Supporting Information

A High Loaded Catalyst of Highly Dispersed Nickel Species on Acid-Treated Mesoporous Clay Layers for Efficient CO and CO_2 Methanation

Feifei Li [a], Junbo Zhang [a], Yufu Liu [a], Guanjun Gao [a], Yi He [a], and Xuzhuang Yang [a, b*]

[a] College of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot 010021, China

[b] Inner Mongolia Key Lab of Rare Earth Materials Chemistry and Physics, Inner Mongolia University, Hohhot, Inner Mongolia, 010021, P. R. China;

[*]Corresponding author: Xuzhuang Yang

E-mail address: xzyang@imu.edu.cn

1. Orthogonal experimental design.

To screen catalysts, we investigated the effects of four factors: (1) two types of clays, raw montmorillonite (A0) and acid-modified montmorillonite (A1); (2) four nickel loadings of 5% (B5), 10% (B10), 15% (B15), and 20% (B20); (3) four types of amino acids, L-lysine (C1), L-alanine (C2), L-serine (C3), and glycine (C4); and (4) four amino acid to nickel molar ratios of 0 (D0), 1 (D1), 2 (D2), and 3 (D3). Table S1 illustrates the orthogonal experimental scheme created by the statistical program Statistical Product and Service Solutions (SPSS).

Table S1 Orthogonal experimental scheme

Catalysts	Clays	Ni loadings	Amino acids	Molar ratio
1	A0	B10	C1	D1
2	A1	B20	C1	D3
3	A1	B15	C1	D2
4	A0	B5	C3	D3
5	A0	B20	C2	D1
6	A1	B10	C4	D0
7	A0	B15	C4	D3
8	A0	B15	C2	D0
9	A0	B10	C3	D2
10	A0	B20	C4	D2
11	A1	B20	C3	D0
12	A0	B5	C1	D0
13	A1	B15	C3	D1
14	A1	B5	C4	D1
15	A1	B10	C2	D3
16	A1	B5	C2	D2

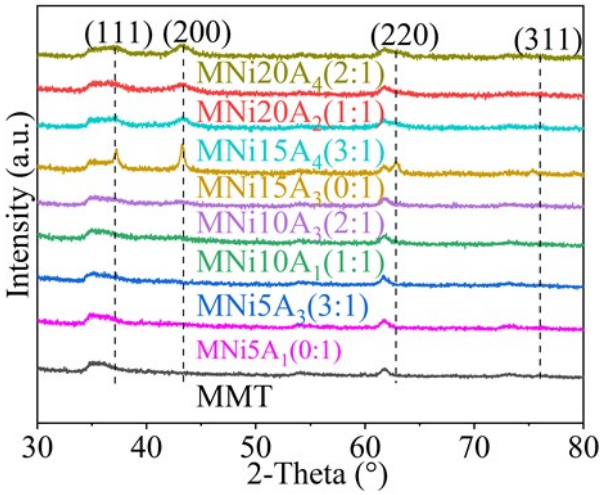


Fig. S1. XRD patterns of nickel catalysts supported on the M ($MNiaA_b(D)$)

Table S2 The amount of Ni in the catalyst and the size of NiO particles

Catalyst	Ni loading (wt.%)	NiO particle size (nm)
$MNi5A_1(0:1)$	5	-
$MNi5A_3(3:1)$	5	-
$MNi10A_1(1:1)$	10	-
$MNi10A_3(2:1)$	10	-
$MNi15A_3(0:1)$	15	56.32
$MNi15A_4(3:1)$	15	13.36
$MNi20A_2(1:1)$	20	9.28
$MNi20A_4(2:1)$	20	15.94

