Electronic Supplementary Information

Synergetic effect of Ni and Co in Ni-Co/SBA-15-CD catalysts and their catalytic performance in carbon dioxide reforming of methane to syngas

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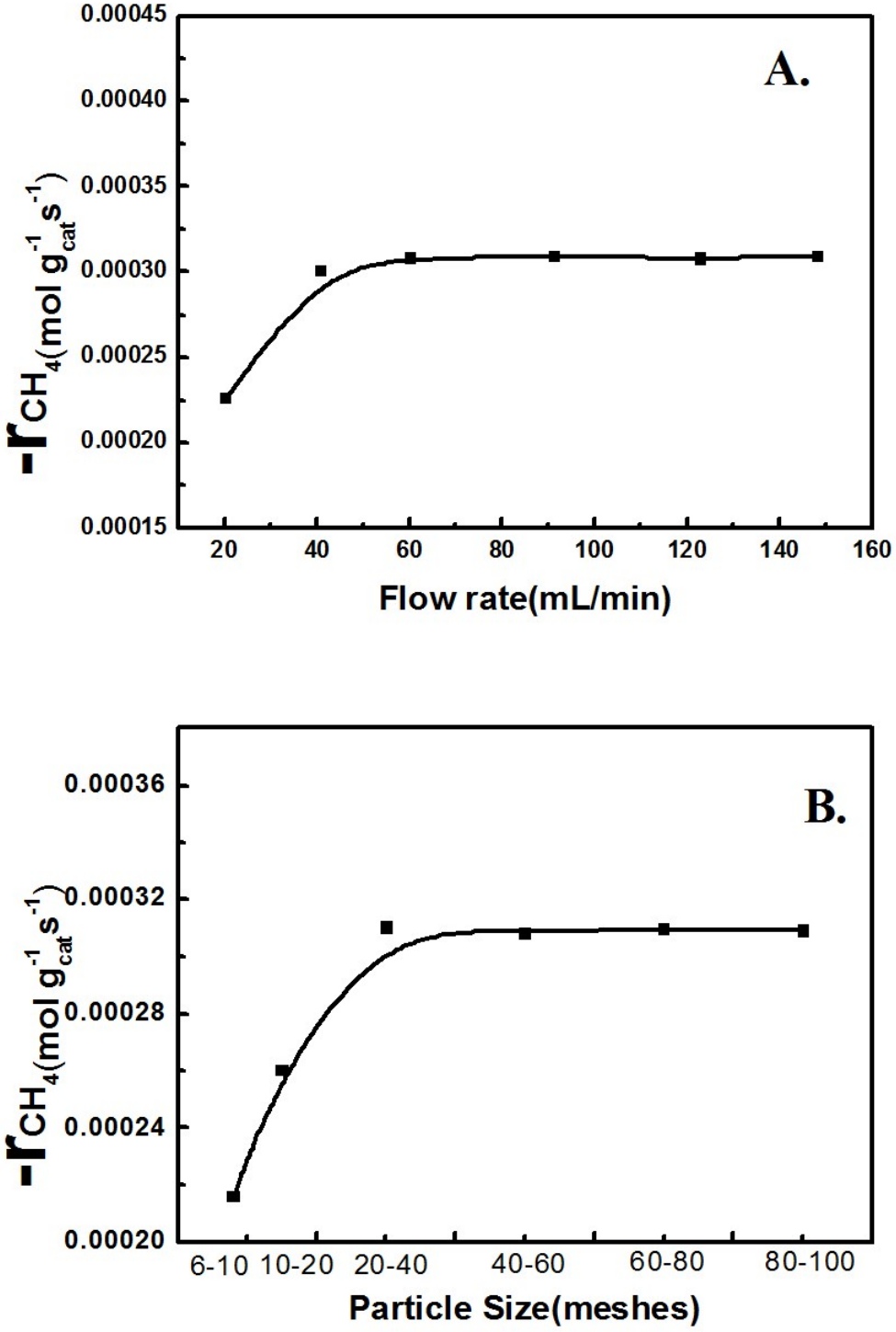


Fig. S1 Elimination of transport artifacts (A) external diffusion (B) internal diffusion of 5Ni/SBA-15-CD catalysts

