Supporting information for

Modulating Oxidation State of Ni/CeO_2 Catalyst for Steam Methane Reforming: A Theoretical Prediction with Experimental Verification

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Experimental methods

Catalyst preparation

Synthesis of CeO_2: CeO_2 support was synthesized by a simple sol-gel method. Briefly, 5.332 g of $Ce(NO_3)_3 \cdot 6H_2O$ were first added into deionized water (20 ml) and stirred 30 min to obtain a dissolved solution. Then, 4.719 g of citric acid was added into the above solution. The solution was stirred for another 12 h at 60 °C. Then, a water bath was used to evaporate the residual. A spongy solid was obtained after drying for 12 h at 120 °C. The sample was then heated to 400 °C at a heating rate of 5 °C/min, and calcined at 400 °C for 4 h.

Synthesis of NiO/CeO_2: NiO/CeO_2 with a 10 wt% Ni content loading in the final catalyst were prepared by a traditional impregnation method. Typically, 1.101 g of $Ni(NO_3)_2 \cdot 6H_2O$ was dissolved into deionized water (2 ml) and then mixed with the as-prepared CeO_2 support (2.000 g) and kept at room temperature for 12 h, followed by drying at 120 °C for another 12 h and calcining at 600 °C for 4 h in static air.

Synthesis of NiO/CeO_2 with different ratios of Ni and NiO: In order to obtain different ratios of Ni and NiO, the as-prepared NiO/CeO_2 catalyst was treated at different reduction temperatures under H_2 atmosphere for 1 hour. NiO/CeO_2-364°C was the catalyst obtained after treating NiO/CeO_2 at 364 °C under H_2 atmosphere for 1 hour. The same method was adopted to synthesize NiO/CeO_2-600°C.

Characterization of the catalysts

The phase structure of the as-prepared catalysts was characterizated by XRD on a Rigaku D8-Focus diffractometer using the graphite filtered Cu Kα radiation (λ = 1.54056 Å) with the 2θ value ranging from 20° to 85°. H_2-TPR was performed on an AMI-300 apparatus. For the measurement of H_2-TPR, the sample (100 mg) was first pretreated at 400 °C by Ar (30 ml/min) for 1 hour. Then, the samples was cooled to 50

°C by air. Finally, the temperature of the furnace was heated from 50 °C to 900 °C at a ramp of 10 °C/min under the mixture of 10 vol% H_2-Ar (30 ml/min). X-ray photoelectron spectroscopy (XPS) was measured on an ESCALAB 250Xi spectrometer (Thermo Fisher Scientific) with an Al *Kα* (hν = 1486.6 eV) X-ray source. The peak of C 1s (284.6 eV) was used as an internal reference to correct all spectra.

The reaction of methane steam reforming

The reaction of methane steam reforming was carried out in a fixed-bed reactor (6 mm ID) at atmospheric pressure. 0.15 g of the catalyst (20 - 40 mesh) was diluted with SiC (1.2 g) and loaded in the tubular reactor. Before reaction, the catalyst was pre-reduced in situ in a flow of H_2 (50 ml/min) at certain temperature (364 °C or 600 °C) for 1 h. For instance, in order to obtain NiO/CeO_2-364°C, the pristine NiO/CeO_2 was pre-reduced in situ in a flow of H_2 (50 ml/min) at 364 °C for 1 h. Then, water was pumped into reactor, and CH_4/N_2 (Vol(CH_4)/Vol(N_2) = 1:1) were simultaneously injected into the reactor. Water was vaporized completely and mixed with CH_4 and N_2 in the heated chamber (300 °C). The flows of steam and methane had an H_2O/CH_4 of 2. The reaction temperature was controlled by three K-type thermocouples centering in the furnace to maintain stable reaction temperature. The produced gas was analyzed by an on-line gas chromatograph (Varian Micro-GC 490) equipped with three columns (PPU column, activated alumina column and 5Å molecular sieve column) and a TCD detector. The flow rate of nitrogen was fixed (60 ml/min) in each experiment. Thus, the production rate of H_2, CO, CO_2 and CH_4 can be calculated according to the content of nitrogen. The conversion of methane and formation rate of gas products were calculated using the following equations.

