SUPPORTING INFORMATION

for

Reversal of methanation-oriented to RWGS-oriented Ni/SiO_2 catalyst by the exsolution of Ni^{2+} confined in silicalite-1

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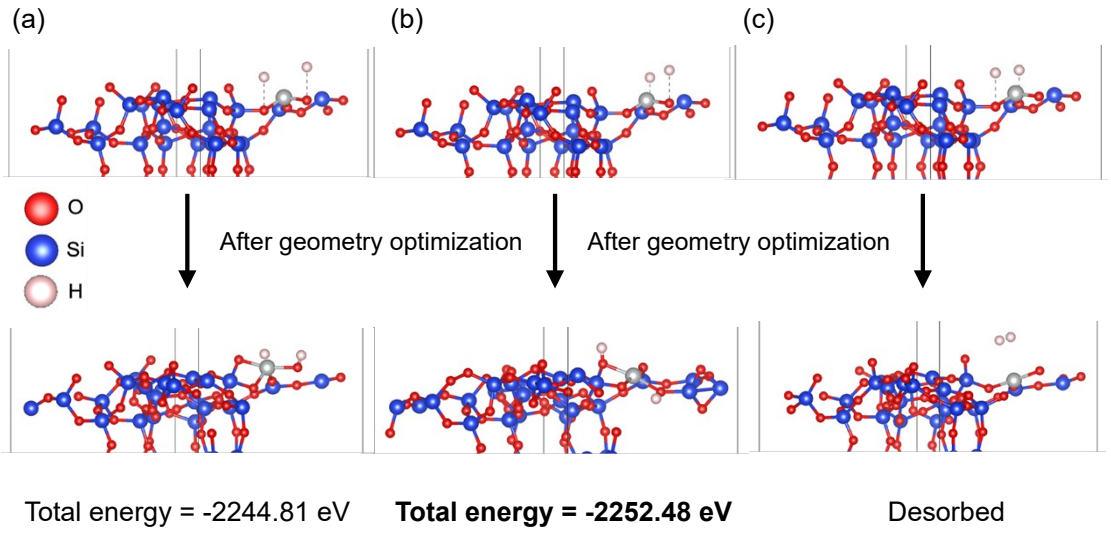


Figure S1. Three different configurations of the two H atoms on the surface of Ni@S-1, (a), (b), and (c). These configurations arise from the presence of three O atoms surrounding the Ni atom, resulting in three possible combinations. The (c) configuration did not yield a stable absorbed structure. On the other hand, the (b) configuration exhibited a relatively lower energy, making it the selected configuration for further analysis.

