Supplementary Information (SI) for Journal of Materials Chemistry A.

Electronic Supplementary Information

Nickel-Catalyzed Simultaneous Iron and Cerium Redox Reactions for Durable Chemical Looping Dry Reforming of Methane

Minjung Kim, [a] Michael Tomechko [b] and Shang Zhai *[a,c]

[a] Department of Mechanical and Aerospace Engineering, The Ohio State University, Columbus, Ohio, 43210, United States

[b] William G. Lowrie Department of Chemical and Biomolecular Engineering, The Ohio State University, Columbus, OH 43210, United States

[c] School of Earth Sciences, The Ohio State University, Columbus, Ohio, 43210, United States

*Corresponding author: Shang Zhai (zhai.218@osu.edu)

Material Naming Protocol

In this study, the naming of materials is based on the molar composition of the metal elements. Nickel was found to be metallic throughout the cycles, so we have Ni at the beginning of the material chemical formula, while iron and cerium are redox active with varying oxygen stoichiometry x. The stoichiometry of cerium (Ce) was set to 0.5 in each formula. The stoichiometries of Fe and Ni were then calculated based on their molar ratios to Ce. The number following the material name indicates the temperature (in °C) at which it was synthesized and tested. For example, $Ni_{0.50}$-($Fe_{0.50}Ce_{0.50}O_x$)-800 refers to $Ni_{0.50}$-($Fe_{0.50}Ce_{0.50}O_x$) material was synthesized and tested at 800°C.

For Ni_β-($Fe_\alpha Ce_{0.5}O_x$) samples,

If the calculated moles of Fe, Ni, and Ce in a 0.5 g fresh sample were 0.001028, 0.002056, and 0.001552, respectively, the material is denoted as $Ni_{0.66}$-($Fe_{0.33}Ce_{0.50}O_x$). Similarly, for another sample with Fe = 0.002063 moles, Ni = 0.001032 moles, and Ce = 0.001532 moles, the material is named as $Ni_{0.34}$-($Fe_{0.67}Ce_{0.50}O_x$). We included seven different materials across the paper Ni_β-($Fe_\alpha Ce_{0.5}O_x$) where α = 0, 0.15, 0.33, 0.50, 0.67, 0.85, and 1.03, and β = 0.98, 0.85, 0.66, 0.50, 0.34, 0.15, and 0, respectively.

0.5g freshly synthesized materials were used for reactor tests. To determine molar amount of each metal element in a 0.5g sample to write the formula defined above, it was assumed to consist of Fe_3O_4, NiO, and CeO_2 because of high temperature oxidation in air during synthesis. The molar ratio of each metal element was determined by precursors added. The sum of Fe_3O_4, NiO, and CeO_2 components yields the total mass of the 0.5g fresh material.

For Ni_β-($Ce_{0.5}O_x$)-800, and ($Fe_\alpha Ce_{0.5}O_x$)-800 samples,

To test the effect of Fe and Ni separately, Fe-Ce oxides and Ni-Ce oxides were used in a reactor that have the same amounts of Fe or Ni and Ce from the three-metal counterpart. For instance, for $Fe_{0.33}Ce_{0.50}O_x$-800, the same amount of Fe and Ce was used as in the $Ni_{0.66}$-($Fe_{0.33}Ce_{0.50}O_x$)-800 sample but without Ni. Likewise, for $Ni_{0.66}$-($Ce_{0.50}O_x$)-800, the same amount of Ni and Ce was used as in the $Ni_{0.66}$-($Fe_{0.33}Ce_{0.50}O_x$)-800 sample but without Fe. In practice, this meant that 0.3464 g $Fe_{0.33}Ce_{0.50}O_x$-800 contains the same amount of Fe and Ce as 0.5 g of $Ni_{0.66}$-($Fe_{0.33}Ce_{0.50}O_x$)-800, while 0.4207 g $Ni_{0.66}$-($Ce_{0.50}O_x$)-800 contained the same amount of Ni and Ce as 0.5 g of $Ni_{0.66}$-

$(Fe_{0.33}Ce_{0.50}O_x)$-800. Six materials, $Fe_{0.33}Ce_{0.5}O_x$-800, $Fe_{0.50}Ce_{0.50}O_x$-800, and $Fe_{0.67}Ce_{0.50}O_x$-800, and $Ni_{0.34}$-$(Ce_{0.50}O_x)$-800, $Ni_{0.50}$-$(Ce_{0.50}O_x)$-800, and $Ni_{0.66}$-$(Ce_{0.50}O_x)$-800 were tested in the reactor.