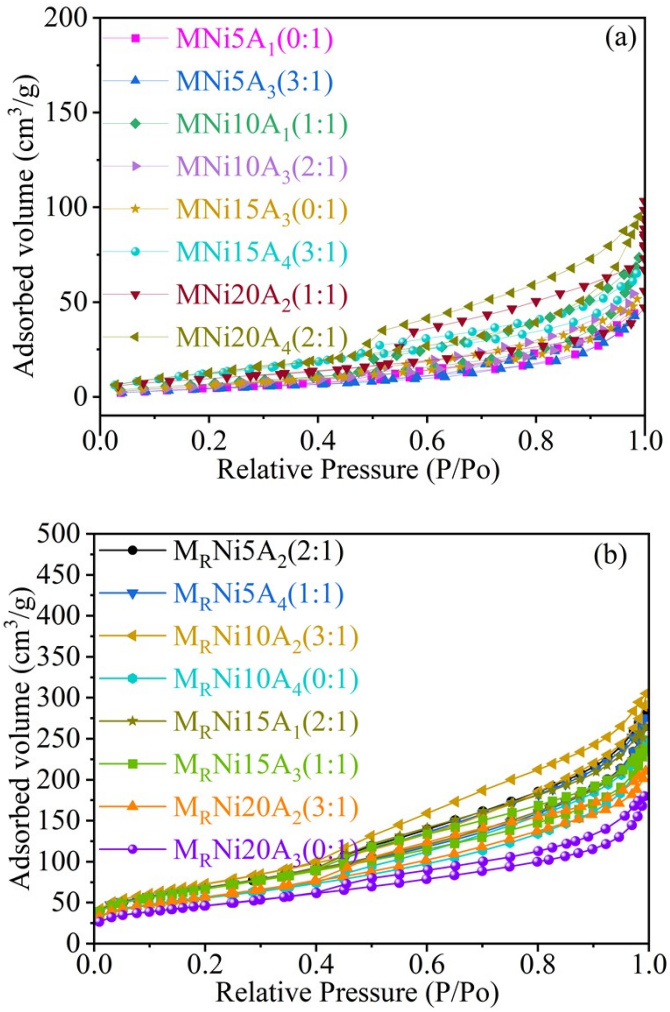


Fig. S2. N_2 adsorption-desorption isotherms and pore size distribution curves of (a, b) the catalysts designed for orthogonal experiment

2.Catalyst activity

Table S3 Orthogonal experiment CO conversion, CH_4 selectivity, and formation rate for the CO methanation

Catalysts	Factor				CO Conv. (%)	S_{CH4} (%)	Formation rate (%)
	A	B	C	D			
1	0	10	1	1	98.8	75.3	74.2
2	1	20	1	3	99.5	78.7	78.2
3	1	15	1	2	99.7	79.7	79.3
4	0	5	3	3	83.0	76.8	51.2
5	0	20	2	1	99.7	81.2	80.9
6	1	10	4	0	98.4	72.4	69.9
7	0	15	4	3	99.5	77.7	77.2
8	0	15	2	0	98.5	73.9	72.8
9	0	10	3	2	99.0	75.7	74.9
10	0	20	4	2	99.7	81.0	80.8
11	1	20	3	0	98.9	76.4	75.6
12	0	5	1	0	71.5	62.8	44.8
13	1	15	3	1	99.5	79.4	79.0
14	1	5	4	1	94.5	69.0	64.9
15	1	10	2	3	98.5	73.4	71.9
16	1	5	2	2	92.6	67.7	62.7

Table S4 CO conversion range analysis data for the CO methanation

Value name	A	B	C	D
K1	93.7	85.4	92.2	91.8
K2	97.6	98.7	97.3	98.1
K3		99.3	95.1	97.8
K4		99.2	91.8	94.9
Rj	3.9	13.9	5.9	6.3
Importance		B>D>C>A		

Table S5 CH_4 Selectivity range analysis data for the CO methanation

Value name	A	B	C	D
K1	73.9	65.9	74.1	71.4
K2	74.6	74.2	74.0	76.2
K3		77.7	73.9	76.0
K4		79.3	75.0	73.5
Rj	0.6	13.5	0.9	4.9
Importance		B>D>C>A		

Table S6 CH_4 Formation Rate range analysis data for the CO methanation

Value name	A	B	C	D
K1	69.6	55.9	69.1	65.7
K2	72.7	72.7	72.1	74.8
K3		77.0	70.2	74.4
K4		78.9	73.2	69.6
Rj	3.1	22.9	4.1	9.0
Importance		B>D>C>A		