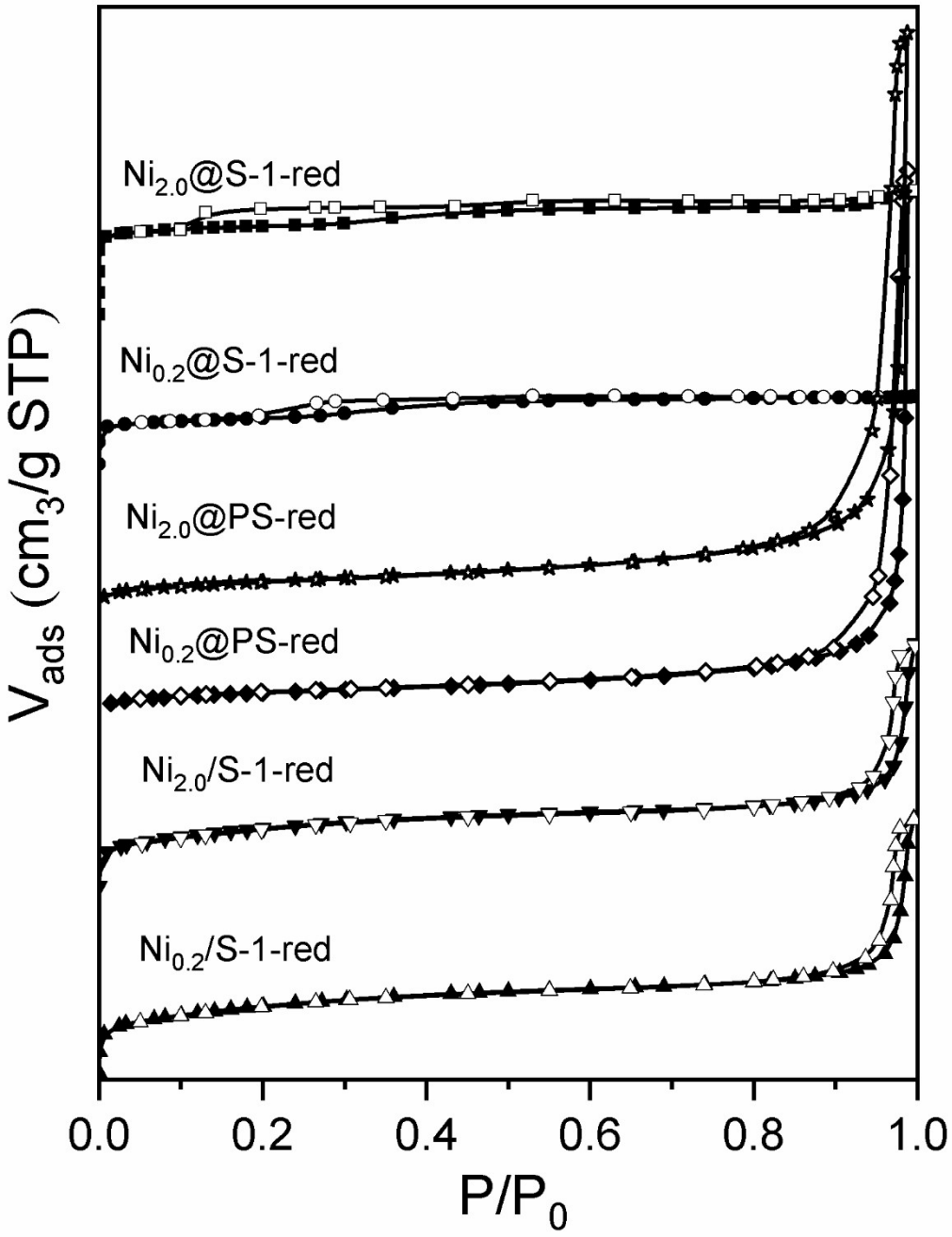


Figure S2. N_2 isotherms of tested catalysts.