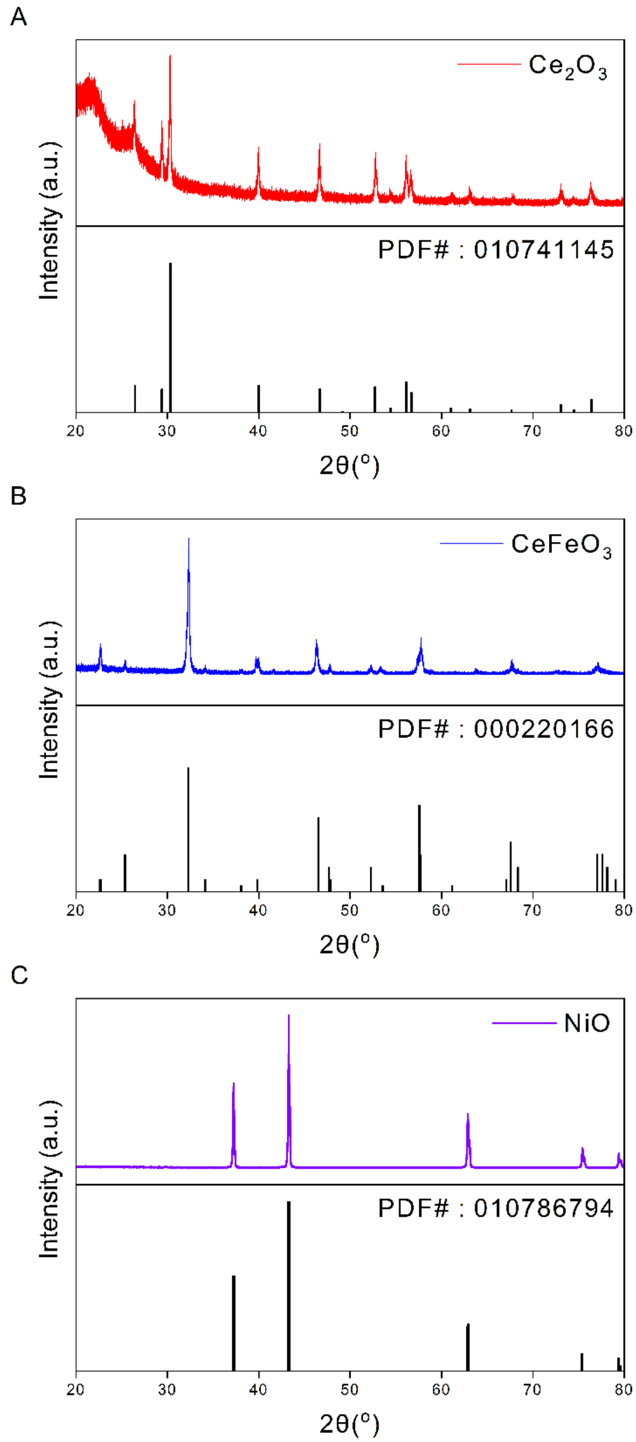

Figure S1: XRD of synthesized reference materials for XAS. CeO_2 was completely reduced for 20 hours under 25 sccm of H_2 at 1100°C to get Ce_2O_3. For $CeFeO_3$, iron, iron (III) oxide, and cerium (IV) oxide were physically mixed, pressed as a pellet and calcined at 850°C for 48 hours under the vacuum. NiO was synthesized via sol-gel method by using nickel nitrate hexahydrate and citric acid with ethanol. The solution was covered and stirred for 6-10 hours, evaporated for 10-15 hours at 90°C, and calcined for 5 hours at 900°C. The red, blue, and purple lines represent the measured data for Ce_2O_3, $CeFeO_3$, and NiO respectively. The references are provided below the measured data.

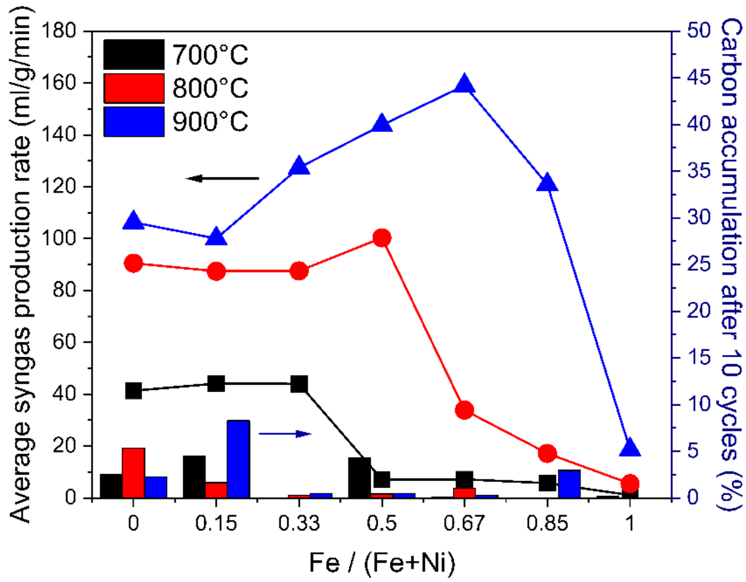

Figure S2: Influence of Fe/(Fe+Ni) ratio and temperature on average syngas production rate (over the 3rd to the 10th cycle, solid lines, left axis) and accumulated carbon deposition percentages (carbon accumulation divided by the total carbon in supplied CH_4 over the 10 cycles, bars, right axis). All samples contain 60wt% ceria.