$$\text{Methane conversion (wt\%)} = \frac{F_{cH4}^{in} - F_{CH4}^{out}}{F_{cH4}^{in}} \times 100 \qquad (1)$$

H_2 selectivity (%)= $\frac{F_{H2}^{out}}{4*F_{cH4}^{in}} \times 100$ (2)

Gas product rate (umol/min) $R(H_2) = \frac{A_{H2} \cdot f_{H2}}{A_{N2} \cdot f_{N2}} \times R(N_2)$ (3)

A is the peak area, which was obtained from gas chromatograph. *f* is the response factor, which was determined by the property of gas species. *R* is the gas flow rate.

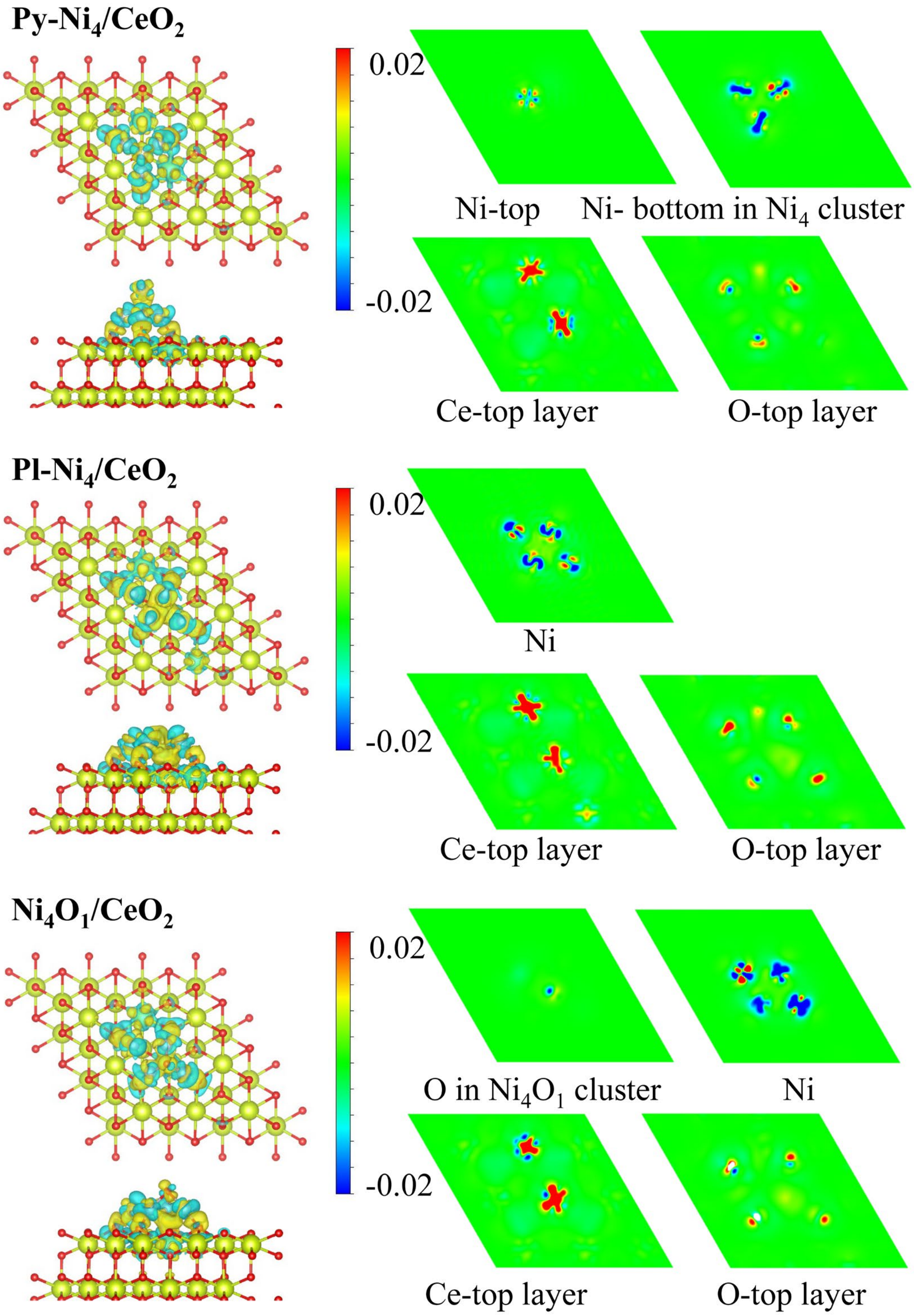


