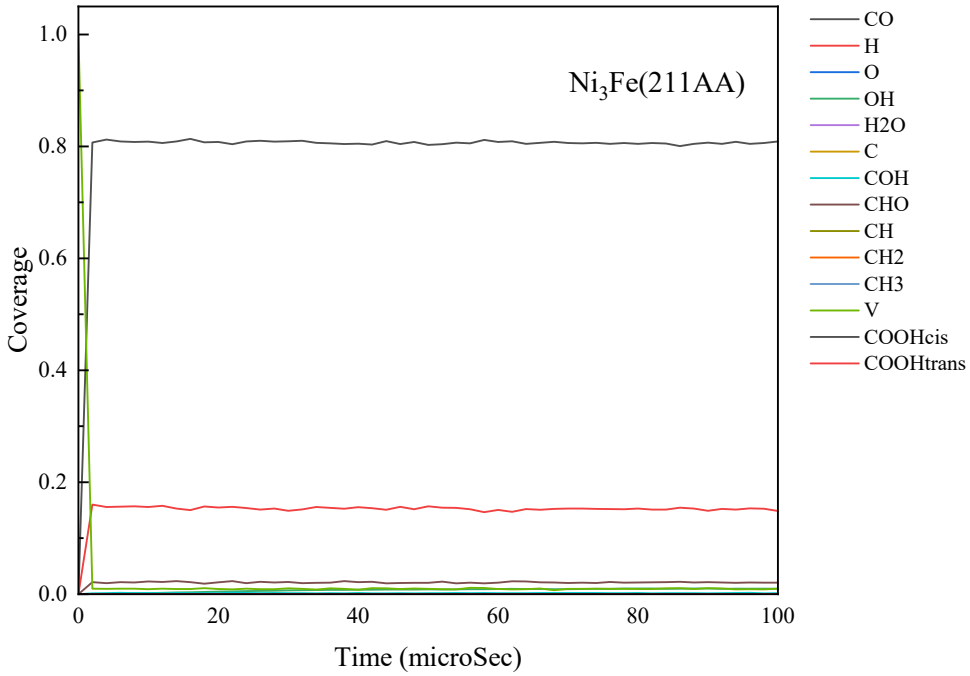

Figure S3 The variation of coverage in simulation time at 100 microSec on $Ni_3Fe(211AA)$ at 673 K

As can be seen from the figure, in a few microseconds, the coverage of each species has reached stability. The surface of Ni(211) is almost covered by CO, and the coverage of other intermediate species and H is very small. The surface of $Ni_3Fe(211AB)$ and $Ni_3Fe(211AA)$ is almost covered by CO and H, and the coverage of other intermediate species is very small. The figures indicate that the residence time of the intermediate is short, and the reaction system reaches stability at this time. The dissociation and hydrogenation of CO occur simultaneously on the catalyst surface, but the surface of Ni(211) is almost covered by CO, which is not conducive to hydrogenation reaction compared with $Ni_3Fe(211AB)$ and $Ni_3Fe(211AA)$.