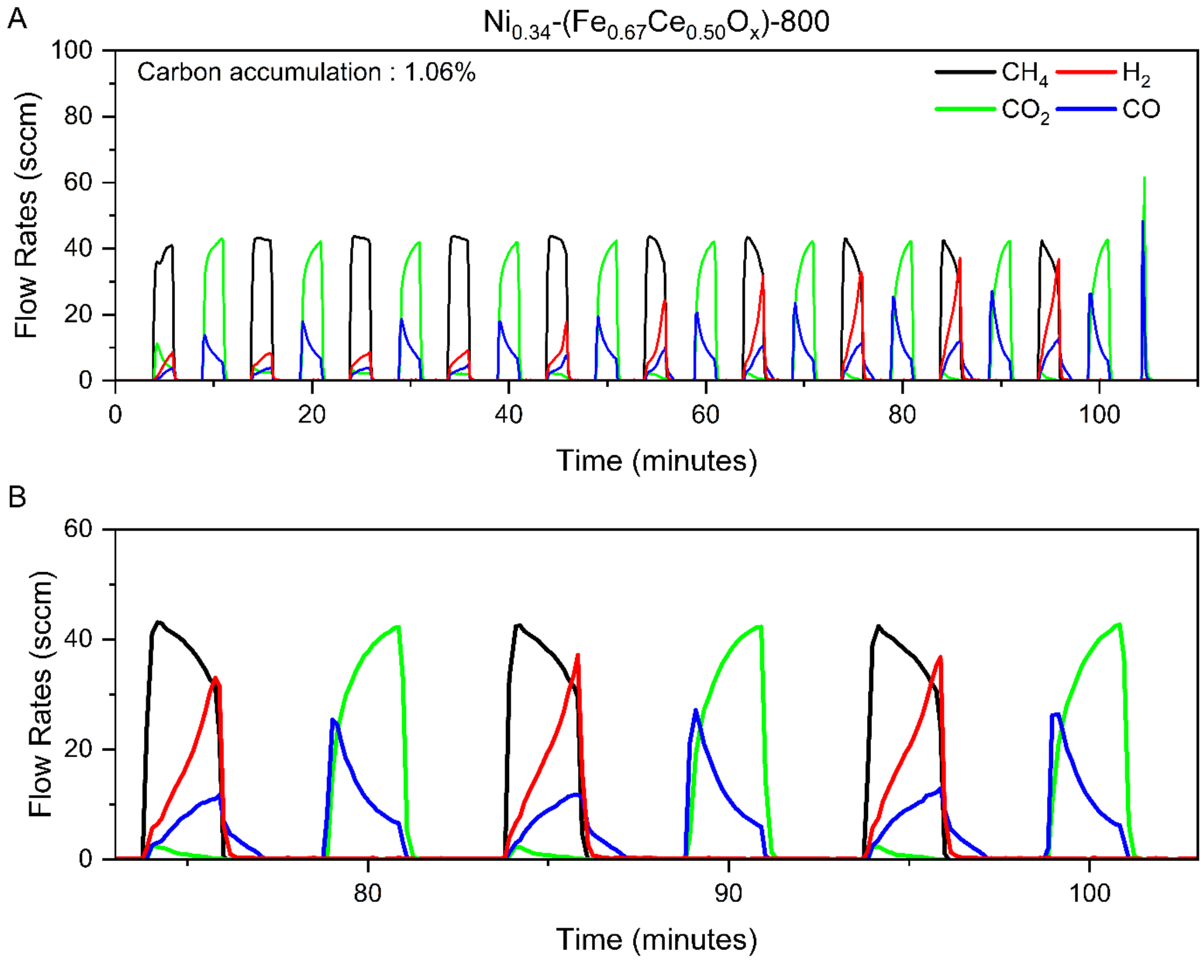

Figure S3: CLDRM reactor exhaust gas profiles for $Ni_{0.34}$-($Fe_{0.67}Ce_{0.50}O_x$)-800 over A) 10 cycles and B) a zoomed-in view of the final three cycles at 800°C. The black curve is unreacted methane. Hydrogen (red), carbon monoxide (blue), and carbon dioxide (green) are the products during the methane step. In the following CO_2 step, CO (blue) is the product, and green curve is unreacted CO_2 in the exhaust. At the end of the 10 cycles, 20% O_2 diluted in Ar was fed into the reactor to combust and help quantify accumulated carbon deposition by the formed CO_2 and CO.

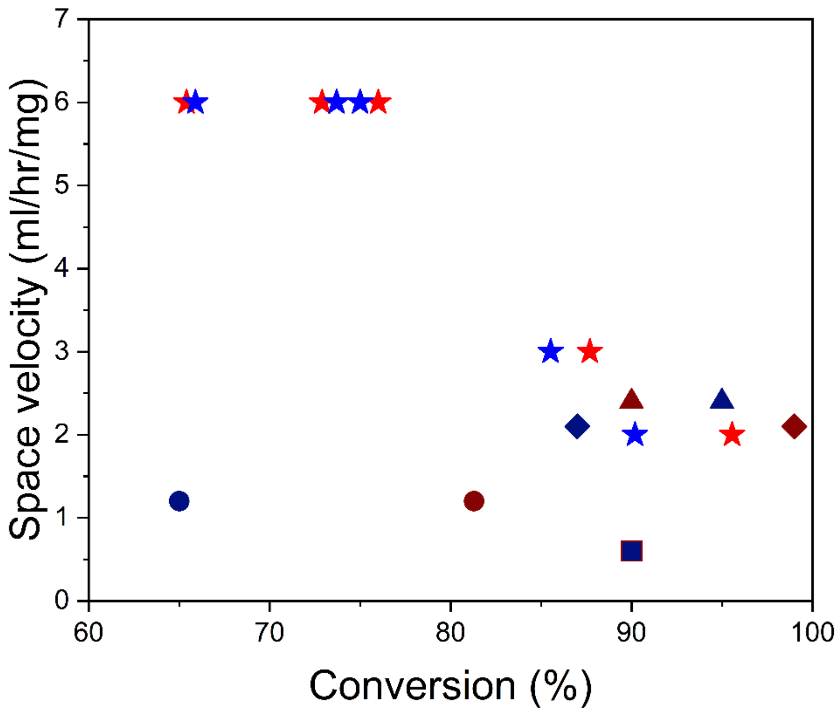

Figure S4: Comparison between materials in this paper and previously published materials in terms of space velocity and conversions in CLDRM. Red and blue tones represent CH_4 and CO_2 steps, respectively. Space velocity is calculated using gas flow rate (ml/hr) divided by the total mass of solid material (mg). $Fe_{0.88}Ni_{0.12}O_x$ with CeO_2 (square) achieved 90% conversion for both CH_4 and CO_2 at 1000°C.[1] $SrFeO_3/CaO$ (triangle) demonstrated 90% and 95% of CH_4 and CO_2 conversions at 980°C.[2] Ni-Fe-Al oxide (diamond) exhibited 99% CH_4 and 87% CO_2 conversions at 900°C.[3] Fe_2O_3/CeO_2 (dot) at 875°C showed 81% and 65% methane and CO_2 conversions.[4] One of our reported materials, $Ni_{0.34}$-($Fe_{0.67}Ce_{0.50}O_x$)-900 (star), showed about 76% of both CH_4 (red) and CO_2 (blue) conversions at a higher space velocity of 6 mL/hr/mg-material. In this paper, 50 sccm of CH_4 or CO_2 was fed with 150 sccm of Ar over 500mg material. The conversions of $Ni_{0.34}$-($Fe_{0.67}Ce_{0.50}O_x$)-900 (star) increase as the space velocity decreases. For lower space velocity experiments, 25 or 16.67 sccm of CH_4 or CO_2 was introduced with 75 or 50 sccm of Ar, respectively, over 500mg material. All conversions are averaged across reaction duration rather than peak conversion.