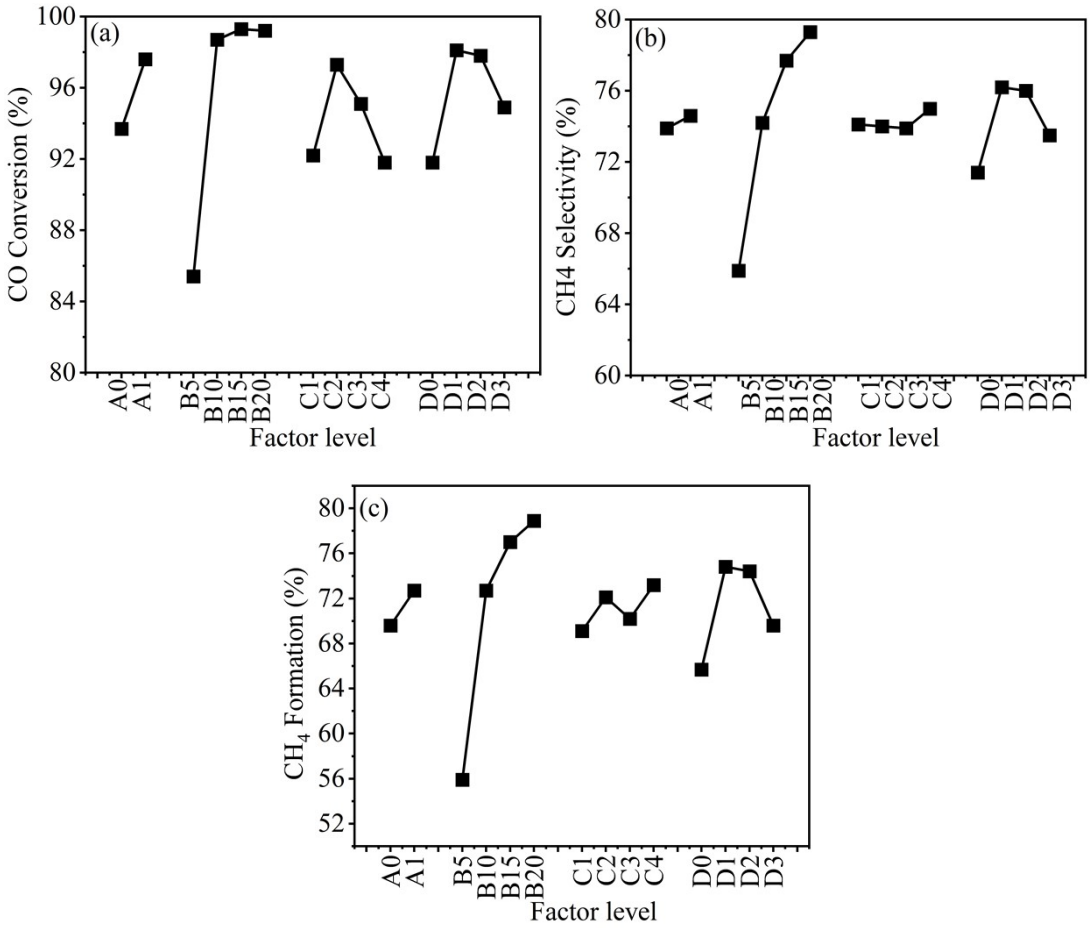


Fig. S3. Factor level diagram for the CO methanation.

Table S7 Orthogonal experiment CO_2 conversion, CH_4 selectivity, and formation rate for the CO_2 methanation

Catalysts	Factor				CO_2 Conv. (%)	S_{CH4} (%)	Formation rate (%)
	A	B	C	D			
1	0	10	1	1	82.1	99.1	81.2
2	1	20	1	3	88.4	99.5	87.9
3	1	15	1	2	88.0	99.6	87.6
4	0	5	3	3	64.3	93.8	60.3
5	0	20	2	1	89.5	99.6	89.1
6	1	10	4	0	76.0	97.0	72.9
7	0	15	4	3	84.0	99.3	83.2
8	0	15	2	0	77.0	98.5	75.5
9	0	10	3	2	78.0	98.3	76.4
10	0	20	4	2	88.4	99.6	88.1
11	1	20	3	0	83.8	99.3	82.9
12	0	5	1	0	60.4	90.8	54.8
13	1	15	3	1	88.0	99.5	87.1
14	1	5	4	1	66.0	94.0	62.0
15	1	10	2	3	80.8	98.9	79.6
16	1	5	2	2	72.5	95.9	69.1

Table S8 CO_2 conversion range analysis data for the CO_2 methanation

Value name	A	B	C	D
K1	77.9	67.1	79.8	77.3
K2	81.1	79.2	79.9	82.7
K3		84.3	78.5	81.7
K4		87.5	79.9	79.4
Rj	3.1	20.5	1.4	5.3
Importance		B>D>A>C		

Table S9 CH_4 Selectivity range analysis data for the CO_2 methanation

Value name	A	B	C	D
K1	97.4	93.6	97.2	96.4
K2	97.9	98.3	98.2	98.1
K3		99.2	97.7	98.3
K4		99.5	97.5	97.9
Rj	0.6	5.9	0.9	1.9
Importance		B>D>C>A		

Table S10 CH_4 Formation Rate range analysis data for the CO_2 methanation

Value name	A	B	C	D
K1	76.1	61.6	77.9	71.5
K2	78.7	77.5	78.3	81.0
K3		83.3	76.7	80.3
K4		87.0	76.6	77.7
Rj	2.6	25.4	1.8	9.5
Importance		B>D>A>C		