Reaction conditions: atmospheric pressure, 800 ^{o}C, CO_2/CH_4=1

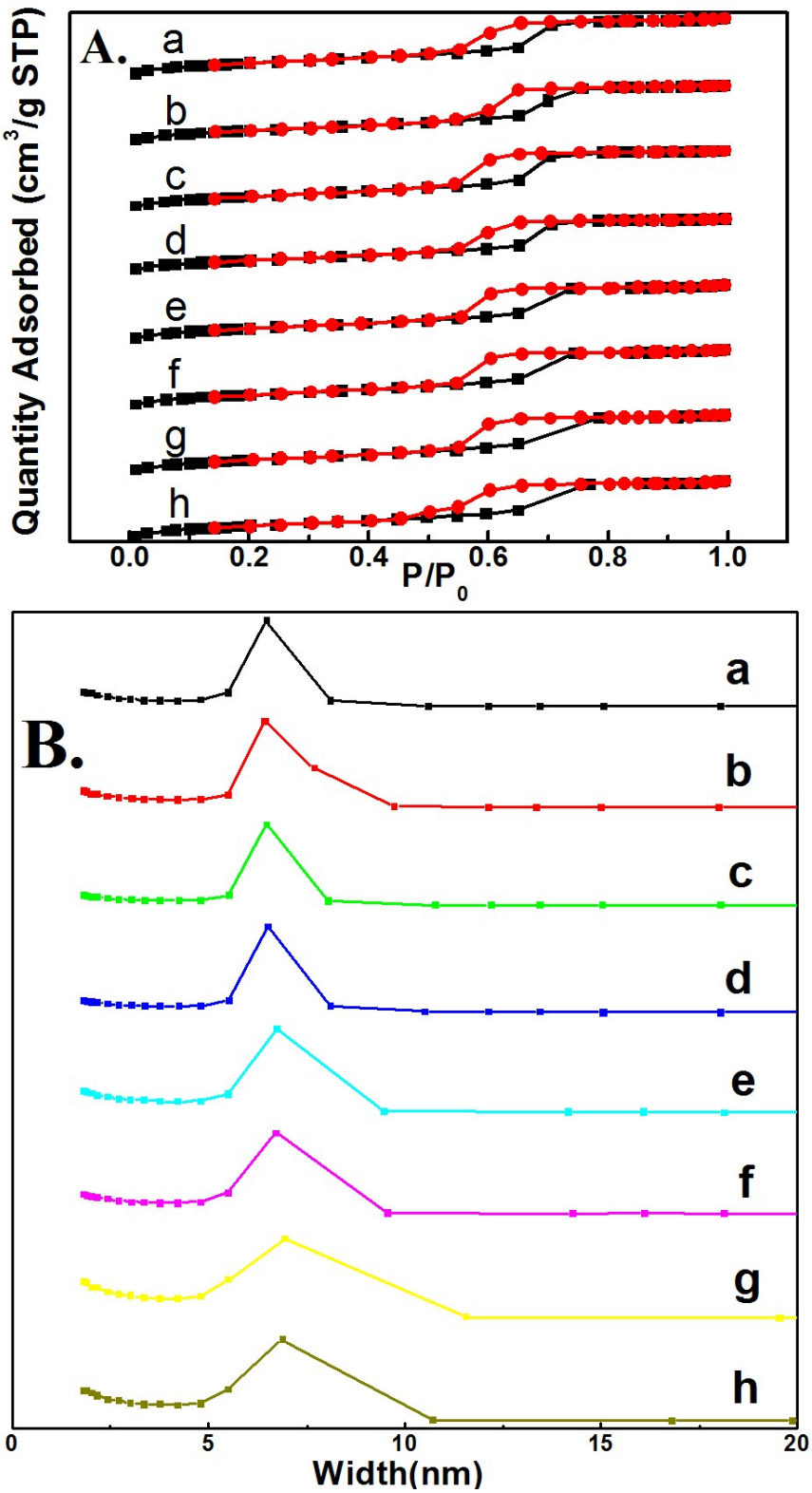


Fig. S2 N_2 adsorption-desorption isotherms (A) and pore size distributions (B) of fresh xNiyCo/SBA-15-CD

a, 5Ni; b, 4.5Ni0.5Co; c, 4Ni1Co; d, 3.5Ni2.5Co; e, 3Ni2Co; f, 2.5Ni2.5Co; g, 2Ni3Co; h, 5Co

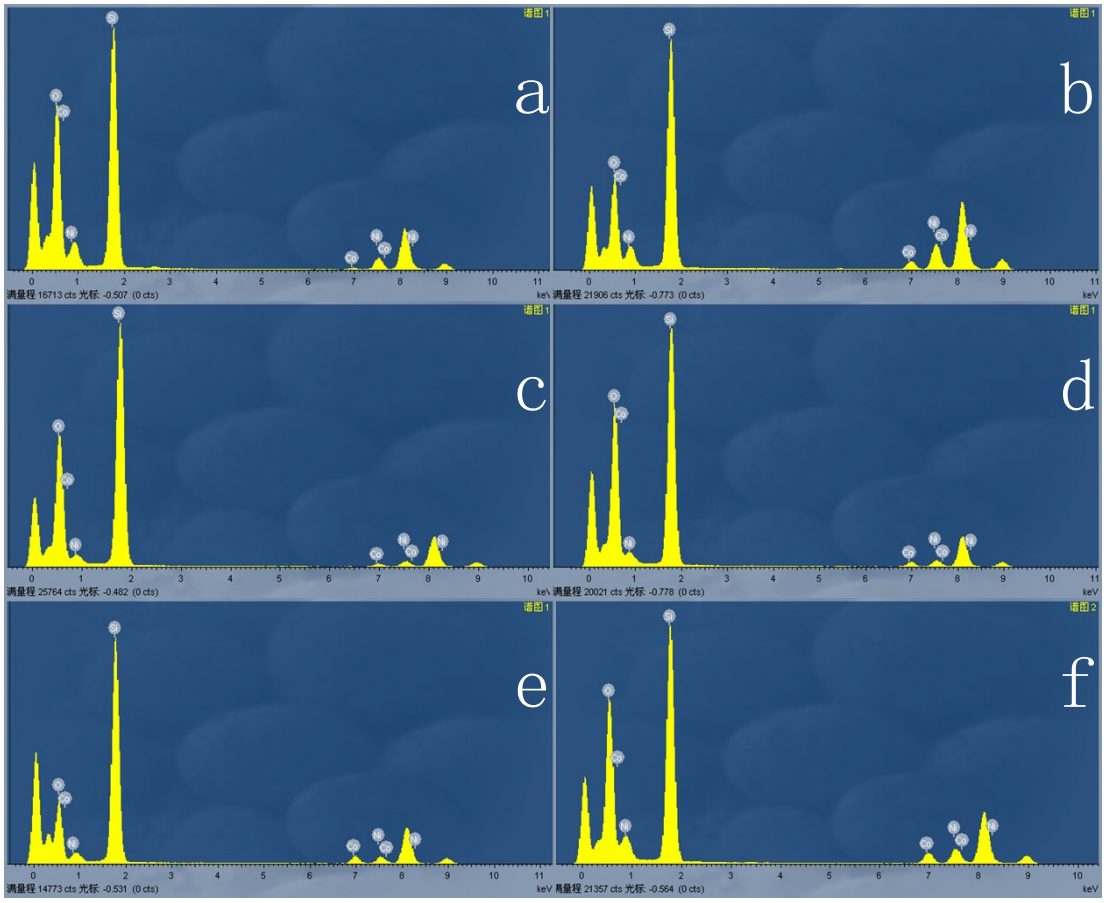
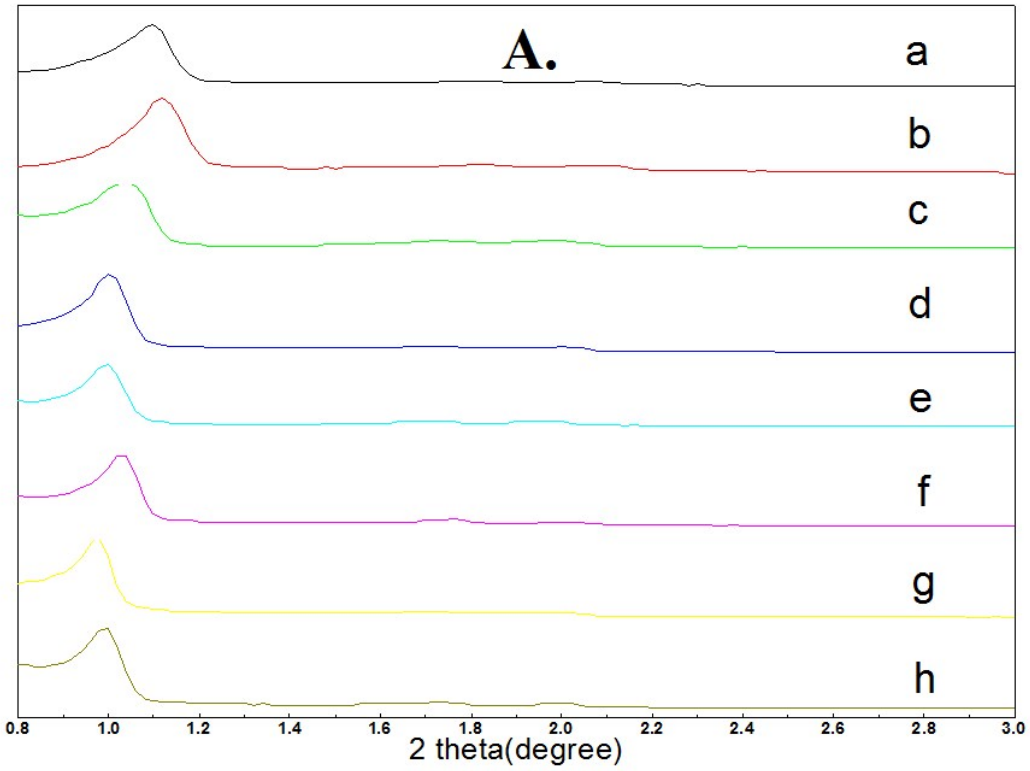