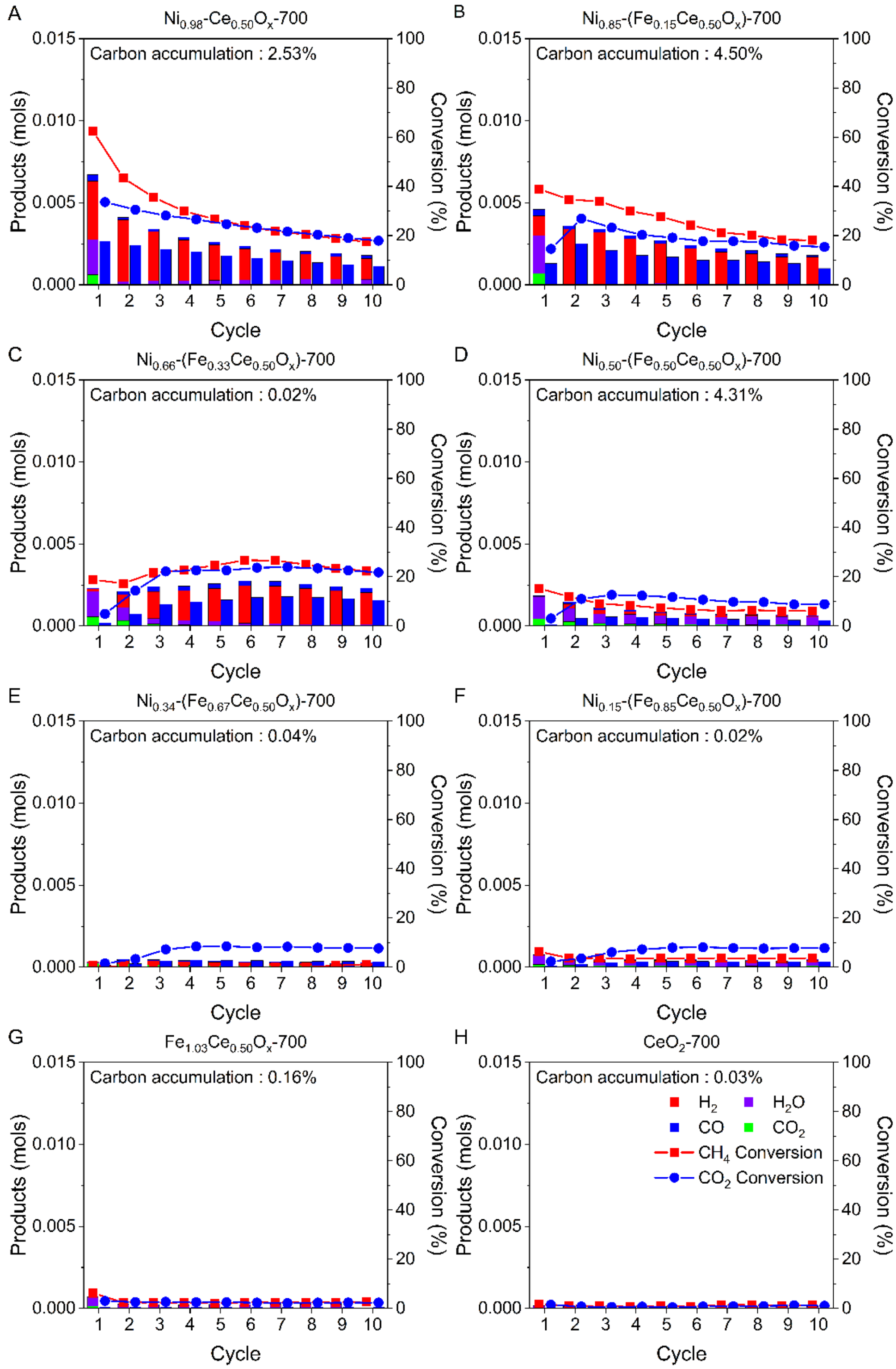

Figure S5: Effect of Fe to Ni ratio in various oxides for CLDRM at 700°C. A) $Ni_{0.98}$-$Ce_{0.50}O_x$-700, B) $Ni_{0.85}$-($Fe_{0.15}Ce_{0.50}O_x$)-700, C) $Ni_{0.66}$-($Fe_{0.33}Ce_{0.50}O_x$)-700, D) $Ni_{0.50}$-($Fe_{0.50}Ce_{0.50}O_x$)-700, E) $Ni_{0.34}$-($Fe_{0.67}Ce_{0.50}O_x$)-700, F) $Ni_{0.15}$-($Fe_{0.85}Ce_{0.50}O_x$)-700, G) $Fe_{1.03}Ce_{0.50}O_x$-700, and H) pure CeO_2-700. Methane step produces CO (blue bar), CO_2 (green bar), H_2O (purple bar), and H_2 (red bar), and CO_2 step produces CO (blue bar). Curves are the conversions of CH_4 (red square) and CO_2 (blue dot).