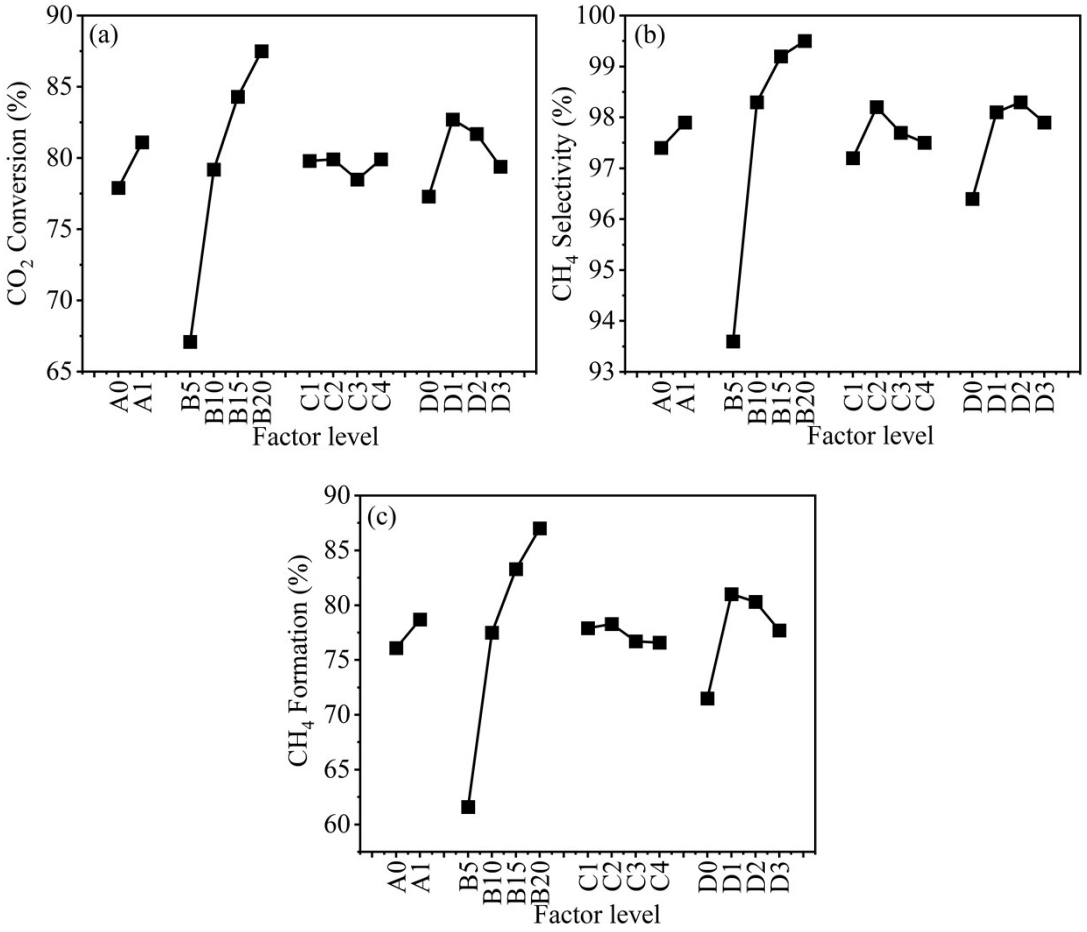
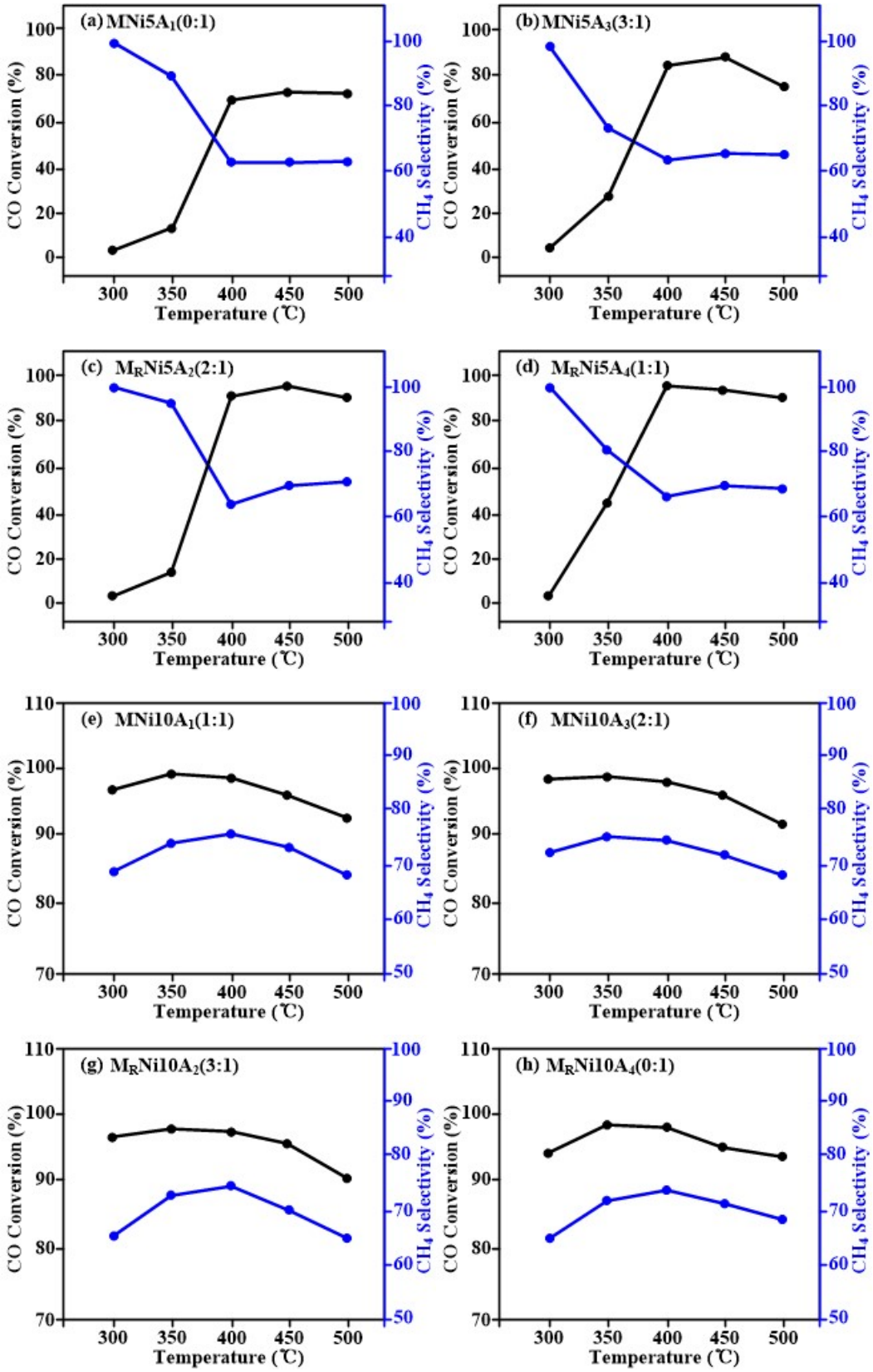