Fig. S3 EDS of fresh xNiyCo/SBA-15-CD

a, 4.5Ni0.5C; b, 4Ni1Co; c, 3.5Ni2.5Co; d, 3Ni2Co; e, 2.5Ni2.5Co; f, 2Ni3Co



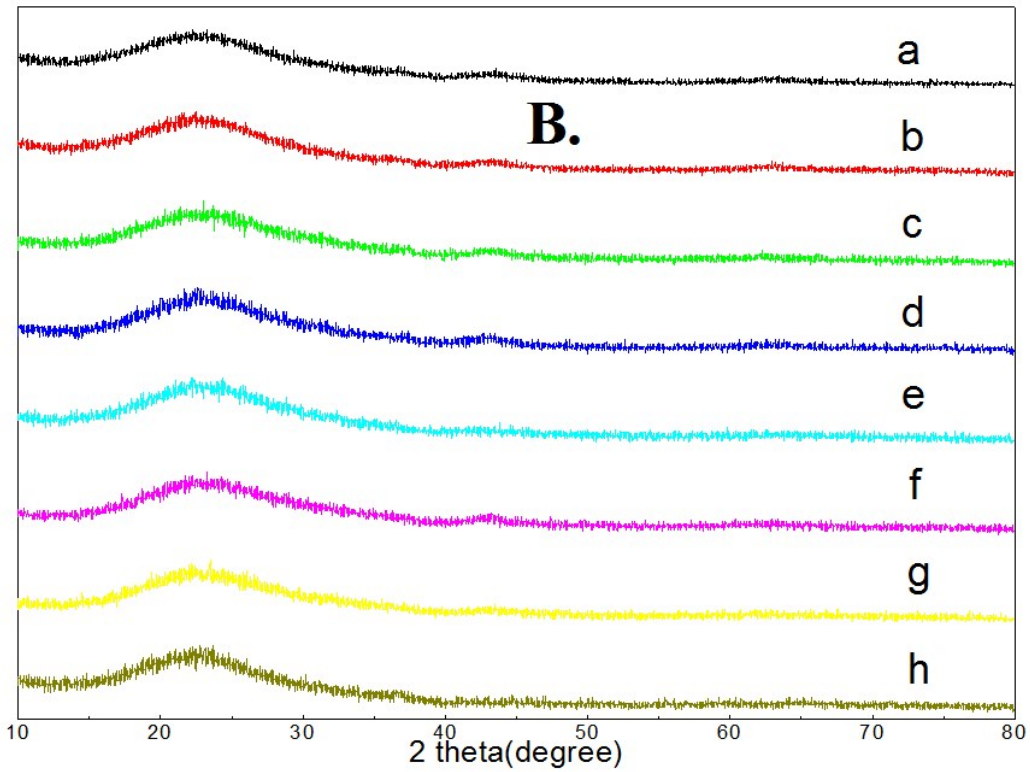


Fig. S4 XRD patterns of fresh xNiyCo/SBA-15-CD
(A) small angle XRD patterns; (B) wide angle XRD patterns
a, 5Ni; b, 4.5Ni0.5Co; c, 4Ni1Co; d, 3.5Ni2.5Co; e, 3Ni2Co; f, 2.5Ni2.5Co; g, 2Ni3Co; h, 5Co

