

Electronic Supplementary Information for

Silica-based micro- and mesoporous catalysts for dry reforming of methane

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Table S1 Microporous silica-based catalysts for DRM reaction

Catalyst	Synthesis method	Catalytic performance			Carbon resistance	Reaction Conditions	Reasons to performance	Metal Loading wt%	Ref
		CH ₄	CO ₂	H ₂ /CO Ratio					
Ni supported on silicalite-1 zeolite coated SiC foam (Ni/S-1/SiC)	Wet impregnation	65	40	1.3	Negligible after 30 h TOS	750 °C, GHSV = 15 L _{gcat} ⁻¹ h ⁻¹ , CH ₄ : CO ₂ : O ₂ = 8: 2: 3	Strong MSI, small Ni particle size (4.5 nm after 100 h reaction) and high Ni dispersion	14	38
10Ni/10MgO-β zeolite	Wet impregnation	90	95	0.9	2mg _{coke} g _{cat} ⁻¹ h ⁻¹	800 °C, GHSV = 60 L _{gcat} ⁻¹ h ⁻¹ , CH ₄ : CO ₂ = 1: 1	Within 7 h, CH ₄ and CO ₂ conversions decreased by 10.5% and 8%, respectively	10	8
Ni-ITQ-6	Incipient wet impregnation	77	90	1.39	2.1% after 7 h	700 °C, GHSV = 30 L _{gcat} ⁻¹ h ⁻¹ , CH ₄ : CO ₂ = 1: 1	Side reactions including Boudouard reaction and steam reforming reaction lead to high H ₂ /CO ratio	5	33
Ni-ZSM-5	Wet impregnation	95	98	0.9	1% after 30 h	800 °C, GHSV = 12 L _{gcat} ⁻¹ h ⁻¹ , CH ₄ : CO ₂ = 1: 1	Higher crystallization lead to higher catalytic performance	5	35
1Ni-2Co-ZSM-5	Wet impregnation	60	65	0.82	5% after 12 h	700 °C, GHSV = 60 L _{gcat} ⁻¹ h ⁻¹ , CH ₄ : CO ₂ : N ₂ = 1: 1: 3	Synergistic effect between Ni and Co decreased carbon deposition	7	36
1.5Ni-0.5Pt@Hollow silicalite-1	Incipient wet impregnation and silicon leaching	75	82	-	1% after 6 h	800 °C, GHSV = 72 L _{gcat} ⁻¹ h ⁻¹ , CH ₄ : CO ₂ = 1: 1	Sintering of Ni outside shell occurred	1.5Ni-0.5Pt	37

Table S2 Mesoporous silica-based catalysts

Catalyst	Synthesis method	Catalytic performance			Carbon resistance	Reaction Conditions	Remarks	Metal Loading wt%	Ref
		CH ₄	CO ₂	H ₂ /C/O					
Ni based catalysts									
Ni-SBA-15	Solid-state grinding	78	86	1.05	6.3% after 100 h	700 °C, GHSV = 22.5 L _{gcat} ⁻¹ h ⁻¹ , CO ₂ : CH ₄ = 1: 1	Strong MSI, small Ni particle size (4.5 nm after 100 h reaction) and high Ni dispersion	5	40
Ni-KIT-6		76	85	1.05	8.1% after 100 h		Strong MSI, small Ni particle size (6.5 nm after 100 h reaction) and high Ni dispersion		
Ni-MCM-41		decrease from 79% to 69%	decrease from 84% to 77%	0.93	38.8% after 100 h		Weak MSI, sintering of Ni, big Ni enwrapped by carbon nanotubes		
Ni-KIT-6	Impregnation	40	53	0.9	-	700 °C, GHSV = 60 L _{gcat} ⁻¹ h ⁻¹ , N ₂ : CO ₂ : CH ₄ =3: 1: 1	Low Ni (0.5 wt%) loading lead to high dispersion but low DRM activity due to the low accessibility of Ni confined within the micropores of KIT-6	2	66
Ni-SBA-15	Impregnation (pretreated Ni precursor with (PEI))	87.5	88	0.92	Negligible after 40 h	750 °C, GHSV = 20 L _{gcat} ⁻¹ h ⁻¹ , CO ₂ : CH ₄ : N ₂ = 2: 2: 1	NH ₂ groups in PEI help Ni precursor bond to the silanol groups on surface of SBA-15 and inhibit their sintering due to steric hindrance	-	55
5-Ni ₄ /SBA-15	Impregnation [Ni ₄ O ₄] cubane cluster	65	-	0.88	5.56%	600 °C, GHSV = 36 L _{gcat} ⁻¹ h ⁻¹ , CO ₂ : CH ₄ : N ₂ = 1: 1: 8	Small and highly dispersed NiO NPs	1.67	56