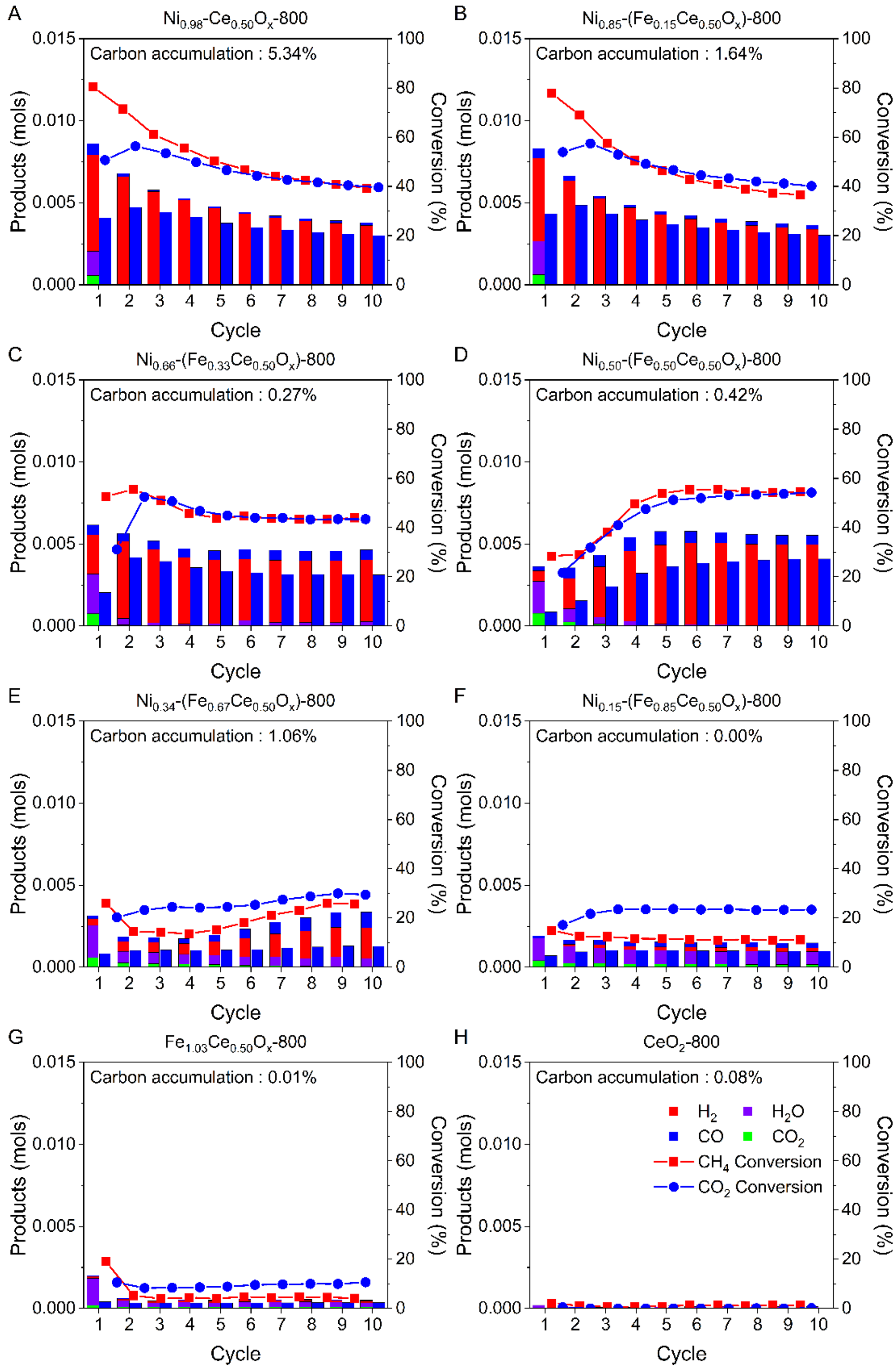

Figure S6: Effect of Fe to Ni ratio in various oxides for CLDRM at 800°C. A) $Ni_{0.98}$-$Ce_{0.50}O_x$-800, B) $Ni_{0.85}$-($Fe_{0.15}Ce_{0.50}O_x$)-800, C) $Ni_{0.66}$-($Fe_{0.33}Ce_{0.50}O_x$)-800, D) $Ni_{0.50}$-($Fe_{0.50}Ce_{0.50}O_x$)-800, E) $Ni_{0.34}$-($Fe_{0.67}Ce_{0.50}O_x$)-800, F) $Ni_{0.15}$-($Fe_{0.85}Ce_{0.50}O_x$)-800, G) $Fe_{1.03}Ce_{0.50}O_x$-800, and H) pure CeO_2-800. Methane step produces CO (blue bar), CO_2 (green bar), H_2O (purple bar), and H_2 (red bar), and CO_2 step produces CO (blue bar). Curves are the conversions of CH_4 (red square) and CO_2 (blue dot).