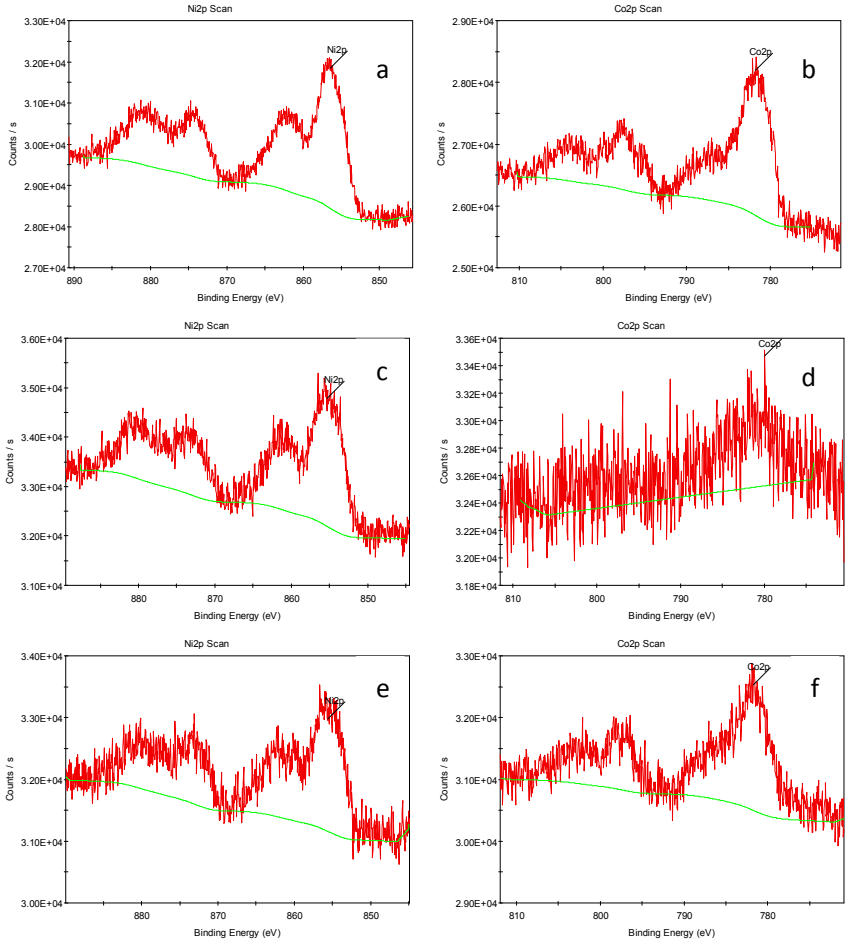


Fig. S5 XPS scan of xNiyCo/SBA-15-CD
a, Ni 2p of 5Ni; b, Co 2p of 5Co; c, Ni 2p of 4.5Ni0.5Co; d, Co 2p of 4.5Ni0.5Co; e, Ni 2p of 3Ni2Co; f, Co 2p of 3Ni2Co

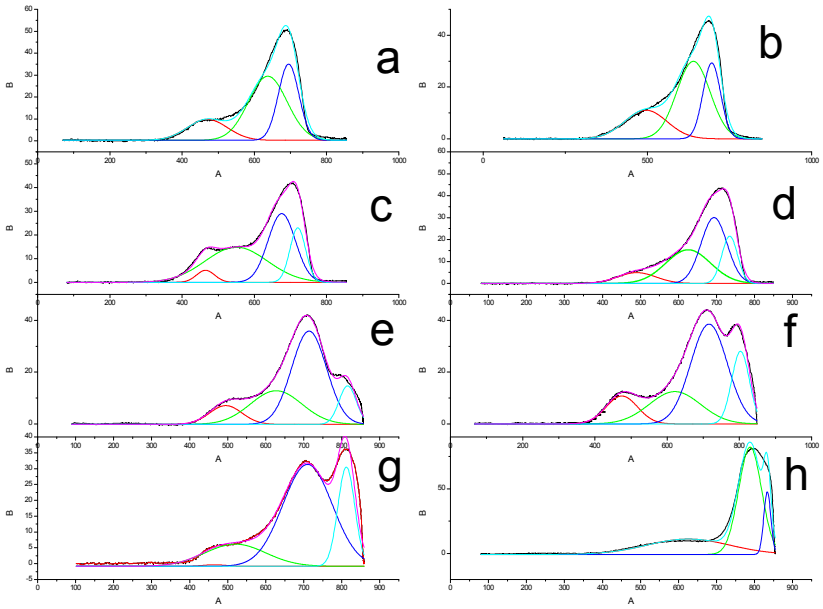


Fig. S6 Curve fitting of TPR of fresh xNiyCo/SBA-15-CD

a, 5Ni; b, 4.5Ni0.5Co; c, 4Ni1Co; d, 3.5Ni2.5Co; e, 3Ni2Co; f, 2.5Ni2.5Co; g, 2Ni3Co; h, 5Co

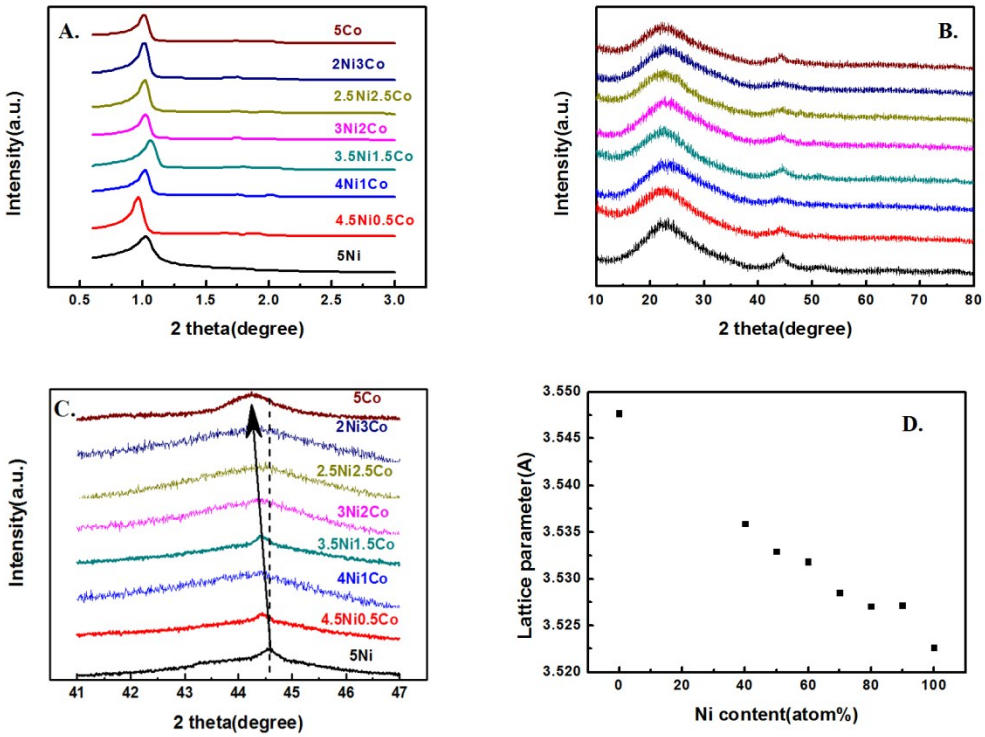


Fig. S7 XRD patterns of reduced xNiyCo/SBA-15-CD
(A) Small angle XRD patterns; (B) wide angle XRD patterns; (C) step scan patterns; (D) lattice parameters