Ni/SBA-15	Impregnation with EG as solvent	87	96	1.1	Negligible after 20 h	750 °C, GHSV = 7.5 L _{gcat} ⁻¹ h ⁻¹ , CO ₂ : CH ₄ = 1: 1	Interesting and effective method to prepare mesoporous silica confined catalysts	-	54
Ni-hexagonal mesoporous silica	One pot self-assembled method	76	84	0.8	5% after 100 h	700 °C, GHSV = 22.5 L _{gcat} ⁻¹ h ⁻¹ , CO ₂ : CH ₄ = 1: 1	Stable conversion within 100 h	7.5	67
Ni based bimetallic catalyst									
Ni9Co1-SBA-15	Urea co-precipitation	60	73	1	Negligible after 50 h	700 °C, GHSV = 72 L _{gcat} ⁻¹ h ⁻¹ , CO ₂ : CH ₄ = 1: 1	High metal dispersion (ca. 17–20%) and small metal particle sizes (ca.4–5 nm), synergetic effect of Co and Ni, confinement effect	10	24
0.5Ru/12Co/SBA-15	Two-solvent impregnation	43	51	1.1	-	550 °C, GHSV = 67 L _{gcat} ⁻¹ h ⁻¹ , CO ₂ : CH ₄ = 1: 1	Ru addition enhanced the reducibility of Co species, stabilized Co from migration and increased active phases	0.5Ru-12Co	68
Perovskite catalyst									
LaNiO ₃ -SBA-15	Wet impregnation	75	67	1.05	4.5	700 °C, GHSV = 36 L _{gcat} ⁻¹ h ⁻¹ , CO ₂ : CH ₄ = 1: 1	Stable structure restricted the agglomeration of Ni	10	48
LaNiO ₃ -MCM-41	with metal citrate complex	77	66	1.0	4.8		MCM-41 structure collapsed after reaction leading to some Ni sintering		
LaNiO ₃ -SiO ₂	precursors	60	61	0.95	5.7		Carbon deposition leads to worse catalytic performance		
La ₂ NiO ₄ -KIT-6	Sol-gel	100	100	0.95	3.75% after 60 h	800 °C, GHSV = 33.6 L _{gcat} ⁻¹ h ⁻¹ , CO ₂ : CH ₄ = 1: 1	Stable cubic structure of KIT-6 and the formation of La ₂ O ₃ prevented Ni sintering	10	69
Ni based catalysts with promoters									
3Sm-10Ni-	Two-solvent impregnation	70	75	H ₂ and	No peaks observed for	700 °C, GHSV = 12 L _{gcat} ⁻¹ h ⁻¹ , CO ₂ : CH ₄ =	High oxygen storage capacity and redox potential of Sm ₂ O ₃ , improved Ni dispersion and MSI	10	71

SBA-15				CO selectivity of 0.88 and 1.05, respectively	TPO after 5 h	1: 1			
1Sm-10Ni-SBA-15	Two-solvent impregnation	56	66	-	20% after 12 h	700 °C, GHSV = 12 L _{gcat} ⁻¹ h ⁻¹ , CO ₂ : CH ₄ = 1: 1	Small NiO size and high dispersion, the findings of opposite effects of Sm upon the catalytic performance of Ni-SBA-15 and Co-SBA-15 is interesting	10	72
Ni-AISBA-15	Impregnation with ethylene glycol as solvent	73	80	0.97	1.5% after 20 h	700 °C, GHSV = 18 L _{gcat} ⁻¹ h ⁻¹ , CO ₂ : CH ₄ = 1: 1	Ultra-small Ni size, high Hydrothermal stability, confinement effect of the mesoporous channels of AISBA-15	7	73
5Co-5Ni/5Sc-SBA-15	Hydrothermal	74% to 65% within 50 h	81% to 70% within 50 h	-	13% weight loss after 7 h	700 °C, CO ₂ : CH ₄ : N ₂ = 2.83:2.83:1, F/W = 133.33 mL _{gcat} ⁻¹ min ⁻¹ , total flow rate = 40 mL min ⁻¹	Better dispersion of Co and Ni, strong MSI	10	26
3B-10Ni/SBA-15	Sequential incipient wet impregnation	78	80	2.6	1.5% 800 °C	800 °C, CH ₄ :H ₂ O:CO ₂ = 3:2:1	Enhancing interaction between the acidic B ₂ O ₃ and basic NiO phases	10	74