Figure S1 Left: Charge density difference (ρ_{diff}) between -3.2×10^{-3} (blue, deficit) and 3.2×10^{-3} (yellow, accumulation) e/Bohr ^{3}. Right: The electron localization function (ELF) maps of Ni atom, top atom layers of O and Ce in CeO_2 between −0.02 (dark blue, deficit) and 0.02 (red, accumulation) for Py-Ni_4/CeO_2, Pl-Ni_4/CeO_2 and Ni_4O_1/CeO_2. Coloring scheme: grey (Ni), red (O), yellow (Ce).

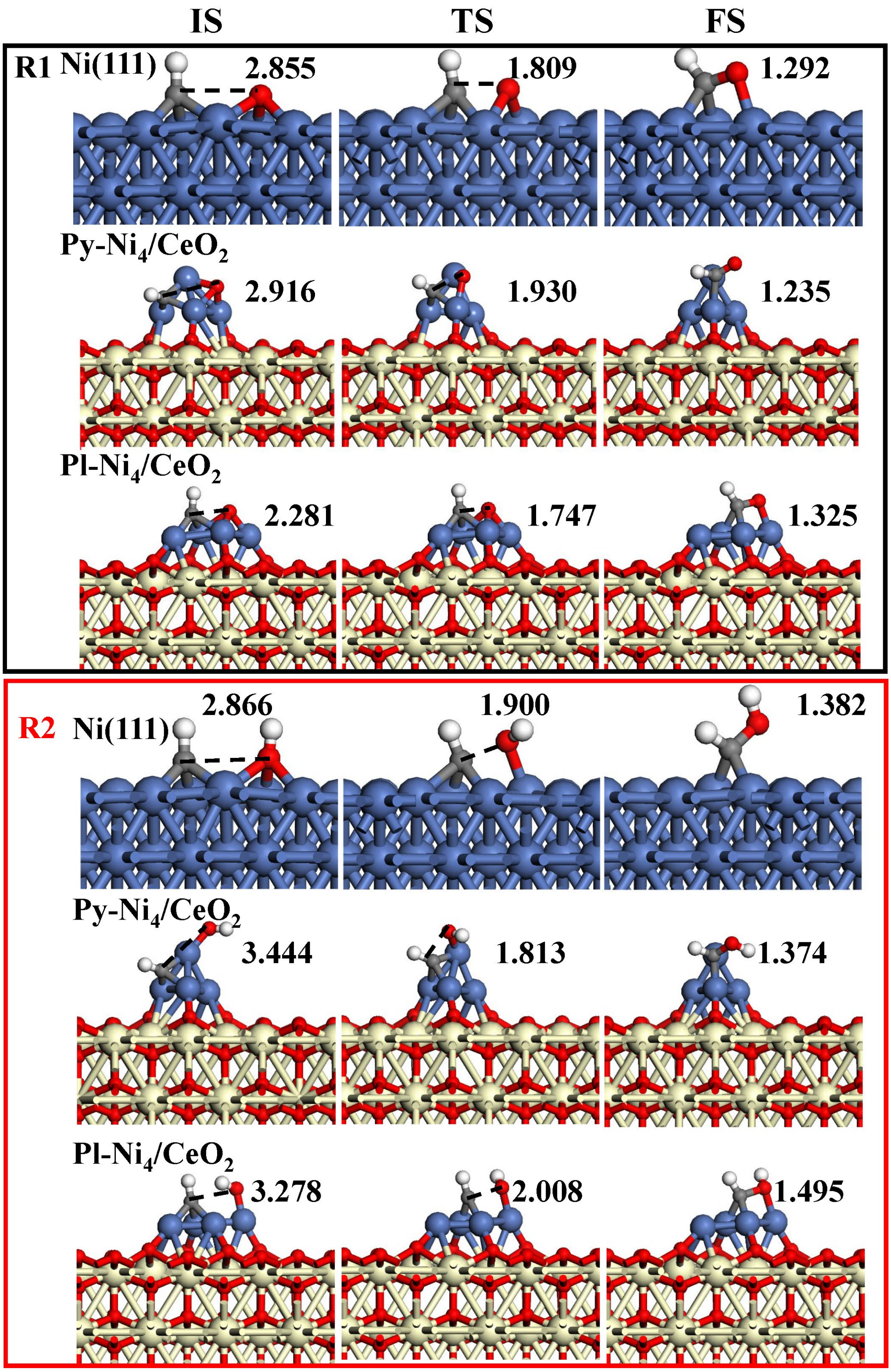
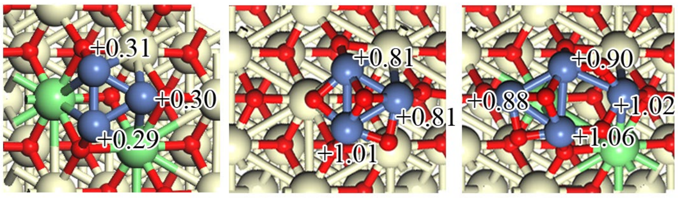