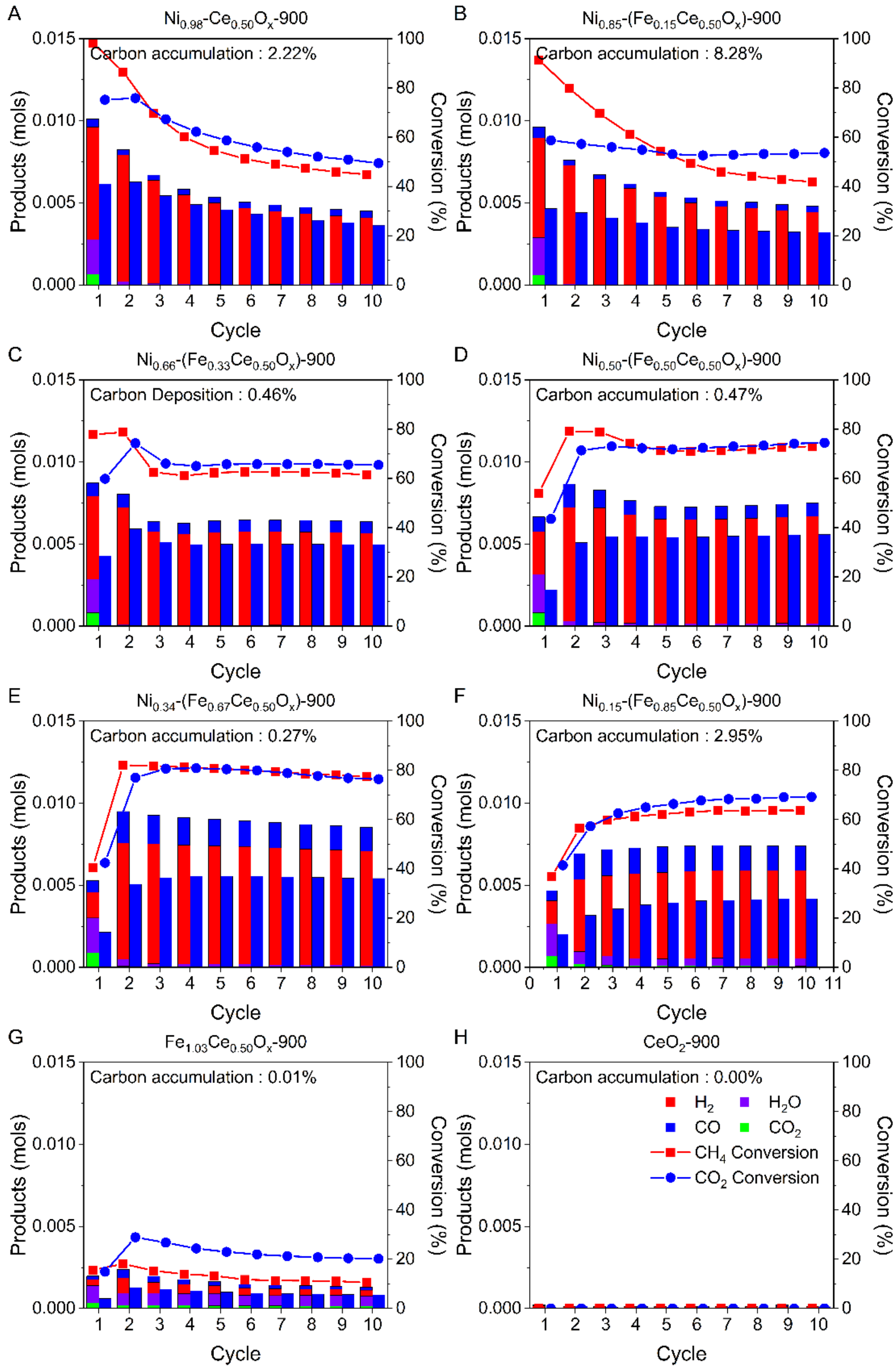

Figure S7: Effect of Fe to Ni ratio in various oxides for CLDRM at 900°C. A) $Ni_{0.98}$-$Ce_{0.50}O_x$-900, B) $Ni_{0.85}$-($Fe_{0.15}Ce_{0.50}O_x$)-900, C) $Ni_{0.66}$-($Fe_{0.33}Ce_{0.50}O_x$)-900, D) $Ni_{0.50}$-($Fe_{0.50}Ce_{0.50}O_x$)-900, E) $Ni_{0.34}$-($Fe_{0.67}Ce_{0.50}O_x$)-900, F) $Ni_{0.15}$-($Fe_{0.85}Ce_{0.50}O_x$)-900, G) $Fe_{1.03}Ce_{0.50}O_x$-900, and H) pure CeO_2-900. Methane step produces CO (blue bar), CO_2 (green bar), H_2O (purple bar), and H_2 (red bar), and CO_2 step produces CO (blue bar). Curves are the conversions of CH_4 (red square) and CO_2 (blue dot).