1La-5Ni/SB A-15	Incipient wet impregnation method with oleic acid as precursor	83	86	0.92	Negligible after 10 h at 700 °C	700 °C, GHSV = 72 L _{gcat} ⁻¹ h ⁻¹ , CO ₂ : CH ₄ : N ₂ = 1: 1: 1	Interesting synthesis method to achieve high Ni dispersion and sintering resistance	5	13
7La-6Ni/SB A-15	Wet impregnation method	73	80	0.8	-	750 °C, GHSV = 20 L _{gcat} ⁻¹ h ⁻¹ , CO ₂ : CH ₄ : N ₂ = 1: 1: 3	Highly dispersed La promotes generation of small Ni and CO ₂ dissociation into oxygen atom, facilitating the formation of different C1 intermediates on Ni surface	6	76
20LaNi-SBA	In situ auto-combustion	48	60	0.61	Carbon balance 91%	600 °C, GHSV = 600 L _{gcat} ⁻¹ h ⁻¹ , CO ₂ : CH ₄ = 1: 1	smaller CH ₄ activation energy of 64.7 kJmol ⁻¹ due to small Ni size of 3 nm	20La NiO ₃	52
10Ni-8Mg-SBA-15	Incipient wetness impregnation	67	57	-	-	700 °C, GHSV = 36 L _{gcat} ⁻¹ h ⁻¹ , CO ₂ : CH ₄ = 1: 1	Mg incorporation promoted Ni dispersion and basic properties of SBA-15 via metal-support interaction, inhibiting carbon formation	10	70
10Ni-8MgO-coated SBA-15	One pot hydrothermal and wet impregnation	73	65	1.0	6% after 40 h	700 °C, GHSV = 36 L _{gcat} ⁻¹ h ⁻¹ , CO ₂ : CH ₄ = 1: 1	Better order in the meso-structure and more medium basic sites were formed, enhanced Ni dispersion and improved catalytic performance and carbon resistance.	10	47
NiCe/SBA-16	Incipient wetness impregnation	72	77	0.72	3.8% after 100 h	700 °C, GHSV = 45 L _{gcat} ⁻¹ h ⁻¹ , CO ₂ : CH ₄ : He = 1: 1: 1	CeO ₂ confinement effect of stable cage-like pores	5	43
2Ni-1Zr-MCM-41	One pot hydrothermal	92	-	0.98	6% after 72 h	750 °C, GHSV = 45 L _{gcat} ⁻¹ h ⁻¹ , CO ₂ : CH ₄ : He = 1: 1: 1	Addition of Zr ⁴⁺ enhanced the structural stability, increased Ni dispersion, partial activation of CO ₂	2	50
9Y-9Ni-SBA-15	Sol-gel	85	90	0.9	1.2% after 50 h	700 °C, GHSV = 24 L _{gcat} ⁻¹ h ⁻¹ , CO ₂ : CH ₄ = 1: 1: 1	Stable conversions of CH ₄ and CO ₂ within 50 h TOS with a 6% and 4% decrease, respectively	9	75

Table S3 SiO₂-based catalysts for DRM reaction

Catalyst	Synthesis method	Catalytic performance			Carbon resistance	Reaction Conditions	Remarks	Metal Loading wt%	Ref
		CH ₄	CO ₂	H ₂ /CO					
Ni/SiO ₂ (OAm)	Incipient wetness impregnation	70	75	0.95	17 h & negligible carbon formation on Ni/SiO ₂ OAmc	700 °C GHSV = 72 L g _{cat} ⁻¹ h ⁻¹	A stronger steric hindrance is given by the more complex aliphatic chain network of the pair, retarding the growth of Ni particle.	5	53
Ni/SiO ₂ (OAc)		32	40	0.8					
Ni/SiO ₂ (OAmc)		12	25	0.5					
Ni-Cu/SiO ₂	Wetness Impregnation	90	90	-	140 h	-	The addition of Cu into Ni fine-tuned the catalytic activity by balancing the CH ₄ cracking and coke oxidation by CO ₂	8Ni-1Cu	82
Ni-Cu/SiO ₂	Incipient Wetness impregnation	60	70	0.9	30 h & 8% carbon formation	700 °C GHSV = 16 Lh ⁻¹ , CH ₄ :CO ₂ :He = 1:1:8	Strong metal-support interaction and the well dispersed small metal-nanoparticles	5.5Cu-20.9Ni	83
NiFe ₂ O ₄ Spinel/ SiO ₂	Sol-Gel Hydrothermal	66	93	1.1	-	800 °C, GHSV=54 Lh ⁻¹ , CH ₄ :CO ₂ : He =2:1:6	NiFe ₂ O ₄ on silica has more acidic properties provides a more active and selective catalyst that seems less prone to coking.	10	84
NiFe ₂ O ₄ /SiO ₂	Modified hydrothermal	80	72	0.88	60 h and 7.24 mg carbon. g _{cat} ⁻¹	200 W (Plasma assisted) CH ₄ : CO ₂ = 1: 1 GHSV = 12 Lg _{cat} ⁻¹ h ⁻¹	The special structure of the as-synthesized NiFe ₂ O ₄ #SiO ₂ catalyst prevented the carbon formation in the process and restrained aggregation of Ni-Fe alloy.	Ni/Fe = 0.5	85