Figure S2. Configurations of the initial state (IS), transition state (TS), and final state (FS) of the C-O bond formation for R1 pathway (CH*+O*-CHO*, in the black frame) and R2 pathway (CH*+OH*-CHOH*, in the red frame) on Ni(111), Py-Ni$_4$/CeO$_2$, and Pl-Ni$_4$/CeO$_2$. The C-O bond distances of IS, TS and FS are given in Å. Coloring scheme: dark blue (Ni), red (O), yellow (Ce), white (H) and grey (C).



Ni_3/CeO_2 R= 0 Ni_3O_3/CeO_2 1 Ni_4O_4/CeO_2 1

Figure S3. The structures of Ni_3/CeO_2, Ni_3O_3/CeO_2, and Ni_4O_4/CeO_2. The Bader charge of Ni atoms was labeled nearby. "+" represents the loss of electrons. The values of NiO/(Ni+NiO) ratio (R) were provided below the figures. Coloring scheme: dark blue (Ni), red (O), yellow (Ce^{4+}) and light green (Ce^{3+}).

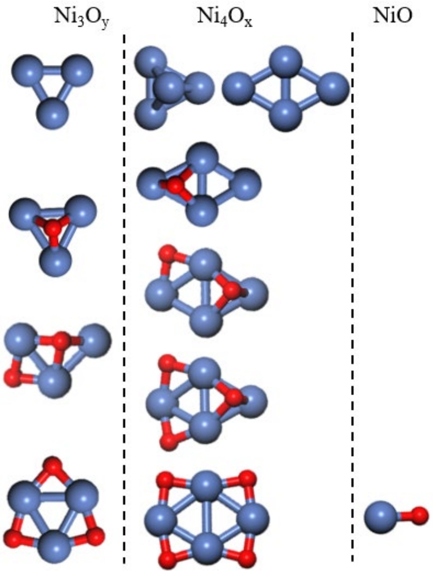


Figure S4. The structures of Ni_4O_x (x = 0-4), Ni_3O_y (y = 0-3) and NiO in gas phase. Coloring scheme: dark blue (Ni), red (O).