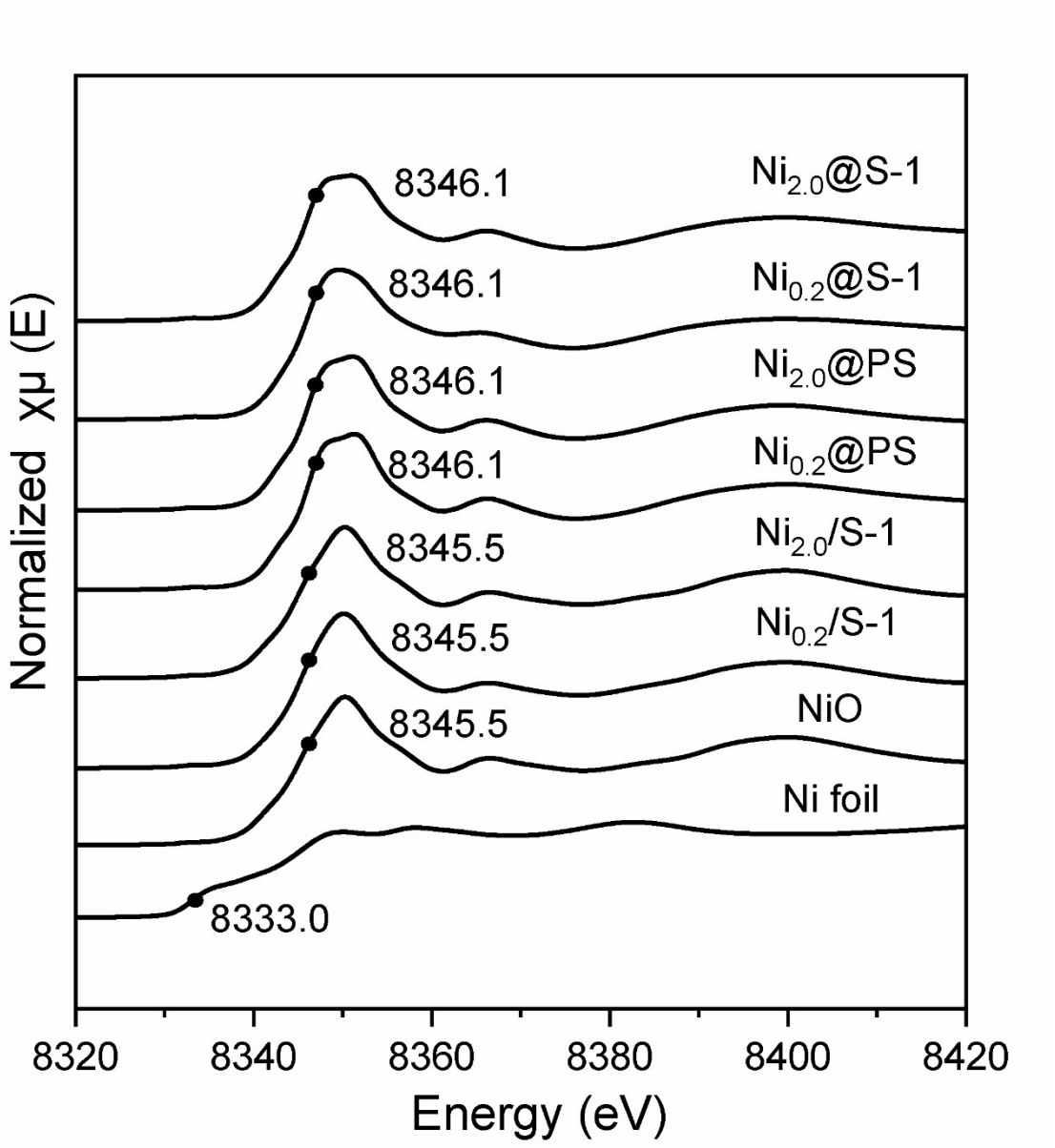


Figure S3. XANES spectra of the catalyst precursors at Ni *K*-edge.