Fe-Ni/MgAl ₂ O ₄	co-precipitation and incipient wetness impregnation	51	-	-	-	800 °C CH ₄ : CO ₂ = 1: 1 W _{cat} /F _{CH₄} = 0.40–0.71 kg _{cat} smol ⁻¹)	The Fe-Ni alloy is the active phase where Fe segregates to form FeOx. It reduces the surface carbon accumulation through interaction with FeOx lattice oxygen, producing CO.	8Ni-5Fe	87
Ni-Co/SiO ₂	Incipient wetness impregnation	80	82	-	30 h & 0 mg carbon/mg _{cat} h	700 °C, CH ₄ : CO ₂ = 1: 1, GHSV= 72Lg _{cat} ⁻¹ h ⁻¹	Ni-Co are uniformly distributed and thus led to strong metal support interaction	4Ni-1Co	88
Ni/SiO ₂	on using oleic acid	75	78	-	30 h & 0 mg carbon/mg _{cat} h		-	5	
Co/SiO ₂	and oleylamine	30	30	-	30 h & 0 mg carbon/mg _{cat} h		-	5	
Ni-Co/SiO ₂ derived from phyllosilicates	One pot hydrothermal method	85	90	0.85	100 h & Negligible coke formation	750 °C CH ₄ : CO ₂ =1: 1 GHSV = 60000 mLg _{cat} ⁻¹ h ⁻¹	Addition of Co enhanced metal support interaction and thus prevented carbon formation for 100 h operation	7Ni-3Co	89
Co-Ru-Zr/ SiO ₂	Wetness impregnation	70	83	0.82	-	700 °C, CH ₄ : CO ₂ =1:1, GHSV=20L g _{cat} ⁻¹ h ⁻¹	An appropriate support and amount of Ru played crucial role in activity and stability of the catalyst	0.4Ru	90
Co-Ru-Zr/γ-Al ₂ O ₃		81	90	0.92	-				
Co-Ru-Zr/ MgO		59	71	0.76	-				
Sn, Ce, Mn, Co promoted Ni _x Mg _{1-x} O	A bottom up approach	75	85	0.9	100 h & 26.65% coke deposition	750 °C, CH ₄ :CO ₂ =1: 1, GHSV= 20L g _{cat} ⁻¹ h ⁻¹	Distribution of promoters in crucial to enhance the performance of the catalyst.	1promoters-10 Ni	91
Sn modified Ni/Al ₂ O ₃	Co-impregnation method	60	-	-	8 h & 17 mg g _{cat} ⁻¹ .h ⁻¹	800 °C CH ₄ : CO ₂ =1: 1 GHSV = 72 mL g _{cat} ⁻¹ h ⁻¹	Sn ⁴⁺ enriched the NiO particle surface and facilitated the formation of Ni-Sn alloy and increased the reducibility of NiAl ₂ O ₄	11.3 Ni-0.45Sn	92