Table S1 Magnetic moment of Ni atom (μ_b/atom) and total Ni-NiO clusters (μ_b) of Ni-NiO clusters in gas phase and supported on CeO_2; binding energy (eV) and the number Ce^{4+} to Ce^{3+} for Ni-NiO clusters supported on CeO_2

		Gas cluster		Supported on CeO_2			
		Magnetic Moment		Magnetic Moment			
cluster	R	Ni (μ_b/atom)	Ni-NiO cluster (μ_b)	Ni (μ_b/atom)	Ni-NiO cluster (μ_b)	Binding energy (eV)	Ce^{4+} to Ce^{3+}
Ni_3	0	1.62	4.85	1.07	3.22	-5.86	2
Ni_3O_1	0.33	0.59	1.84	1.06	3.41	-6.83	2
Ni_3O_2	0.67	0.49	1.77	0.77	2.53	-5.50	1
Ni_3O_3	1	0.41	1.91	0.49	1.69	-3.38	0
Py-Ni_4	0	0.85	3.40	0.54	2.15	-6.63	2
Pl-Ni_4	0	0.97	3.87	1.08	4.32	-6.29	2
Ni_4O_1	0.25	0.89	3.74	0.88	3.62	-7.29	2
Ni_4O_2	0.50	0.81	3.64	0.77	3.54	-6.69	2
Ni_4O_3	0.75	0.77	3.68	0.33	1.75	-5.14	2
Ni_4O_4	1	0.67	3.79	0.32	1.81	-2.97	2
NiO	1	1.11	1.83	-0.03	0.06	-2.81	0

R= NiO/(Ni+NiO)