Fig. S4. Factor level diagram for the CO_2 methanation.


(a) MNi5A1(0:1)
(b) MNi5A3(3:1)
(c) MRNi5A2(2:1)
(d) MRNi5A4(1:1)
(e) MNi10A1(1:1)
(f) MNi10A3(2:1)
(g) MRNi10A2(3:1)
(h) MRNi10A4(0:1)
CO Conversion (%)
CH4 Selectivity (%)
Temperature (℃)
300
350
400
450
500

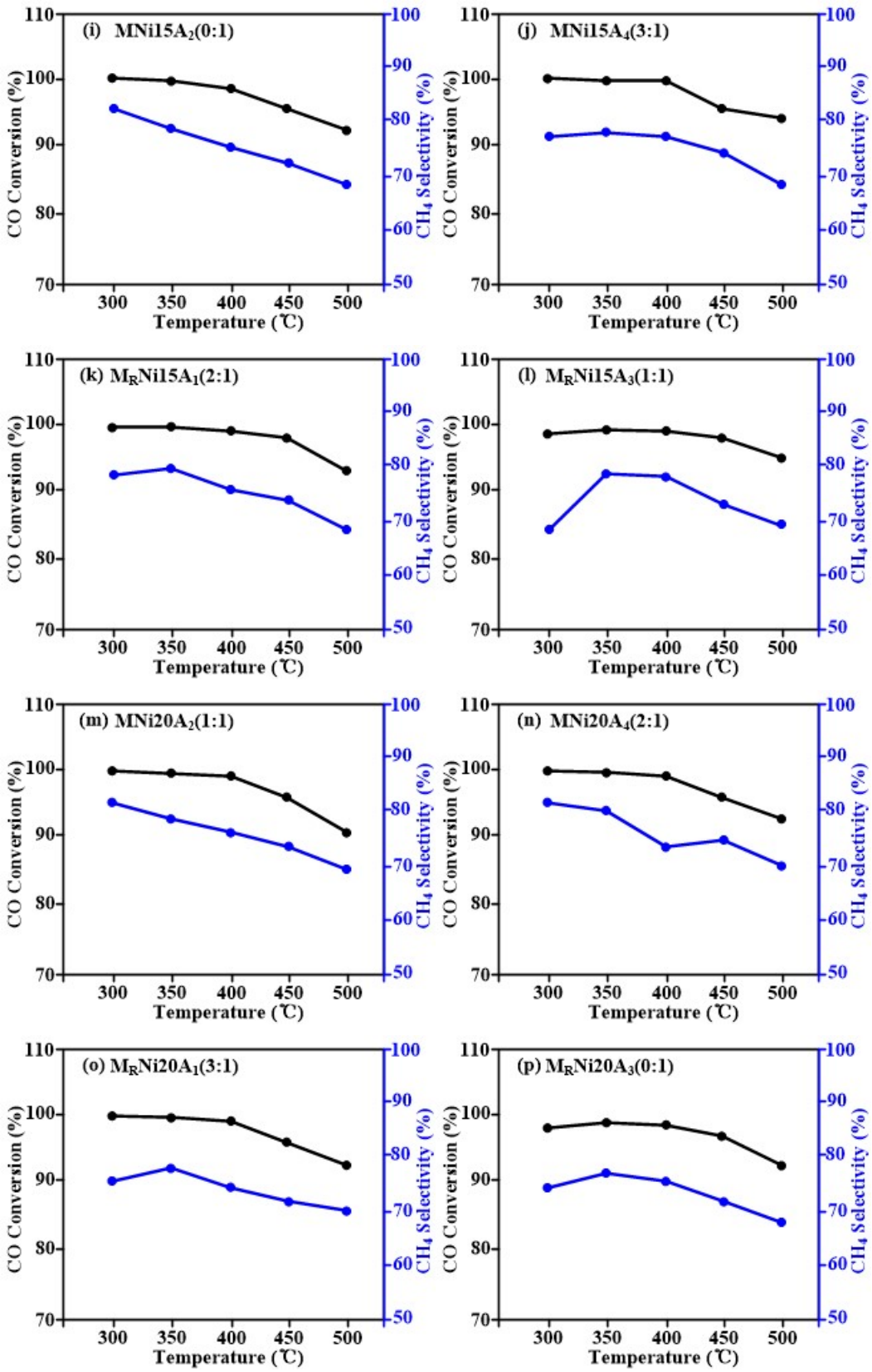
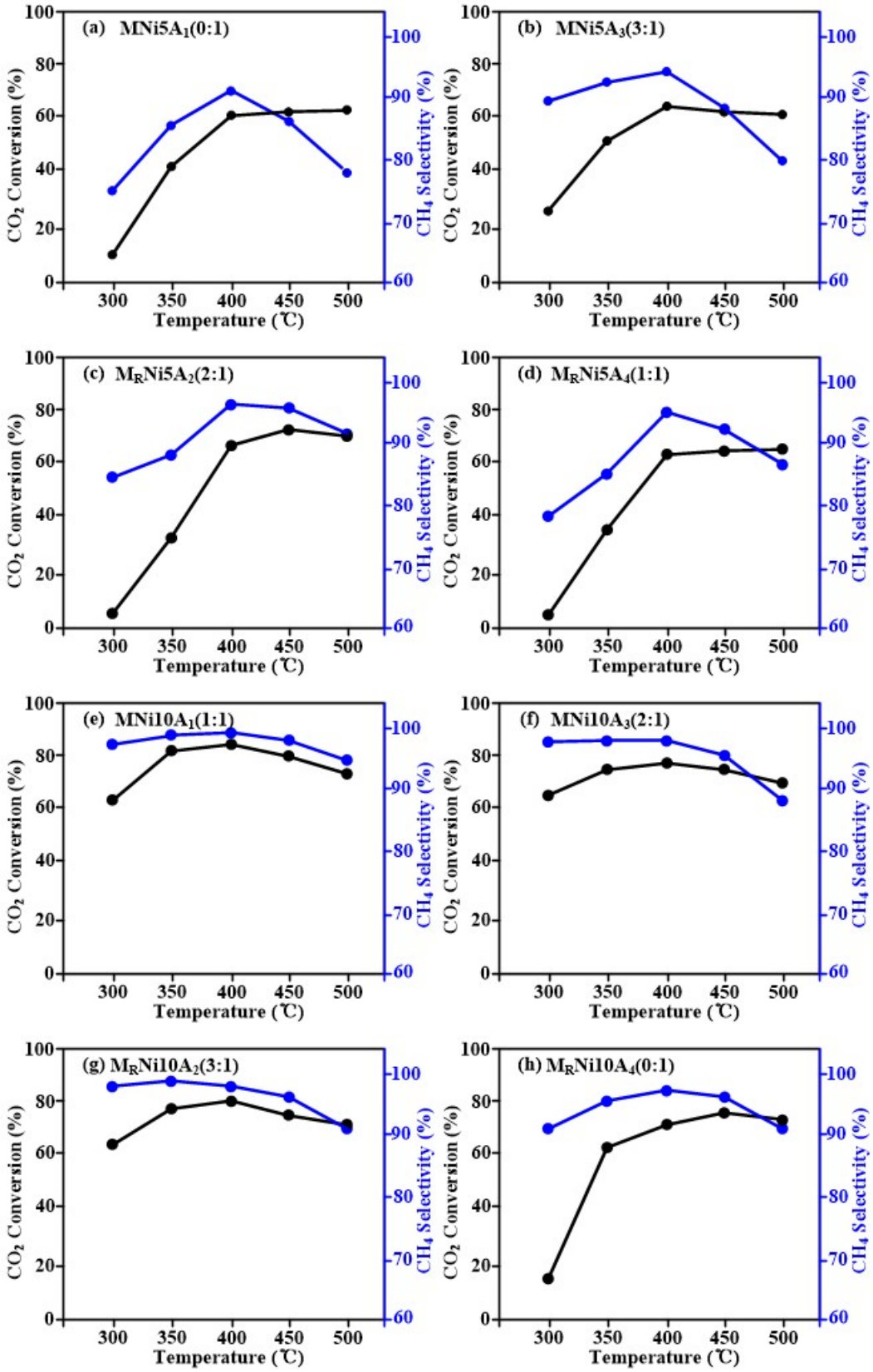


Fig. S5. CO Conversion and CH_4 selectivity of different catalysts for CO methanation.