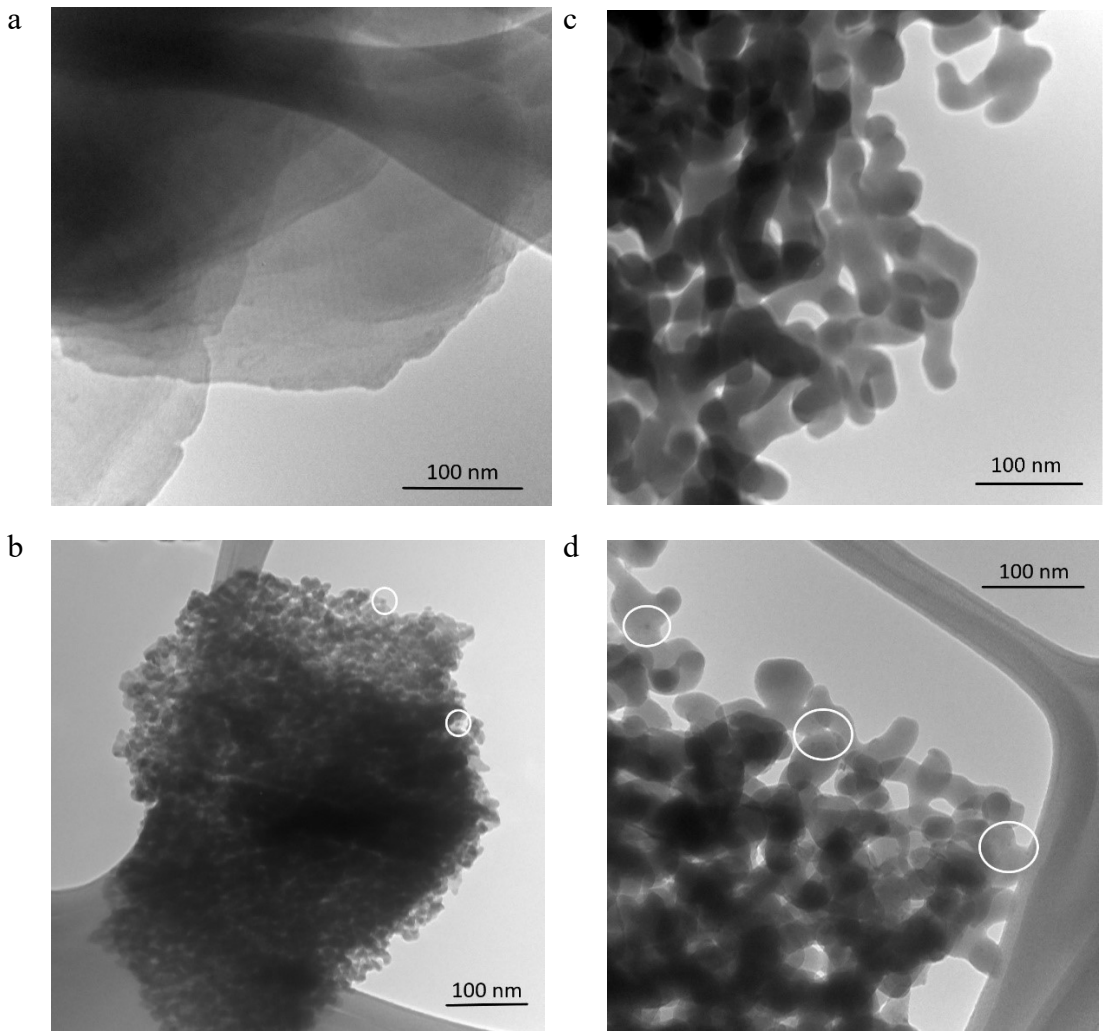
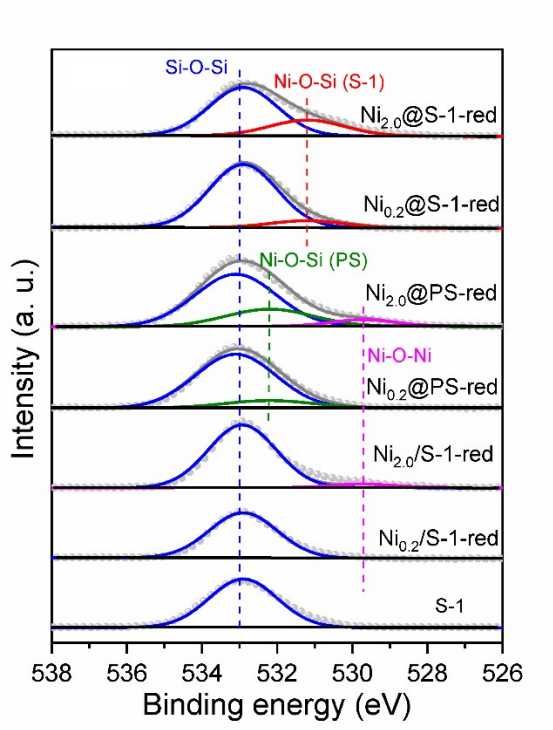


Figure S4. The TEM images of (a) $Ni_{0.2}$/S-1-red, (b) $Ni_{2.0}$/S-1-red, (c), $Ni_{0.2}$@PS-red, and (d) $Ni_{2.0}$@PS-red.