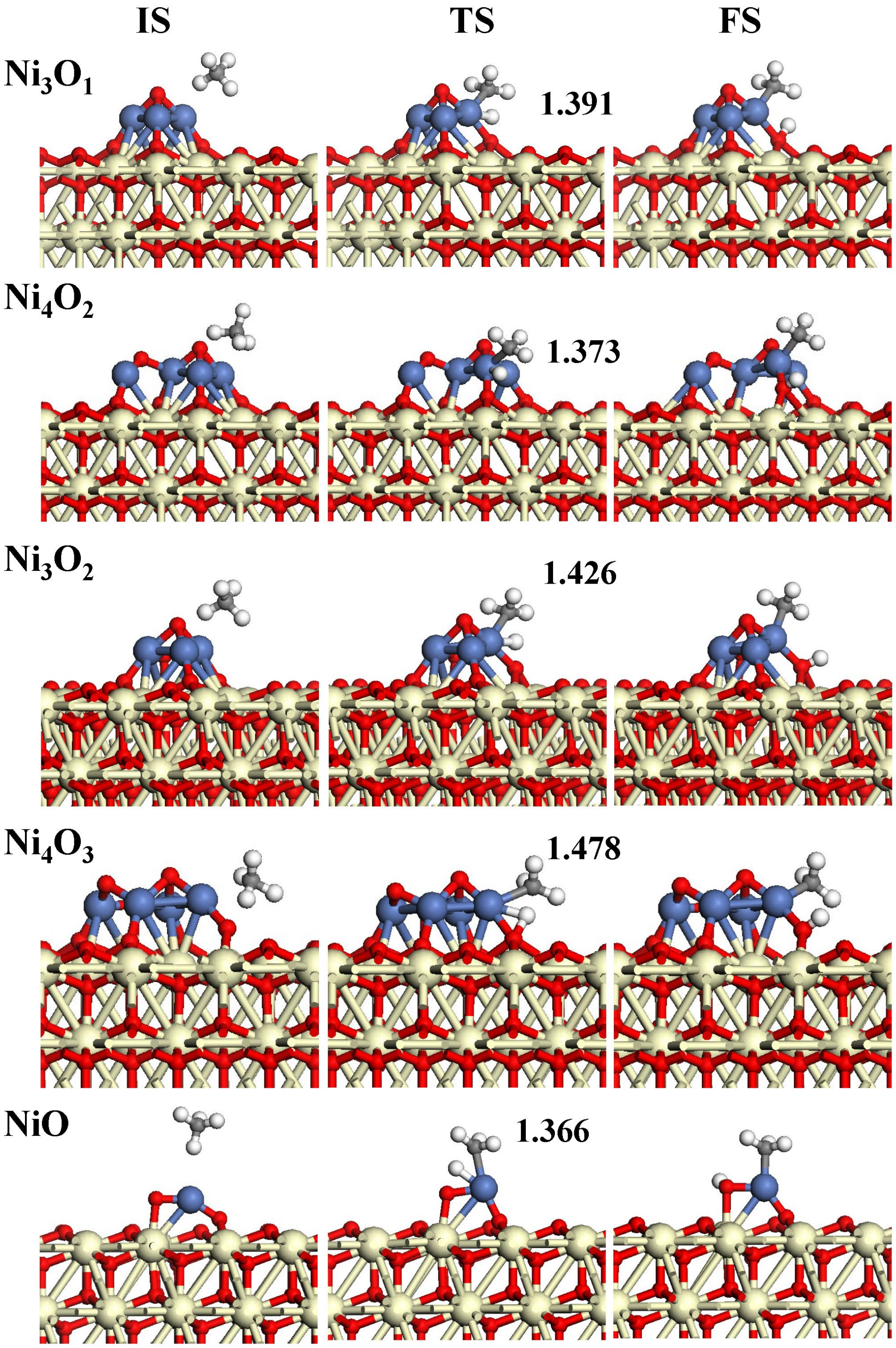


Figure S5. Configurations of the initial state (IS), transition state (TS), and final state (FS) of CH_4* dehydrogenation on $CeO_2(111)$ supported Ni_4O_x (x=2-3), Ni_3O_y (y=1-2) and NiO. The C-H bond distances of TS are given in Å. Coloring scheme: dark blue (Ni), red (O), yellow (Ce), white (H) and grey (C).