(a) MNi5A1(0:1)
(b) MNi5A3(3:1)
(c) MRNi5A2(2:1)
(d) MRNi5A4(1:1)
(e) MNi10A1(1:1)
(f) MNi10A3(2:1)
(g) MRNi10A2(3:1)
(h) MRNi10A4(0:1)
CO2 Conversion (%)
CH4 Selectivity (%)
Temperature (℃)
0
20
40
60
80
100
60
70
80
90
100
300
350
400
450
500

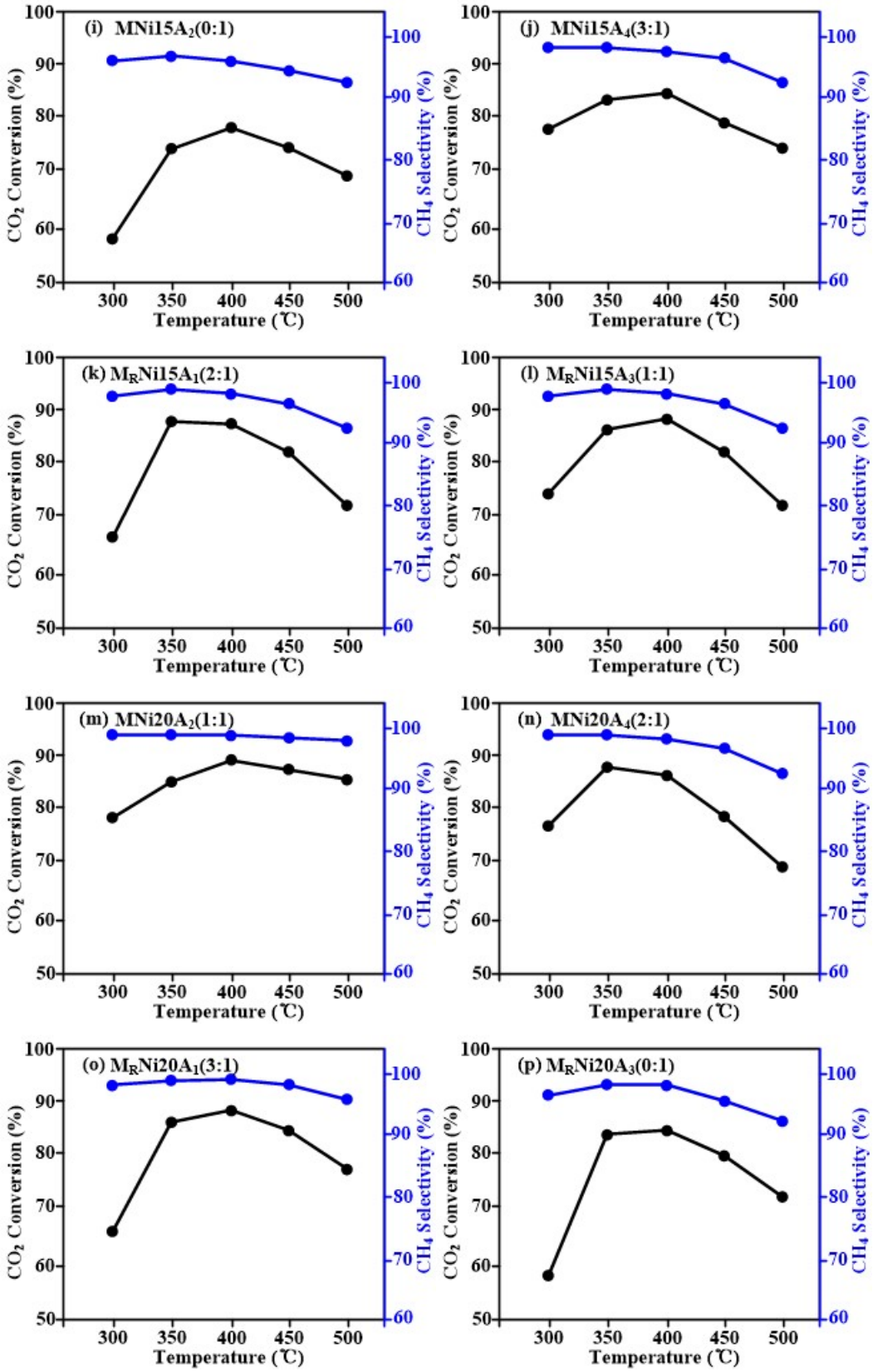


Fig. S6. CO_2 Conversion and CH_4 selectivity of different catalysts for CO_2 methanation.