Sn doped Ni/SiO ₂	Wetness impregnation	-	-	0.4	25 h & 1.8 mol _{carbon} /mol _{Ni}	500 °C, CH ₄ : CO ₂ =2.3: 1.8 GHSV=6000 mol _{reactant} ·h ⁻¹ ·mol ⁻¹ _{totNi}	Addition of Sn showed to have negative effect on Ni atoms decreasing 3-4-fold the intrinsic activity	0.87Ni-0.014Sn	93
Ni-In/SiO ₂	Deposition - precipitation method	30	78	0.73	-	675 °C CH ₄ : CO ₂ = 2.3: 1	Indium atom dilute the surface of the nickel forming multiple bonded carbon species and thus prevent carbon formation	3Ni-2In	94
Ni/α-Al ₂ O ₃	Co - impregnation	62	78	-	45 (mg _{coke} g _{cat} ·h ⁻¹)	800 °C CH ₄ :CO ₂ =1: 1 GHSV = 60L g _{cat} ⁻¹ h ⁻¹	Sn increased the dispersion of Ni, retarded sintering of Ni thus retarding the coke formation	0.02Sn-10 Ni	95
Sn0.02Ni/α-Al ₂ O ₃		38	58	-	0(mg _{coke} g _{cat} ·h ⁻¹)				
One step Ni on Al (OsNiAl)	Solvothermal and sequential impregnation	98	98	1	Weight loss is observed in different regions of temperature	700 °C GHSV = 5000–50000 mLg _{cat} ⁻¹ h ⁻¹ CH ₄ : CO ₂ =1: 1	Catalysts with more acidic or basic surfaces were found to be more prone to deactivation and metal sintering.	-	96
One step Ni on Si (OsNiSi)		98	99	0.6					
Two step Ni on Al (TsNiSi)		90	90	0.65					
Two step Ni on Al (TsNiAl)		25	25	0.82					
Ni-phyllsilicate structure derived Ni-SiO ₂ -MgO	Ammonia Evaporation method	80	62	2.0	135 h /Small amount of coke formation	750 °C, GHSV=100 Lg _{cat} ⁻¹ h ⁻¹ , CH ₄ :CO ₂ :H ₂ O =2:1:2	enhanced basicity strength, reasonable moderate acidity strength and structural stability	15Ni-30-SiO ₂ -55MgO	97

Ni supported on Silica/Ceria-Zirconia particles	Flame spray pyrolysis (FSP)	80	-	1.0	24 h / 0.5 g _{carbon} /g _{cat}	700 °C WHSV = 144 L _{g_{cat}} ⁻¹ h ⁻¹ CH ₄ : CO ₂ = 1: 1	Introducing silica to the ceria-zirconia enabled the mixed supports to outperform the neat ceria-zirconia by decreasing susceptibility toward the RWGS and preventing deactivation.	10-Si/CeZr ratio of 2:1	98
Ni immobilized (NPs) Ce-mesoporous SiO ₂	sublimation-deposition strategy	90	98	1.2	20 h & Negligible coke formation	750 °C GHSV=6 L _{g_{cat}} ⁻¹ h ⁻¹	The confinement effect deriving from the mesoporous channels of silica support, as well as the high dispersion and reducibility of Ni NPs.	10.1	99
Rh/CaO-SiO ₂	Incipient wetness impregnation	46	-	0.88	-	550 °C CH ₄ : CO ₂ = 1: 1 W/F = 2.67 × 10 ⁻⁵ g h mL ⁻¹	The incorporation of CaO increased metal dispersion	8	100
Ni-La ₂ O ₃ /SiO ₂	Wetness impregnation using oleic acid	80	85	0.8	100 h and small amount of coke formation	700 °C CH ₄ : CO ₂ = 1: 1 GHSV = 72 L _{g_{cat}} ⁻¹ h ⁻¹	The addition of La ₂ O ₃ enhanced the interaction between NiO and the silica support to form a more stable nickel silicate.	10	19
Ni-La ₂ O ₃ /SiO ₂	Poly(ethylene glycol)-assisted sol-gel route	98	98	1.04	40 h & coke deposition = 236 mg /g _{cat}	800 °C CH ₄ : CO ₂ = 1: 1 GHSV = 2.4 × 10 ⁴ mL _{g_{cat}} ⁻¹ h ⁻¹	The presence of La significantly inhibited the reverse water gas shift reaction, resulting in a H ₂ /CO ratio close to unity.	17.5	101
Alumina coated Ni nanoparticle	Atomic layer deposition	80	-	-	-	700 °C GHSV = 3600 L _{g_{cat}} ⁻¹ h ⁻¹ CH ₄ : CO ₂ = 1: 1	The formation of alumina coating strongly inhibits catalyst sintering thus significantly increases the activity and stability of the NiO-5 catalyst.	5	105