a



b

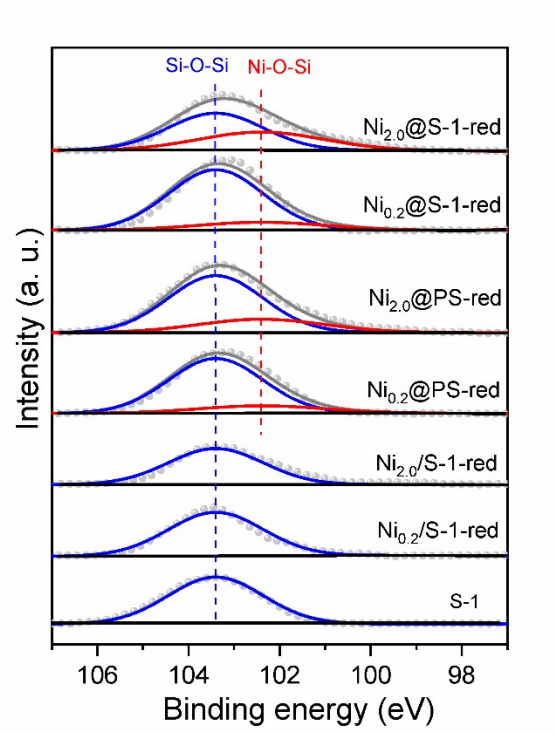


Figure S5. XPS spectra of (a) O 1s and (b) Si 2p photolines of the tested catalysts.

