Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Geometric art of a Ni@silica nano-capsule catalyst with superb methane dry reforming stability: enhanced confinement effect over nickel site anchoring inside capsule shell with appropriate inner cavity

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Supporting Information.

1. Supplementary material preparation

Preparation of Ni/SBA-15 catalyst. SBA-15 was synthesized according to a previously publication [1]. The incorporation of Ni to the calcined SBA-15 was carried out by incipient wetness impregnation using aqueous solutions of $Ni(NO_3)_2$ with the proper concentration to obtain a desired loading similar to the theoretical Ni content of 1.5Ni@SNC. Impregnated catalysts were followed by drying and calcination at 650 ^oC in flowing air for 2 h and it was labeled as 1.5Ni/SBA-15.

Preparation of Ni/SiO_2 catalyst. The $1.5Ni/SiO_2$ catalyst was also prepared by incipient wetness impregnation with above specific nickel nitrate aqueous solutions at room temperature overnight on a fumed silica support (Sigma-Aldrich), followed by drying and calcination at 650 ^oC in flowing air for 2 h.

ref1. D. Y. Zhao, J. L. Feng, Q. S. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548-552.

2. Characterizations

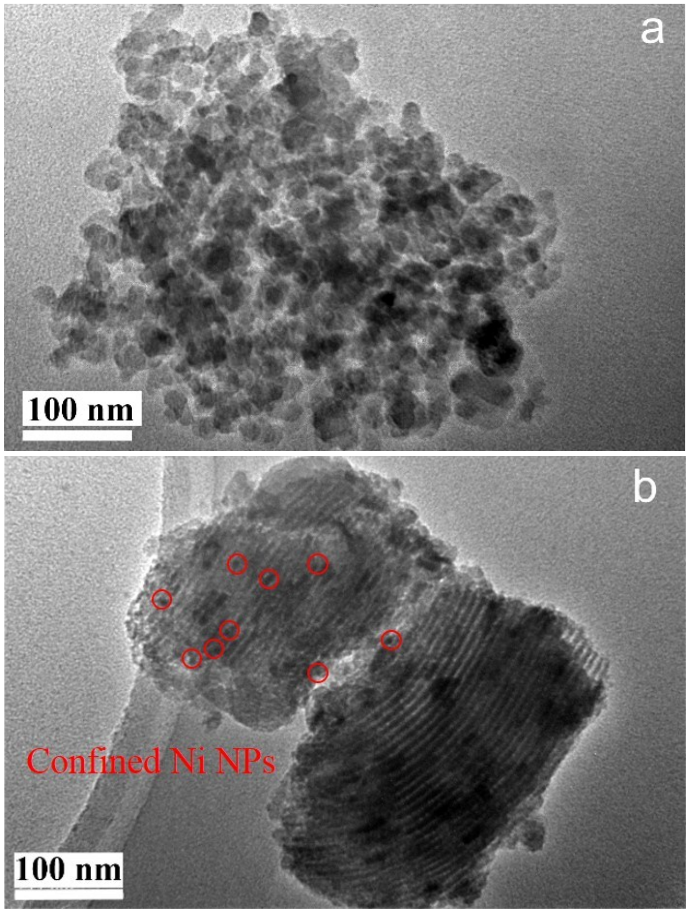

Figure S1. TEM images of calcined a) 1.5Ni/SiO_2, b) 1.5Ni/SBA-15.

Figure S1a showed the TEM image of the referential supported cal-1.5Ni/SiO_2 catalyst. Due to the absence of specific geometric construction for SiO_2 support, 1.5Ni/SiO_2 showed the worst metal dispersion and possessed large metal particle size. For 1.5Ni/SBA-15 catalyst, it shows an obvious ordered mesoporous structure with some nickel particles well embedding in the silica framework. However, also amount of large nickel particles are emerged outside the mesoporous channels, which makes the nickel particle size distribution split into two different ranges, corresponding to the confined and unconfined nickel particles, respectively.