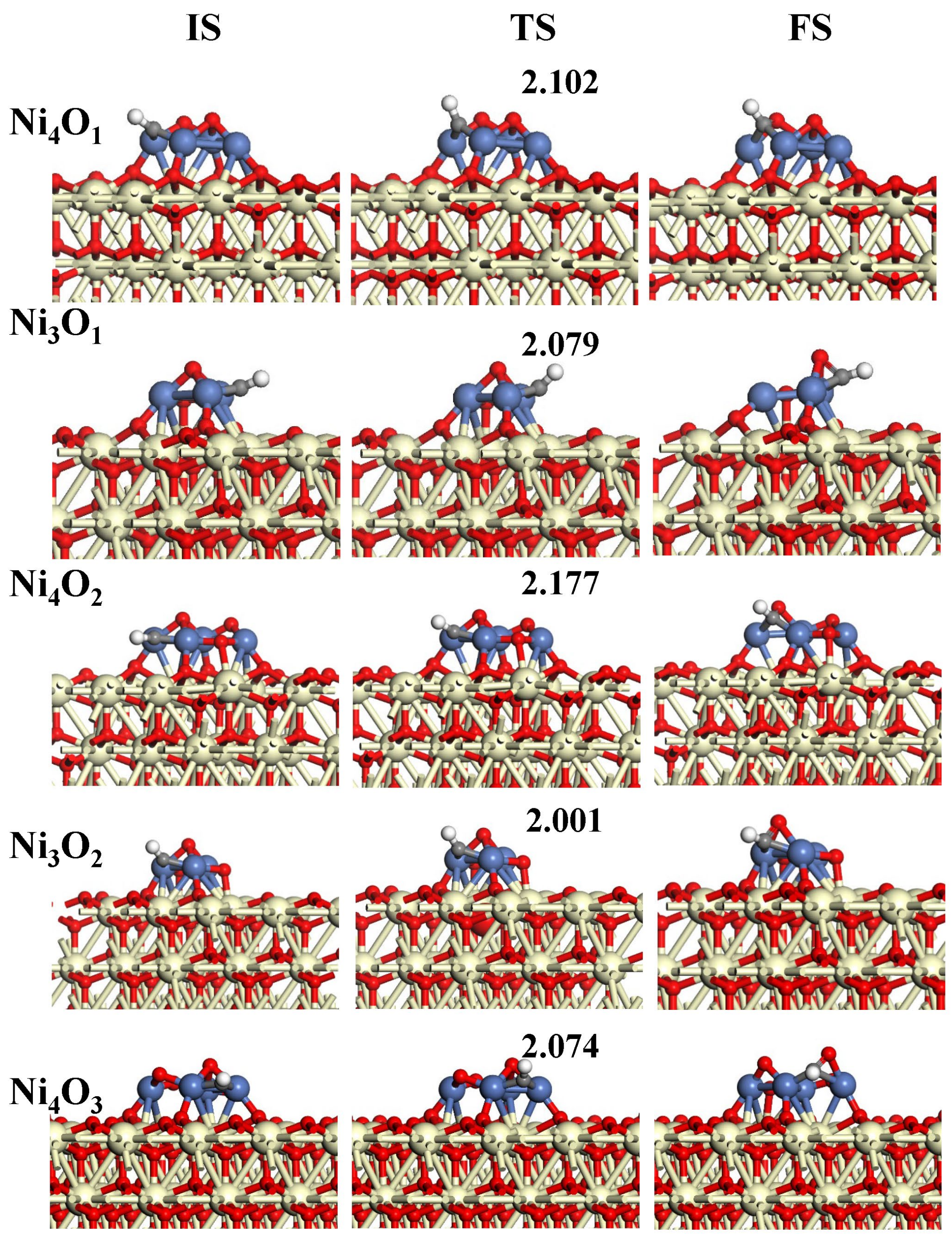


Figure S6. Configurations of the initial state (IS), transition state (TS), and final state (FS) of C-O bond formation on CeO$_2$(111) supported Ni$_4$O$_x$ (x=1-3), Ni$_3$O$_y$ (y=1-2). The C-O bond distances of TS are given in Å. Coloring scheme: dark blue (Ni), red (O), yellow (Ce), white (H) and grey (C).