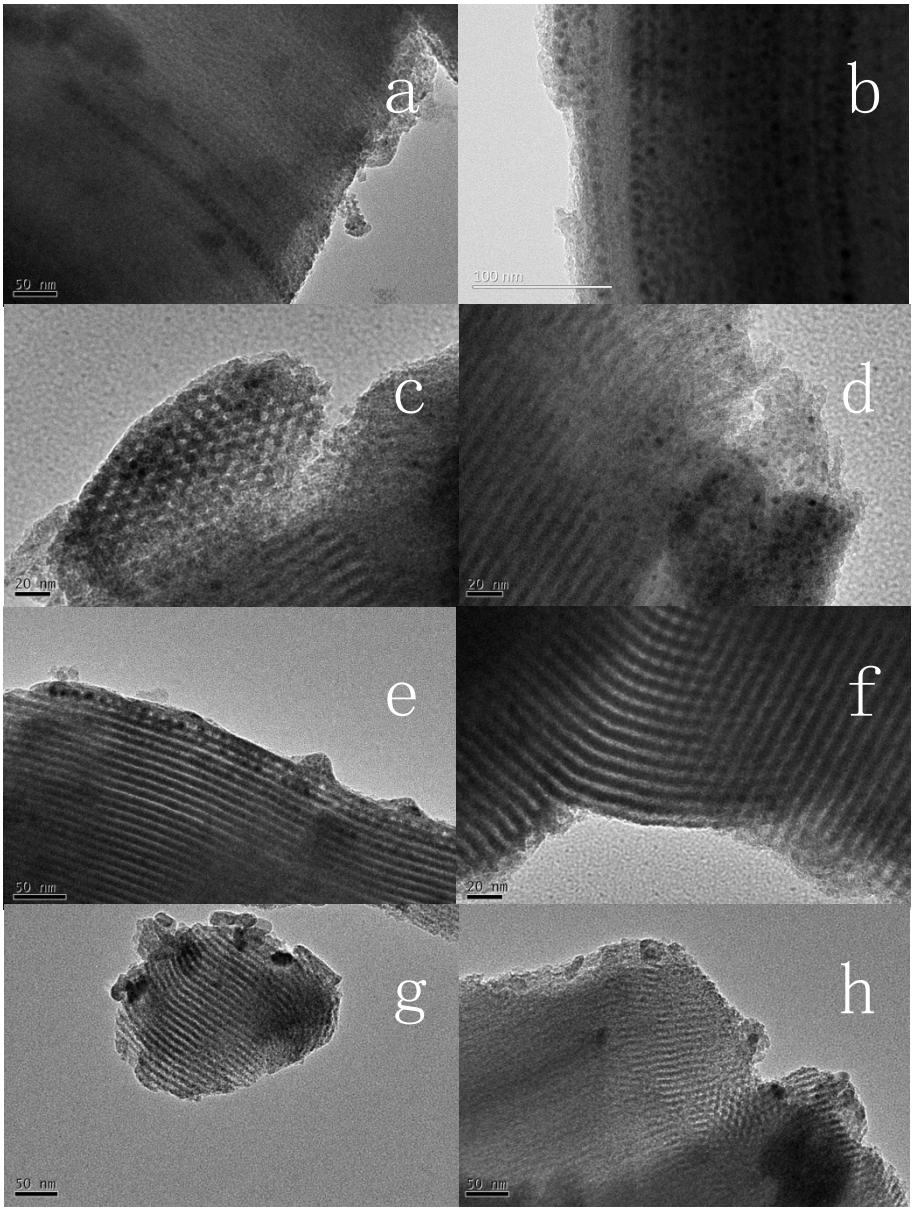


Fig. S8 TEM images of reduced xNiyCo/SBA-15-CD

a, 5Ni; b, 4.5Ni0.5Co; c, 4Ni1Co; d, 3.5Ni2.5Co; e, 3Ni2Co; f, 2.5Ni2.5Co; g, 2Ni3Co; h, 5Co

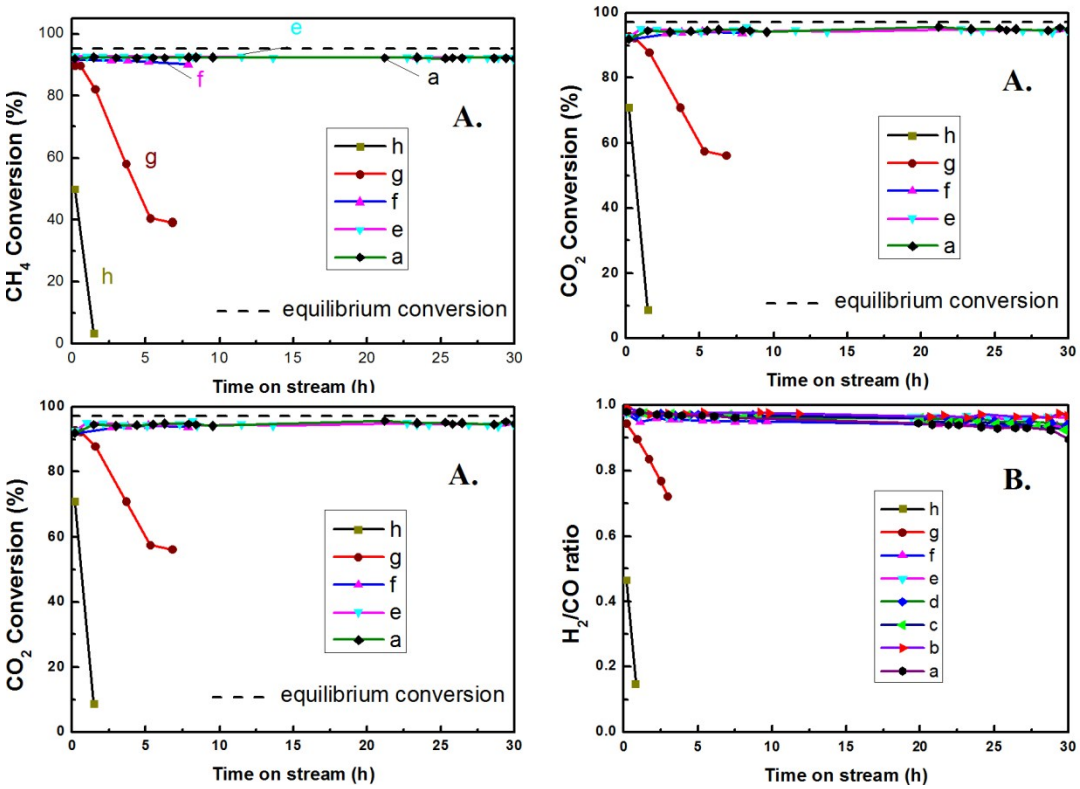


Fig. S9 Catalytic performance of xNiyCo/SBA-15-CD in CRM
(A) GHSV=1.8×10^4 mL/g·h; (B) GHSV=3.6×10^4 mL/g·h

Reaction conditions: atmospheric pressure, 800 ^{o}C, CO_2/CH_4=1

a, 5Ni; b, 4.5Ni0.5Co; c, 4Ni1Co; d, 3.5Ni2.5Co; e, 3Ni2Co; f, 2.5Ni2.5Co; g, 2Ni3Co; h, 5Co