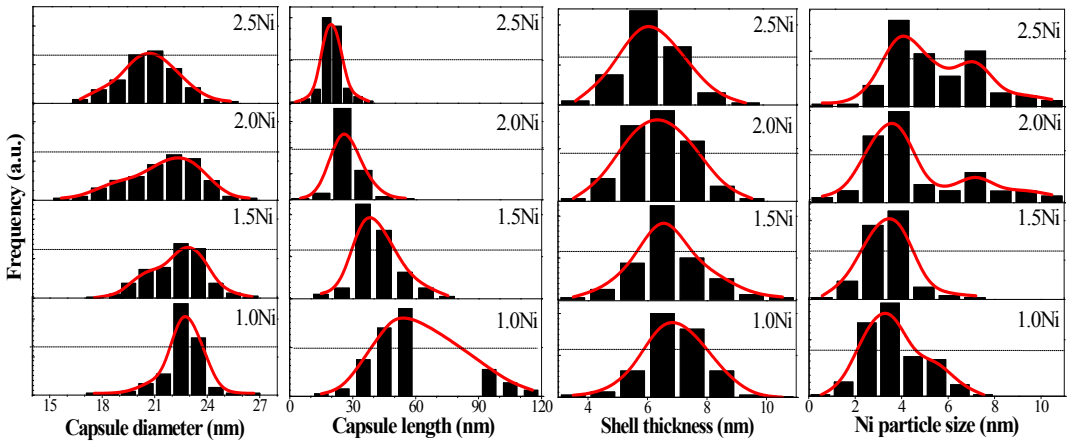

Figure S2. The capsule diameter, capsule length, shell thickness and inner NiO particle size of the calcined x-Ni@SNC samples.

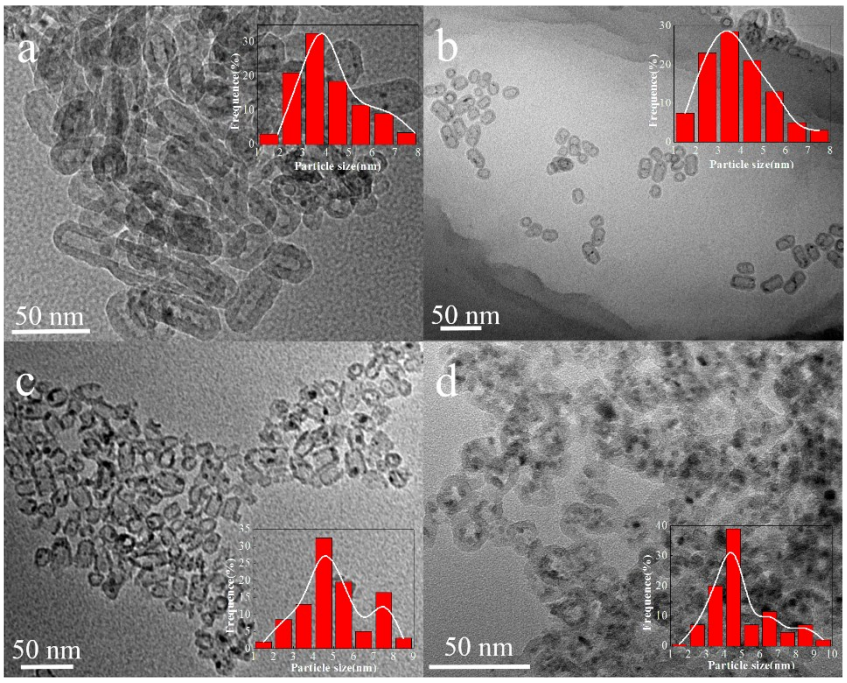

Figure S3. TEM images and the nickel particle size distributions of the reduced x-Ni@SNC catalysts. a) 1.0Ni@SNC, b) 1.5Ni@SNC, c) 2.0Ni@SNC, and d) 2.5Ni@SNC.

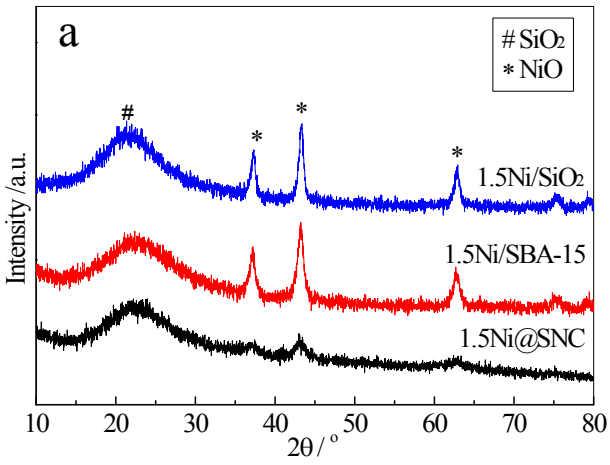

Figure S4. Wide-angle XRD patterns of the calcined 1.5Ni/SiO_2, 1.5Ni/SBA-15 and 1.5Ni@SNC catalysts.