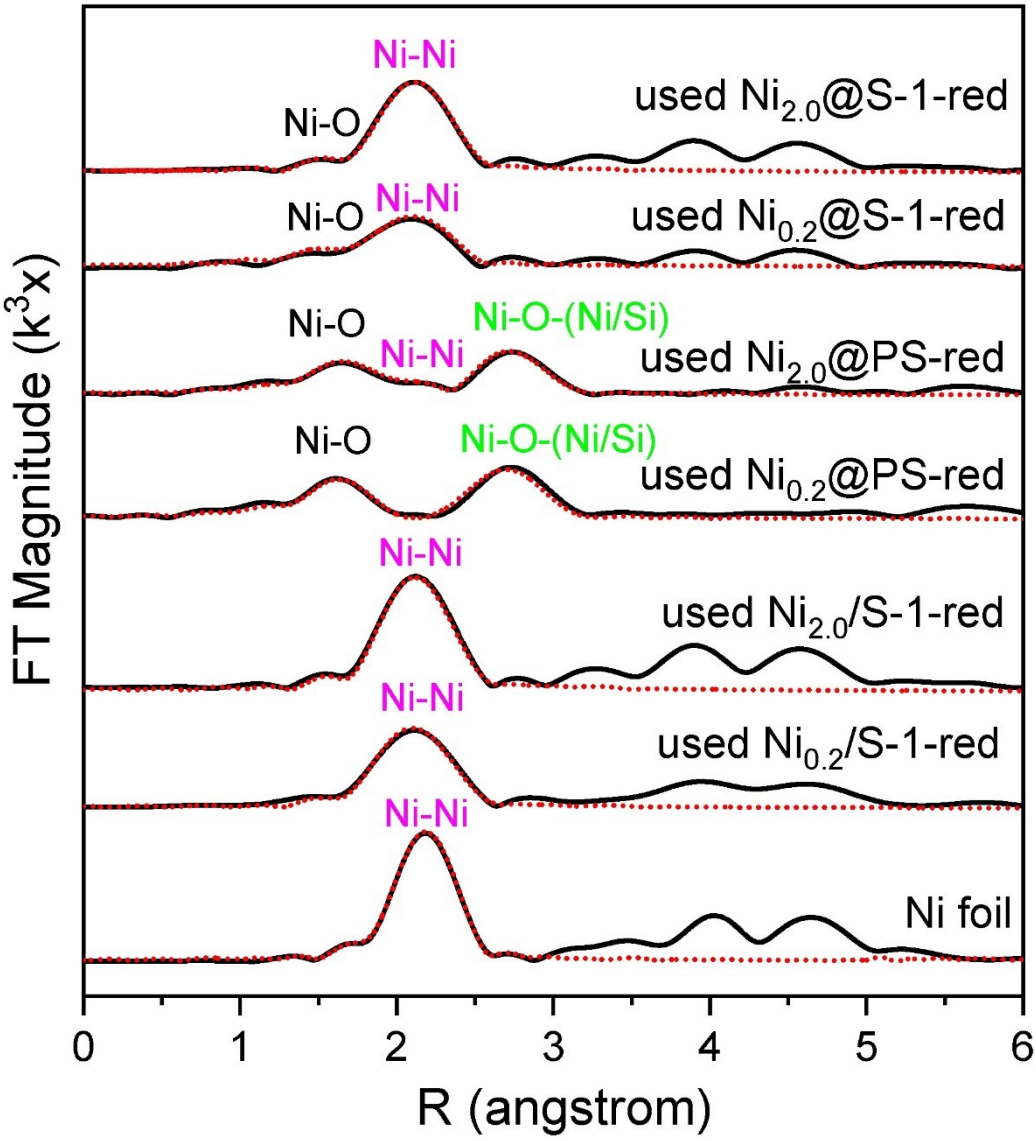


Figure S6. The RDF profiles of the used catalysts. The solid line represents the experimental data, and the dashed line represents the computer fit.

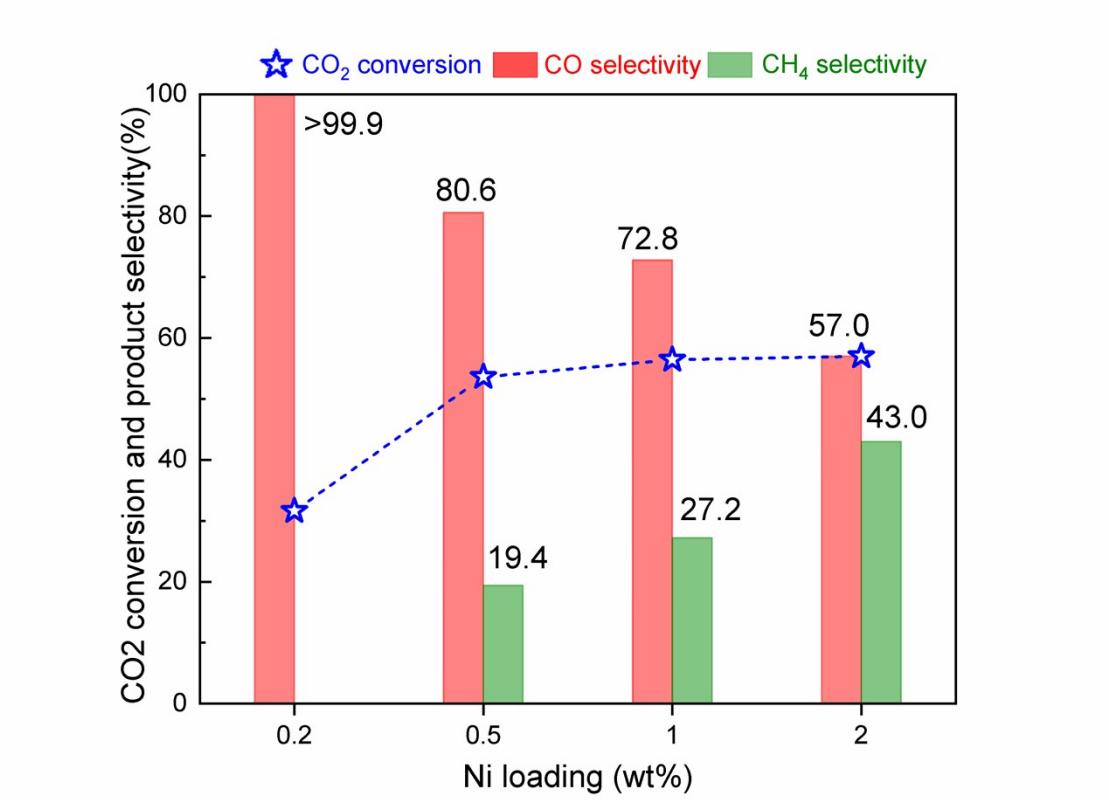
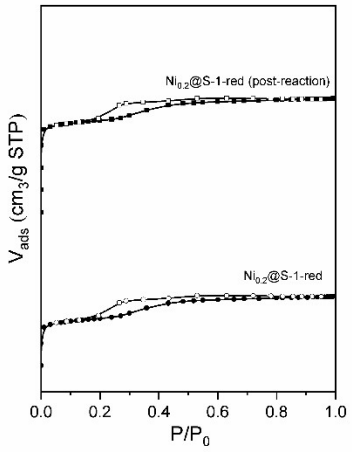
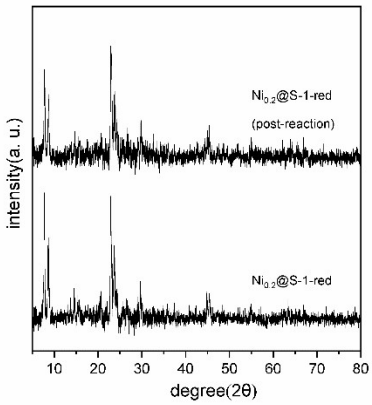