TiO ₂ coated Ni	Atomic layer deposition	58.6	62.6	0.72	-	800 °C CH ₄ : CO ₂ = 1:1 GHSV = 12 L _{g_{cat}} ⁻¹ h ⁻¹	The TiO ₂ layer facilitated the formation of separate carbon filaments rather than the graphitic layer on the Ni, reducing the possibility of the deposited carbon layers to cover and poison the Ni active sites of catalysts.	-	106
Ni@yolk-ZrO ₂	Reverse Micelle	90	-	-	50 h & No coke formation	750 °C GHSV = 50400 mL _{g_{cat}} ⁻¹ h ⁻¹	Amount of micropores in ZrO ₂ hollow shells and the surfactant addition directly affected the physical properties of the ZrO ₂ hollow shell	13.45	107
Ni-Yolk@Ni@SiO ₂	microemulsion	90	95	0.81	90 h & negligible coke formation	800 °C GHSV = 36000 mL _{g_{cat}} ⁻¹ h ⁻¹ CH ₄ : CO ₂ = 1: 1	Highly dispersed Ni nanoparticles in the shell and core imparts dual effects of formation of small satellite Ni particles due to strong Ni-SiO ₂ interactions.	18.68	15
Ni@Ni- phyllosilicate	Mg Hydrothermal	78	81	0.98	90 h & negligible coke formation	700 °C GHSV = 1440 L _{g_{cat}} ⁻¹ h ⁻¹ CH ₄ : CO ₂ = 1: 1	Higher nickel dispersion, strong basicity due to the presence of Mg which prevents carbon deposition by reverse disproportionation	6.3Ni- 21.6Si- 7.8Mg	110
Ni@SiO ₂	Immobilization Ni nanoparticles on silica	42	64	0.70	160 h & no carbon deposition	800 °C GHSV = 19000 mL _{g_{cat}} ⁻¹ min ⁻¹ CH ₄ : CO ₂ : N ₂ = 9: 9: 2	The over-layer of silica as compared to normal supported catalyst allowed the facile mass transfer of the reactants and products.	10.5	108

Ru-Co@SiO ₂ - PVP	Hydrothermal (or impregnation) and modified Stöber processes	74	85	0.98	10h/0.5 mg _{coke} g _{cat} ⁻¹ h ⁻¹	700 °C CH ₄ : CO ₂ = 1: 1 GHSV = 54000 mL g _{cat} ⁻¹ h ⁻¹	Uniform Ru distribution through a hydrothermal approach resulted in more direct Co-Ru interaction, making Co-based cores rather coking- and oxidation-resistant	1.2Ru-82.2 Co	111
Ru-Co@SiO ₂ - CTAB		71.3	77	0.91					
Ru-Co@SiO ₂ -No surfactant		66.3	76.2	0.81					
NiCo@SiO ₂	Micro-emulsion method	87.2	88.9	-	50 h & Negligible coke formation	800 °C CH ₄ : CO ₂ = 1: 1 GHSV = 300 mL g _{cat} ⁻¹ h ⁻¹	The encapsulation of metal nanoparticles by SiO ₂ shell could effectively inhibit the agglomeration of active sites.	10	112
Cu-Ni@SiO ₂	Micro-emulsion	75	-	0.9	18 h & negligible coke formation	700 °C GHSV = 13.33 L g _{cat} ⁻¹ h ⁻¹ CH ₄ : CO ₂ = 1: 1	proper percentage of Cu improved the performance and stability.	1Cu-2.4 Ni	114
Multiple core@shell	One -pot reverse phase microemulsion	90	90	-	100 h & negligible coke formation	800 °C GHSV = 18000 mL g _{cat} ⁻¹ h ⁻¹ CH ₄ : CO ₂ = 1: 1	Ultra-small Ni nanoparticles (4.3 nm) and confinement effect between metal and support.	4.93	115
Sandwich-Like Silica@Ni@Silica Multicore-Shell	Ammonia evaporation	50	60	0.75	24 h & 7.6 % coke formation	800 °C GHSV = 60 000 mLg _{cat} ⁻¹ h ⁻¹	The thickness of the shell was varied by amount of TEOS and catalyst prepared by 0.4 ml TEOS showed higher activity.	3.5	117
Ni-Mg phyllosilicate nanotubes@ SiO ₂	Hydrothermal	86	90	0.8	75 h & no coke formation	750 °C GHSV = 60 L g _{cat} ⁻¹ h ⁻¹ CH ₄ : CO ₂ = 1: 1	confinement effect conferred by stable mesoporous silica shell.	11.6-Ni-9.2 Mg-33.6Si	118