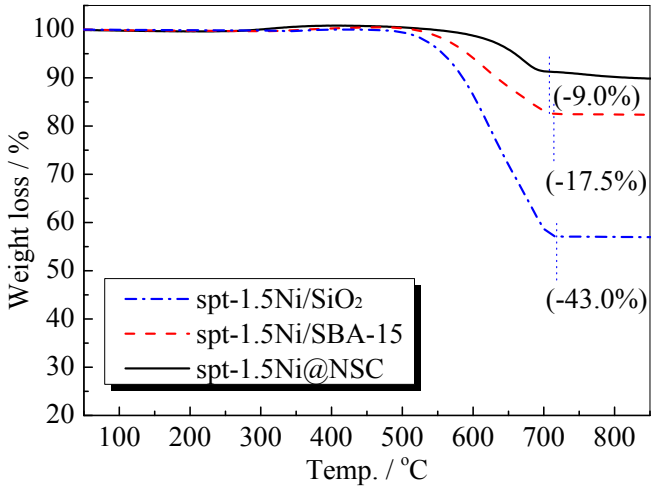

Figure S5. TGA profiles of spt-1.5Ni/SiO_2, spt-1.5Ni/SBA-15, and spt-1.5Ni@SNC catalysts used after 50 h TOS.

Table S1. The fraction of LTP and HTP corresponding to metal support interaction calculated from TPR (Figure 3a).

Catalyst	TPR peak profiles	
	Fraction of LTP / Temp., intensity (fraction)	Fraction of HTP / Temp., intensity (fraction)
1.5Ni/SiO_2	435 ^oC, 1521 (100.0%)	-
1.5Ni/SBA-15	415 ^oC, 893 (60.5%)	575 ^oC, 594 (39.5%)
1.5Ni@SNC	375 ^oC, 492 (39.7%)	575 ^oC, 748 (60.3%)

Table S2. The surface elemental fraction of cal- and spt-Ni@SNC catalyst according to SEM-EDX analysis.

Surface elemental fraction of cal-Ni@SNC				
Elemental	Series	Norm. C [wt.%]	Atom. C [wt.%]	Error (1 Sigma) [wt.%]
O	K-series	53.34	65.81	6.58
Si	K-series	28.39	19.95	1.11
Ni	K-series	12.09	4.07	0.59
C	K-series	6.19	10.17	1.76
Surface elemental fraction of spt-Ni@SNC				
Elemental	Series	Norm. C [wt.%]	Atom. C [wt.%]	Error (1 Sigma) [wt.%]
O	K-series	42.57	55.27	5.74
Si	K-series	38.53	28.49	1.54
Ni	K-series	11.96	4.23	0.55
C	K-series	6.94	12.01	2.08

Table S3. Deactivation and carbon deposition rates of Ni-SiO_2 catalysts.

Catalyst	TOS (h)	Deactivation rate[a](%/h)	Deposited carbon(gC/gCat)	Average coking rate[b] (mgC/gCat/h)	Average coking rate[c] (gC/gNi/h)
1.0Ni@SNC	100	1.82	0.03	1.0	0.02
1.5Ni@SNC	100 (50)[d]	0.01 (0.016)	0.18 (0.09)	1.8 (1.9)	0.02 (0.02)
2.0Ni@SNC	100	0.02	1.78	17.7	0.16
2.5Ni@SNC	100	0.15	2.03	20.3	0.16
1.5Ni/SBA-15	50	0.14	0.22	4.2	0.05
1.5Ni/SiO_2	50	0.42	0.76	15	0.17

[a] Deactivation rate =(CH_4 conversion after 1 h on stream－CH_4 conversion after 100 or 50 h on stream)/99 or 49.

[b] Average coking rate= Deposited carbon /TOS

[c] Average coking rate= Deposited carbon /TOS/Ni content of per gram of catalyst

[d] The data of 1.5Ni@SNC tested for 50h are shown in parentheses.