Figure S7. The activity tests of the Ni_x@S-1-red catalysts (x = 0.2, 0.5, 1.0, and 2.0). Reaction conditions: T = 450 °C, P = 0.1 MPa, H_2/CO_2 = 3, GHSV= 12000 mL/g_{Cat}/h.

a



b



c

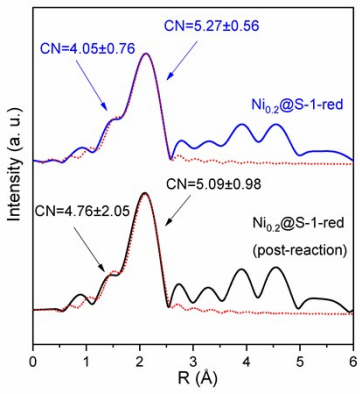


Figure S8. (a) N_2 isotherms, (b) XRD patterns, and (c) RDF profiles of the EXAFS spectra of the fresh and the after 100 h on-stream tested $Ni_{0.2}$@S-1-red catalysts.

Table S1. Parameters obtained from the fitting results of the EXAFS data at Ni *K*-edge of the catalyst precursors.

Sample	Scattering path	CN[a]	R (Å)[b]	σ2 (Å^2)[c]	R-factor
$Ni_{2.0}$@S-1	1st (Ni-O)	5.58 ± 0.66	2.06 ± 0.01	0.004	0.011
	2nd (Ni-O-(Ni/Si))	7.12 ± 1.43	3.06 ± 0.01	0.008	
$Ni_{0.2}$@S-1	1st (Ni-O)	5.75 ± 0.62	2.04 ± 0.01	0.006	0.007
	2nd (Ni-O-Si)	3.12 ± 1.06	3.03 ± 0.01	0.008	
$Ni_{2.0}$@PS	1st (Ni-O)	6.11 ± 0.66	2.07 ± 0.01	0.005	0.009
	2nd (Ni-O-(Ni/Si))	8.07 ± 1.33	3.06 ± 0.01	0.008	
$Ni_{0.2}$@PS	1st (Ni-O)	6.16 ± 0.69	2.07 ± 0.01	0.004	0.009
	2nd (Ni-O-(Ni/Si))	8.69 ± 1.40	3.05 ± 0.01	0.008	
$Ni_{2.0}$/S-1	1st (Ni-O)	6.48 ± 1.02	2.06 ± 0.01	0.005	0.008
	2nd (Ni-O-Ni)	11.79 ± 1.37	2.95 ± 0.01	0.006	
$Ni_{0.2}$/S-1	1st (Ni-O)	6.41 ± 0.73	2.06 ± 0.01	0.006	0.005
	2nd (Ni-O-Ni)	10.41 ± 1.22	2.96 ± 0.01	0.008	
NiO	1st (Ni-O)	6	2.07 ± 0.01	0.006	0.003
	2nd (Ni-O-Ni)	12	2.95 ± 0.01	0.006	

a: coordination number; b: interatomic distance; c: Debye-Waller factor

Table S2. Parameters obtained from the fitting results of the EXAFS data at Ni *K*-edge of the fresh catalysts.