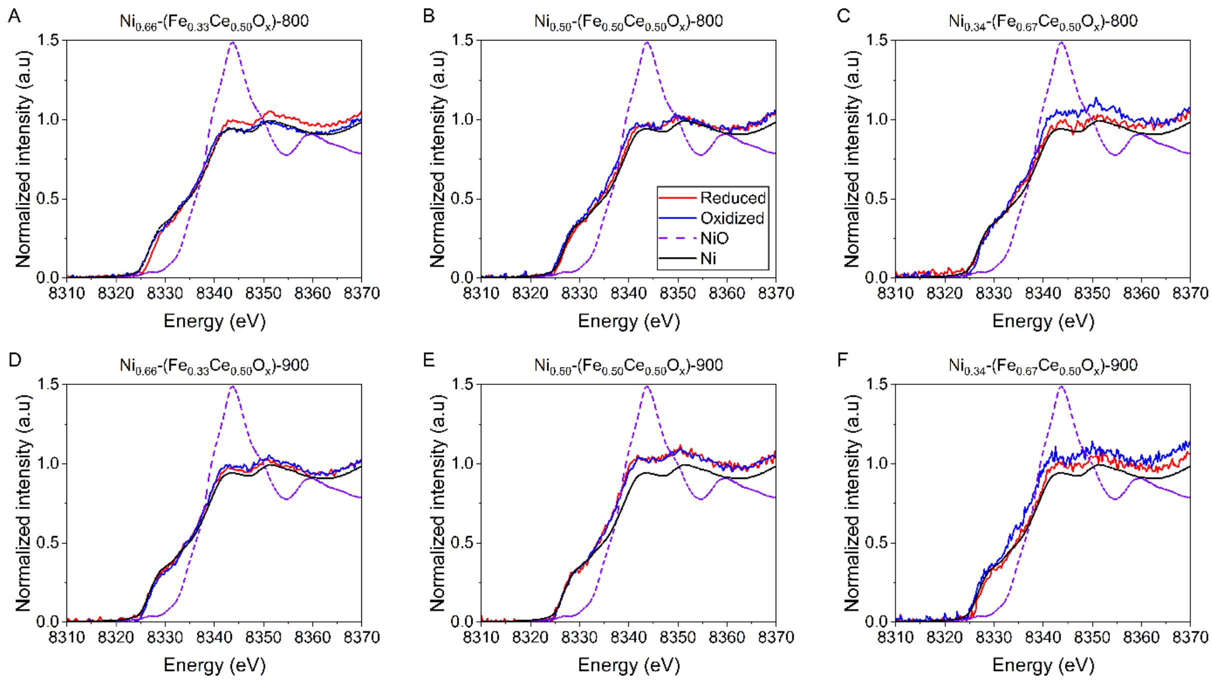

Figure S8: Ni K edge XANES spectra of reduced and oxidized A) $Ni_{0.66}$-($Fe_{0.33}Ce_{0.50}O_x$)-800, B) $Ni_{0.50}$-($Fe_{0.50}Ce_{0.50}O_x$)-800, and C) $Ni_{0.34}$-($Fe_{0.67}Ce_{0.50}O_x$)-800 after cycled at 800°C and D) $Ni_{0.66}$-($Fe_{0.33}Ce_{0.50}O_x$)-900, E) $Ni_{0.50}$-($Fe_{0.50}Ce_{0.50}O_x$)-900, and F) $Ni_{0.34}$-($Fe_{0.67}Ce_{0.50}O_x$)-900 after cycled at 900°C. Red solid lines are for samples in the CH_4-reduced state from the 3rd CLDRM cycle, and blue solid lines are for in the CO_2-oxidized state from the 3rd CLDRM cycle. Two Ni references, metallic nickel (solid black) and nickel oxide NiO (dashed purple) were utilized for data analysis.

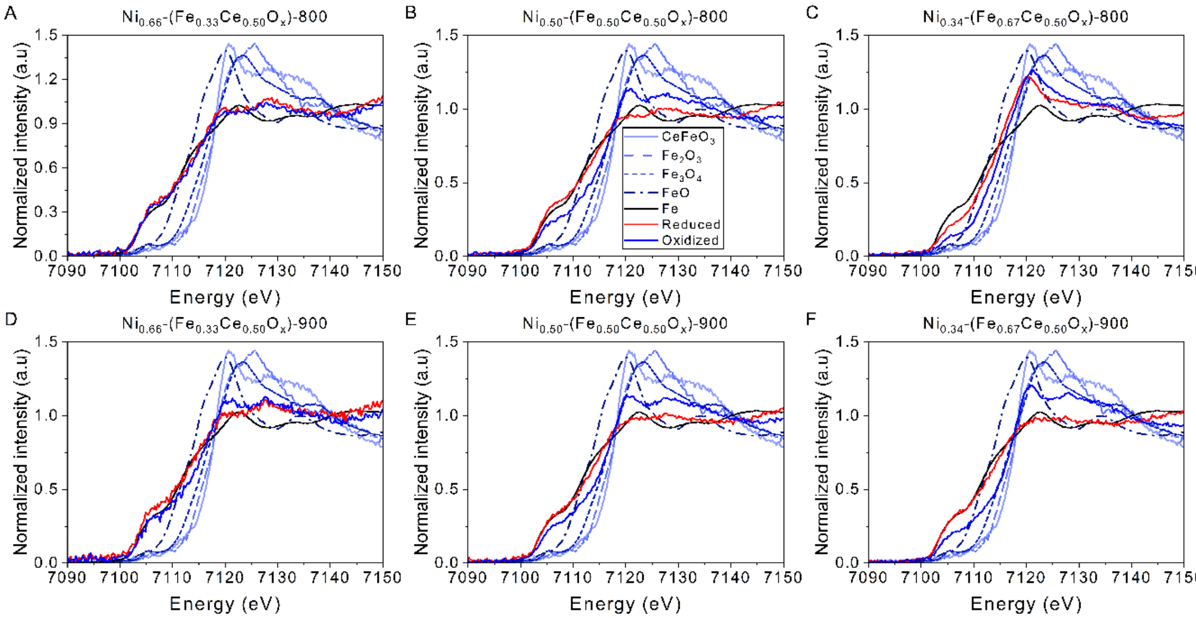

Figure S9: Fe K edge XANES spectra of reduced and oxidized A) $Ni_{0.66}$-($Fe_{0.33}Ce_{0.50}O_x$)-800, B) $Ni_{0.50}$-($Fe_{0.50}Ce_{0.50}O_x$)-800, and C) $Ni_{0.34}$-($Fe_{0.67}Ce_{0.50}O_x$)-800 after cycled at 800°C and D) $Ni_{0.66}$-($Fe_{0.33}Ce_{0.50}O_x$)-900, E) $Ni_{0.50}$-($Fe_{0.50}Ce_{0.50}O_x$)-900, and F) $Ni_{0.34}$-($Fe_{0.67}Ce_{0.50}O_x$)-900 after cycled at 900°C. Red solid lines are for samples in the CH_4-reduced state from the 3rd CLDRM cycle, and blue solid lines are for in the CO_2-oxidized state from the 3rd CLDRM cycle. Five different reference materials were used to help analyze the oxidation state of Fe: cerium orthoferrites (solid pale blue), hematite (long dashed light blue), magnetite (short dashed dark blue), rock salt phase iron oxide (dashed-dotted navy), and metal Fe (solid black).