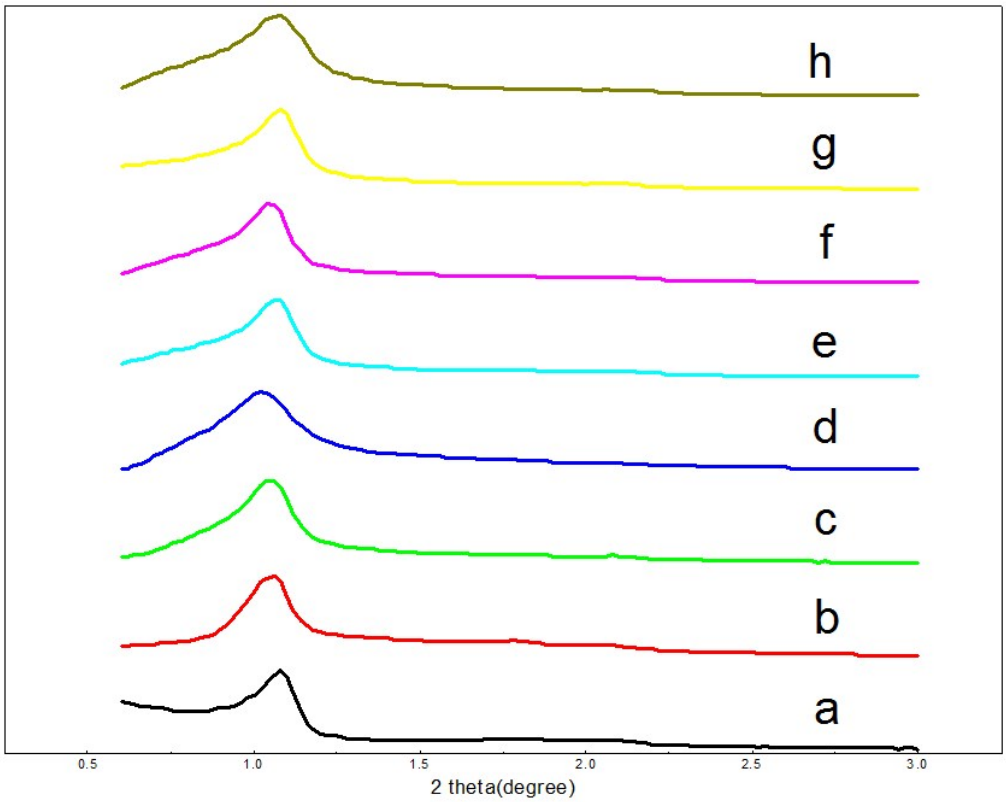


Fig. S10 Small angle XRD patterns of spend xNiyCo/SBA-15-CD

a, 5Ni; b, 4.5Ni0.5Co; c, 4Ni1Co; d, 3.5Ni2.5Co; e, 3Ni2Co; f, 2.5Ni2.5Co; g, 2Ni3Co; h, 5Co

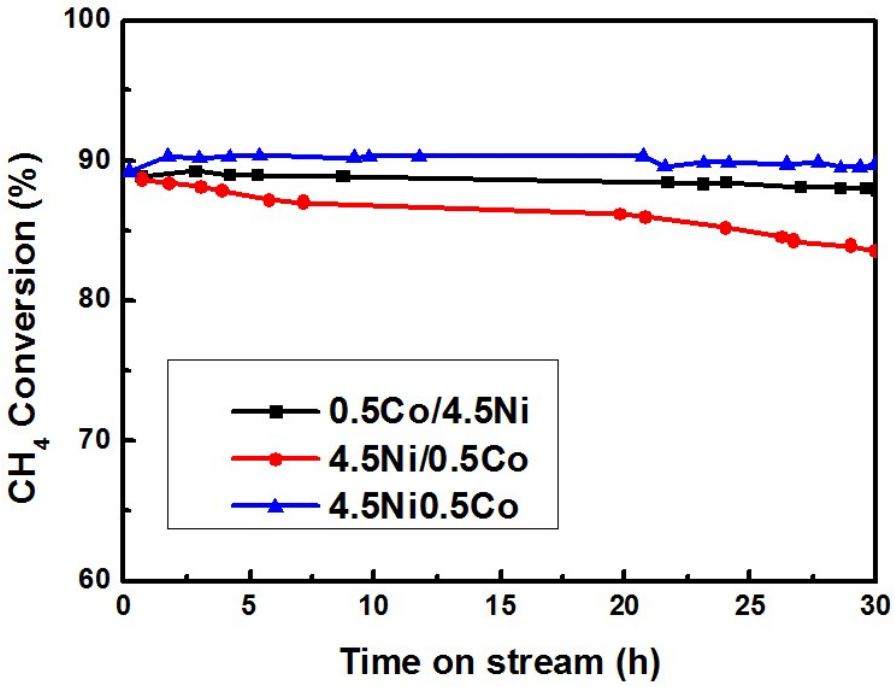


Fig. S11 Catalytic performance of catalysts prepared with different method in CRM Reaction conditions: atmospheric pressure, 800 ^{o}C, CO_2/CH_4=1, GHSV=3.6×10^4 mL/g·h

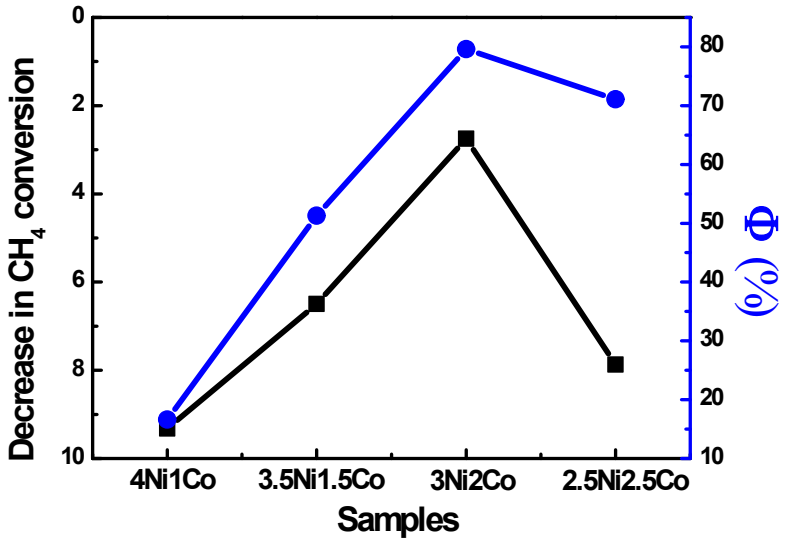


Fig. S12 The trend of Φ and decrease in CH_4 conversion with different Ni/Co ratio