3. Stability

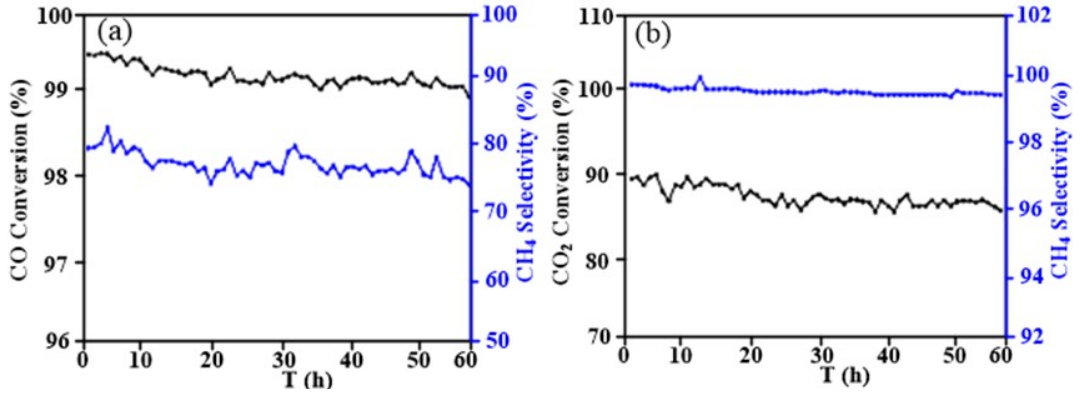


Fig. S7. Time on steam of the catalyst of $MNi20A_2$(1:1) (a) CO methanation and (b) CO_2 methanation. GHSV= 12000 h^{-1}, 0.1MPa and T= 400 ℃ for CO methanation; GHSV= 15000 h^{-1}, 0.1 MPa and T= 400 ℃ for CO_2 methanation.

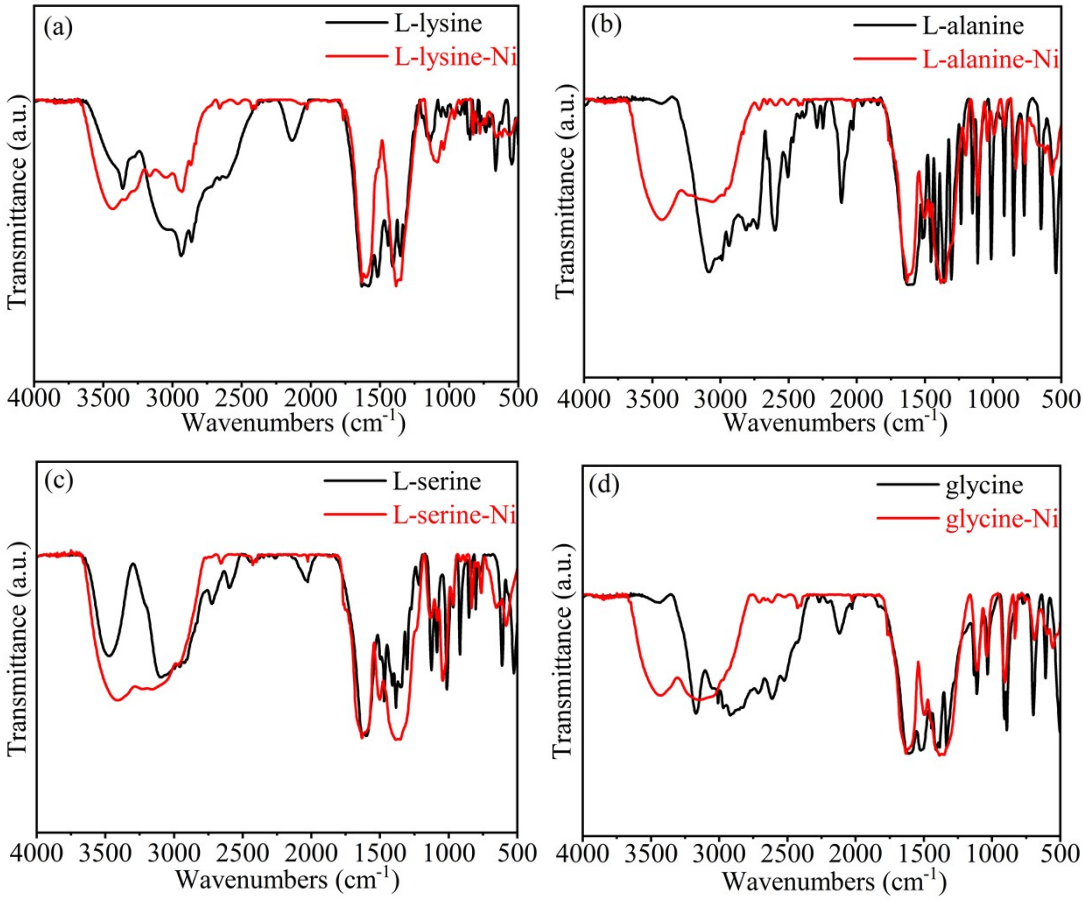


Fig. S8. FT-IR spectra of the samples (a) L-lysine, L-lysine-Ni, (b) L-alanine, L-alanine-Ni, (c) L-serine, L-serine-Ni, (d) glycine, glycine-Ni.