Sample	Scattering path	CN[a]	R (Å)[b]	σ2 (Å²)[c]	R-factor
$Ni_{2.0}$@S-1-red	1st (Ni-O)	1.61 ± 1.05	2.03 ± 0.03	0.011	0.001
	2nd (Ni-Ni)	8.42 ± 0.59	2.48 ± 0.01	0.006	
$Ni_{0.2}$@S-1-red	1st (Ni-O)	4.05 ± 0.76	2.02 ± 0.01	0.009	0.003
	2nd (Ni-Ni)	5.27 ± 0.56	2.48 ± 0.01	0.006	
$Ni_{2.0}$@PS-red	1st (Ni-O)	5.23 ± 0.88	2.07 ± 0.02	0.004	0.007
	2nd (Ni-Ni)	1.39 ± 2.69	2.48 ± 0.03	0.006	
	3rd (Ni-O-(Ni/Si))	6.39 ± 2.47	3.06 ± 0.02	0.007	
$Ni_{0.2}$@PS-red	1st (Ni-O)	5.87 ± 0.70	2.06 ± 0.01	0.004	0.009
	2nd (Ni-O-(Ni/Si))	8.50 ± 1.70	3.05 ± 0.01	0.009	
$Ni_{2.0}$/S-1-red	1st (Ni-Ni)	10.39 ± 0.54	2.48 ± 0.01	0.005	0.002
$Ni_{0.2}$/S-1-red	1st (Ni-Ni)	10.03 ± 1.39	2.48 ± 0.01	0.007	0.013
Ni foil	1st (Ni-Ni)	12	2.48 ± 0.01	0.005	0.001

a: coordination number; b: interatomic distance; c: Debye-Waller factor

Table S3. Parameters obtained from the fitting results of the EXAFS data at Ni *K*-edge of the used catalysts.

Sample	Scattering path	CN[a]	R (Å)[b]	σ2 (Å²)[c]	R-factor
$Ni_{2.0}$@S-1-spent	1st (Ni-O)	1.60 ± 1.09	2.03 ± 0.03	0.011	0.001
	2nd (Ni-Ni)	8.26 ± 0.55	2.48 ± 0.01	0.005	
$Ni_{0.2}$@S-1-spent	1st (Ni-O)	4.76 ± 2.05	2.02 ± 0.02	0.012	0.011
	2nd (Ni-Ni)	5.09 ± 0.98	2.47 ± 0.01	0.006	
$Ni_{2.0}$@PS-spent	1st (Ni-O)	5.27 ± 0.76	2.07 ± 0.02	0.004	0.008
	2nd (Ni-Ni)	1.47 ± 2.43	2.48 ± 0.03	0.007	
	3rd (Ni-O-(Ni/Si))	6.28 ± 2.07	3.06 ± 0.02	0.007	
$Ni_{0.2}$@PS-spent	1st (Ni-O)	5.81 ± 0.68	2.06 ± 0.01	0.004	0.014
	2nd (Ni-O-(Ni/Si))	8.20 ± 1.61	3.06 ± 0.01	0.009	
$Ni_{2.0}$/S-1-spent	1st (Ni-Ni)	10.42 ± 0.68	2.48 ± 0.01	0.005	0.004
$Ni_{0.2}$/S-1-spent	1st (Ni-Ni)	10.12 ± 1.39	2.48 ± 0.01	0.007	0.014
Ni foil	1st (Ni-Ni)	12	2.48 ± 0.01	0.005	0.001

a: coordination number; b: interatomic distance; c: Debye-Waller factor