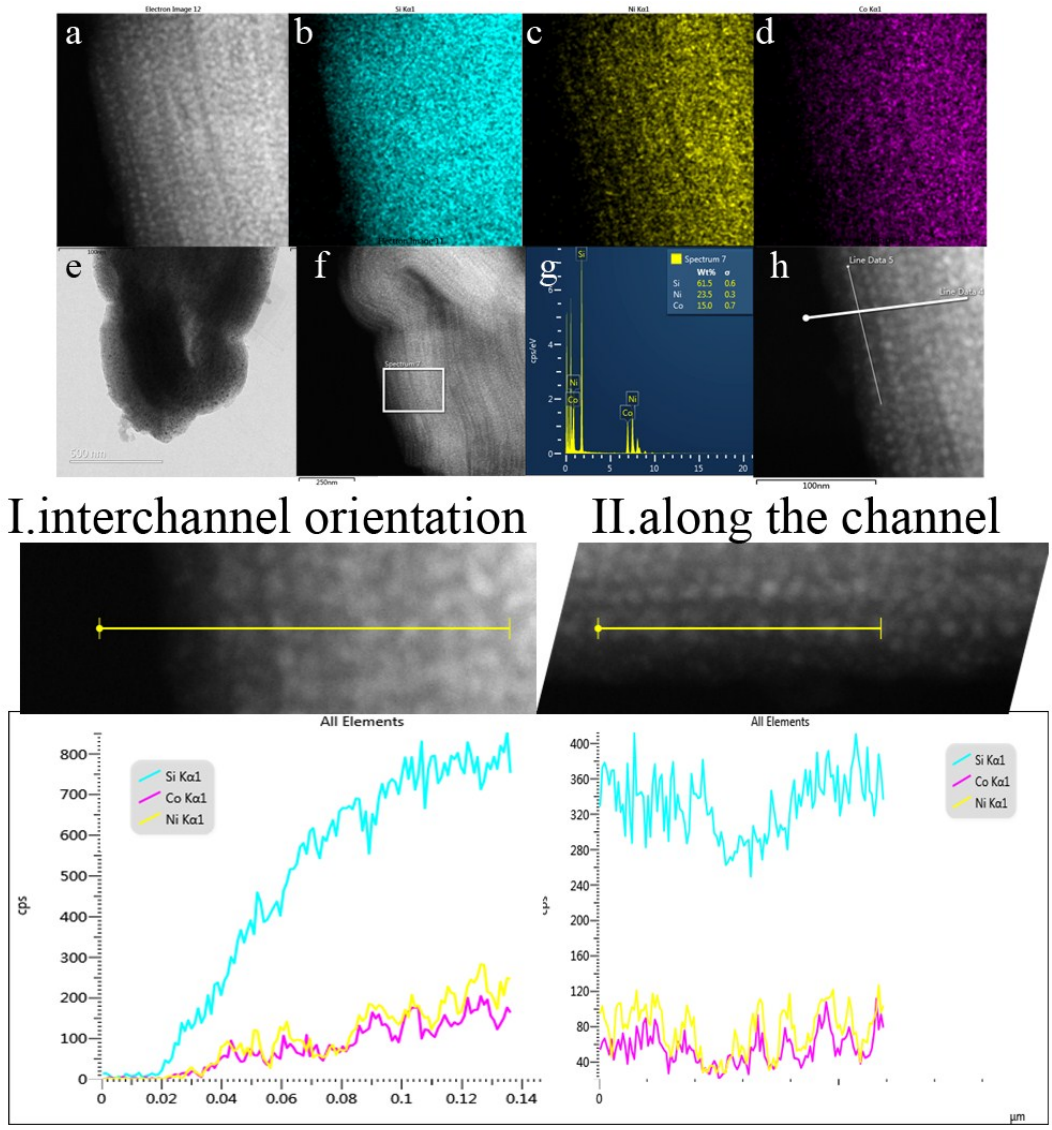


Fig. S13 the HAADF-STEM –mapping of reduced 3Ni2Co catalysts

(a) HAADF-STEM; (b~d) EDX mapping images of Si, Ni and Co, (e) HRTEM; (f~g) HAADF-EDX (h) EDX-line scan (I) interchannel orientation (II)along the channel

Table S1 Textural properties of fresh xNiyCo/SBA-15-CD

Catalysts	Pore volume (cm^3/g)	Average pore width(nm)	Specific surface area (m^2/g)
5Ni/SBA-15	0.61	5.04	534
4.5Ni0.5Co/SBA-15	0.65	5.32	523
4Ni1Co/SBA-15	0.56	5.04	461
3.5Ni1.5Co/SBA-15	0.54	5.11	437
3Ni2Co/SBA-15	0.56	5.02	478
2.5Ni2.5Co/SBA-15	0.55	5.06	454
2Ni3Co/SBA-15	0.55	5.03	466
5Co/SBA-15	0.55	4.78	469

*Measured by N_2 adsorption-desorption method.

Table S2 The results of linear combination of Co K-XANES of fresh xNiyCo/SBA-15-CD with two reference material

Catalysts	CoO	Co_3O_4	R-factor
4.5Ni0.5Co	0.563	0.437	0.0167
4Ni1Co	0.528	0.472	0.0331
3.5Ni1.5Co	0.527	0.473	0.0338
3Ni2Co	0.508	0.492	0.0502
2.5Ni2.5Co	0.490	0.510	0.0611
2Ni3Co	0.451	0.549	0.0733
5Co	0.258	0.742	0.0549

Table S3 the binding energy of fresh xNiyCo/SBA-15-CD

Samples	Binding Energy(eV)	
	Ni 2p $_{1/2}$	Co 2p $_{1/2}$
5Ni	855.4	
4.5Ni0.5Co	855.3	781.4
3Ni2Co	855.5	781.6
5Co		781.9

*Measured by XPS.