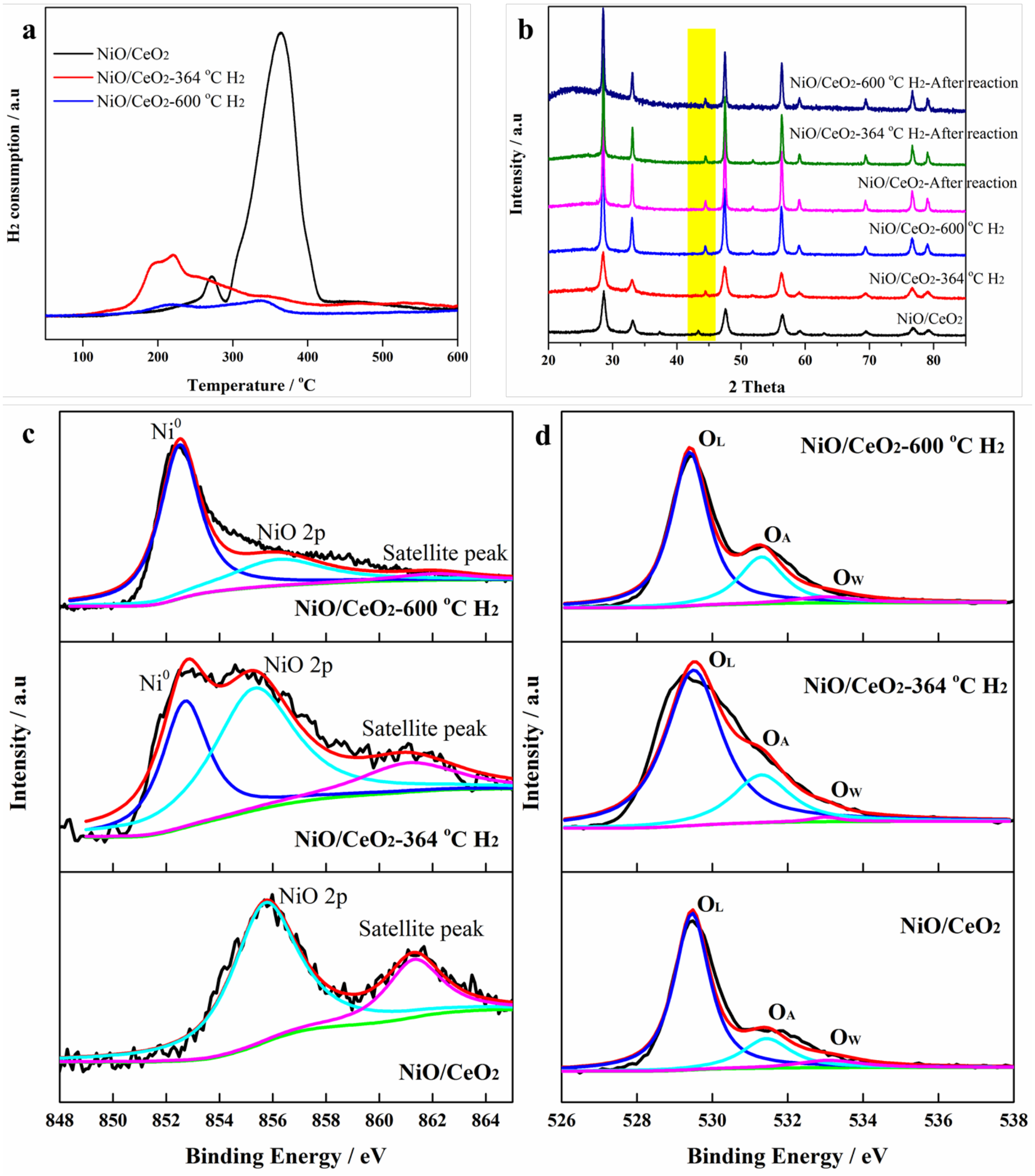


Figure S7. (a) H_2-TPR profiles, (b) XRD patterns, (c) Ni 2p XPS spectra, and (d) O 1s XPS spectra of the fresh catalysts or the spent catalysts.

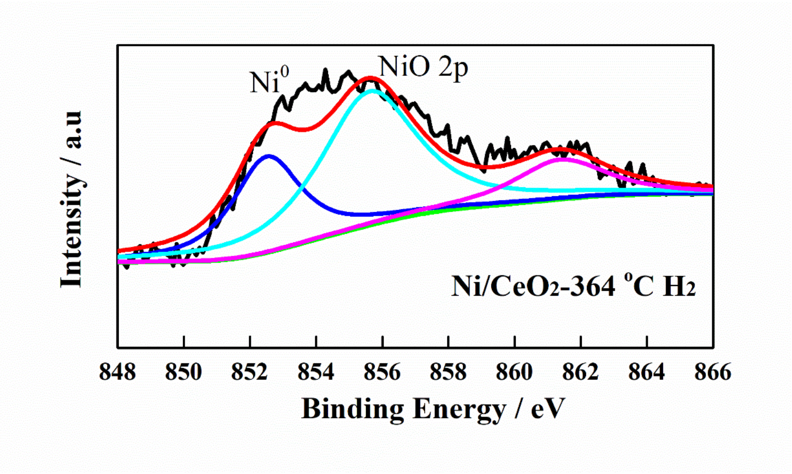


Figure S8. Ni 2p XPS spectrum of the spent NiO/CeO_2-364°C. Reaction conditions: 700°C, $H_2O/CH_4 = 2$, gas hourly space velocity (GHSV) of 20000 g/ml·h, reaction time of 1500 min.