Table S4 Qualitative results of the curve fitting of TPR profiles

Catalysts	Temperature of sub-peaks (°C)						
	<500	**520~550[a]**	**620~640[b]**	**675~700**	**710~735[a]**	**788~815**	**>830**
5Ni	470		637	695			
4.5Ni0.5Co	495		640	696			
4Ni1Co	465	550		676	720		
3.5Ni1.5Co	490		625	693	735		
3Ni2Co	495		627		714	815	
2.5Ni2.5Co	475		622		716	803	
2Ni3Co	465	520			710	812	
5Co			626			788	833

a, absent in mono-metal catalysts but appeared in bimetallic catalysts
b, coexisted in mono-metal and bimetallic catalysts

Table S5 Quantitative results of the curve fitting of TPR profiles

Samples	the amount of hydrogen consumption of sub-peaks(umol)							reduction degree	Φ(%)[c]
	<500	520~550[a]	620~640[b]	675~700	713~734[a]	788~815	829~833		
5Ni	8.7	-	25.5	16.2	-	-	-	0.715	-
4.5Ni0.5Co	12.2	-	26.1	13.5	-	-	-	0.728	-
4Ni1Co	2.5	24.6	-	21.2	9.6	-	-	0.765	16.6
3.5Ni1.5Co	4.5	-	16.5	18.8	8.1	-	-	0.699	51.3
3Ni2Co	4.6	-	13.0	-	24.5	5	-	0.701	79.6
2.5Ni2.5Co	7.8	-	14.8	-	32.6	11.4	-	0.849	71.1
2Ni3Co	0.2	7.3	-	-	27.3	9.1	-	0.668	62.2
5Co	-	-	18.5	-	-	35.5	6.3	0.801	-

a, absent in monometallic catalysts but appeared in bimetallic catalysts

b, coexisted in monometallic and bimetallic catalysts

c, calculated by (peak-A + peak-B)/total hydrogen consumption

Table S6 Structural parameters and estimated uncertainties (in parentheses) from EXAFS of reduced xNiyCo/SBA-15-CD

	Ni-O_1(Å)			Co-O_1(Å)			Co-O_1(Å)			Ni-Ni_2(Å)			Co-Co_2(Å)		
	CN	**R(Å)**	**σ^2(Å^2)**	**CN**	**R(Å)**	**σ^2(Å^2)**	**CN**	**R(Å)**	**σ^2(Å^2)**	**CN**	**R(Å)**	**σ^2(Å^2)**	**CN**	**R(Å)**	**σ^2(Å^2)**
NiO	6	2.08(1)	0.0047(1)												
CoO				6.0	2.11(1)	0.0055(12)									
Ni-foil										12	2.48(1)	0.0061(2)			
5Ni	1.7(3)	2.09(6)	0.0120(36)							4.2(7)	2.47(1)	0.0094(11)			
4.5Ni0.5Co	2.0(2)	2.09(4)	0.0124(27)	2.4(1.1)	2.01(4)	0.0072(35)				4.5(7)	2.47(1)	0.0097(13)	2.7(5)	2.52(2)	0.0068(22)
4Ni1Co	1.9(3)	2.08(5)	0.0124(31)	2.0(1.0)	2.02(5)	0.0072(45)				4.7(8)	2.47(1)	0.0095(15)	2.9(4)	2.50(2)	0.0084(17)
3.5Ni1.5Co	1.8(2)	2.07(4)	0.0125(27)	1.9(9)	2.04(6)	0.0107(51)				5.1(6)	2.48(1)	0.0091(11)	3.6(8)	2.49(2)	0.0083(21)
3Ni2Co	2.9(4)	2.09(5)	0.0123(36)	1.9(9)	2.06(6)	0.0010(55)				4.8(1.5)	2.48(2)	0.0105(27)	2.6(5)	2.5(3)	0.0088(25)
2.5Ni2.5Co	2.5(4)	2.09(5)	0.0126(34)	1.6(8)	2.05(5)	0.0093(50)				5.5(1)	2.47(1)	0.0100(17)	2.7(4)	2.49(2)	0.0088(24)
2Ni3Co	2.7(5)	2.09(7)	0.0124(46)	1.6(5)	2.04(4)	0.0086(35)				6.1(1.7)	2.48(1)	0.0096(23)	3.2(5)	2.5(1)	0.0091(17)
5Co							1.5(5)	2.03(5)	0.0114(38)				2.8(2)	2.50(1)	0.0066(9)
Co-foil													12	2.50(0.2)	0.0068(3)
Co_3O_4							5	1.92(1)	0.0025(10)						

Table S7 The detail of CH_4 conversion of xNiyCo/SBA-15-CD in CRM reaction

Catalysts	CH_4 conversion[a]		decrease in CH_4 conversion[a]	CH_4 conversion[b]		decrease in CH_4 conversion(%)[b]
	initial	final		initial	final	
5Ni	88.5	78.5	10.0	21.7	9.6	55.7
4.5Ni0.5Co	89.2	89.7	-0.5	26.9	18.7	30.7
4Ni1Co	89.2	79.8	9.4	24.9	15.4	38.3
3.5Ni1.5Co	90.8	84.3	6.5	20.9	12.5	40.3
3Ni2Co	90.3	87.5	2.8	24.2	16.3	32.5
2.5Ni2.5Co	88.8	80.9	7.9	19.4	11.4	41.3
2Ni3Co	82.9	46.5	36.4	22.5	8.4	62.5
5Co	16.9	5.7	11.2	3.8	2.0	47.5

a, 800 ^oC, GHSV=3.6×10^4 mL/g·h, atmospheric pressure, CO_2/CH_4=1,30h;
c, 650 ^oC, GHSV=4.4×10^5 mL/g·h, atmospheric pressure, CO_2/CH_4=1, 200min;

Table S8 mass balance of xNiyCo/SBA-15-CD in CRM reaction

Catalysts	mass balance (carbon balance)[a]		
	1[b]	2[c]	3[d]
5Ni	0.969	0.977	0.983
4.5Ni0.5Co	0.972	-	0.979
4Ni1Co	0.964	-	0.964
3.5Ni1.5Co	0.984	-	0.996
3Ni2Co	0.982	0.970	0.999
2.5Ni2.5Co	0.985	0.968	0.998
2Ni3Co	0.973	0.972	0.972
5Co	0.989	1.000	0.983

a, calculated by (molar of carbonic species in outgas)/(molar of feed gas);
b, 650 °C, GHSV=4.4×10^5 mL/g·h, atmospheric pressure, CO_2/CH_4=1;
c, 800 °C, GHSV=1.8×10^4 mL/g·h, atmospheric pressure, CO_2/CH_4=1;
d, 800 °C, GHSV=3.6×10^4 mL/g·h, atmospheric pressure, CO_2/CH_4=1;