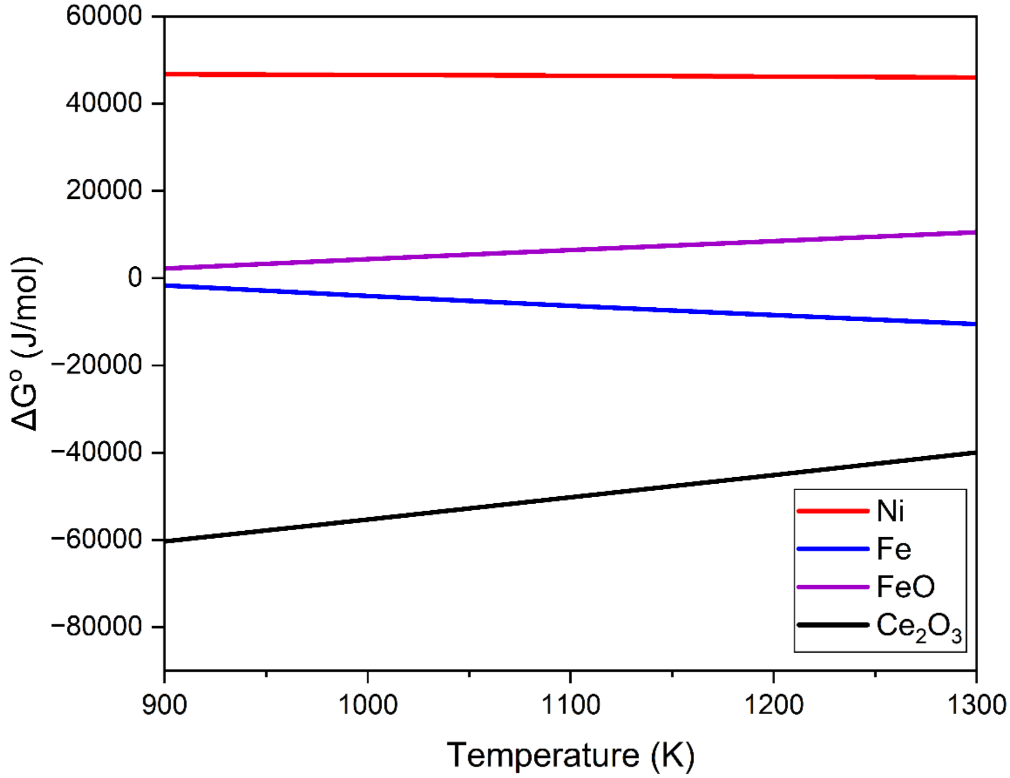

Figure S10: Standard Gibbs free energy change as a function of temperature for the oxidation of Ni ($Ni+CO_2=NiO+CO$), Fe ($Fe+CO_2=FeO+CO$), FeO ($3FeO+CO_2=Fe_3O_4+CO$), and Ce_2O_3 ($Ce_2O_3+CO_2=2CeO_2+CO$) by CO_2 to form CO calculated using FactSage. $CeFeO_3$ and other mixed metal oxides are not included. Each reaction has one mole of oxygen exchange.

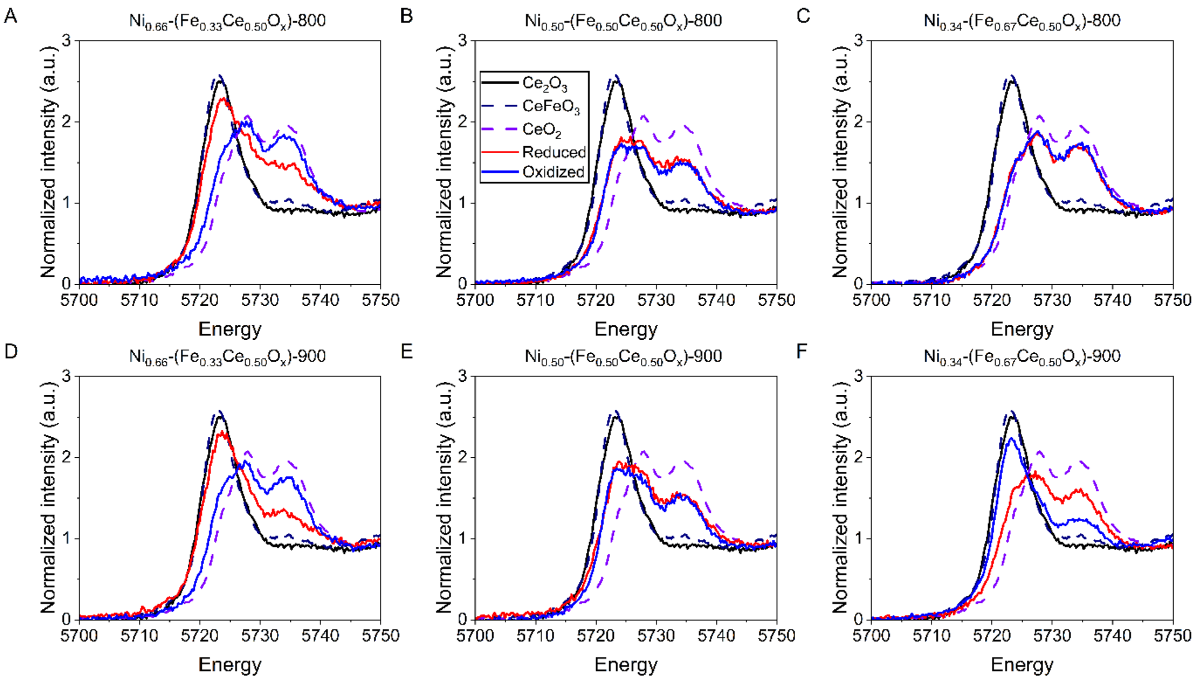

Figure S11: Ce L III edge XANES spectra of reduced and oxidized A) $Ni_{0.66}$-($Fe_{0.33}Ce_{0.50}O_x$)-800, B) $Ni_{0.50}$-($Fe_{0.50}Ce_{0.50}O_x$)-800, and C) $Ni_{0.34}$-($Fe_{0.67}Ce_{0.50}O_x$)-800 after cycled at 800°C and D) $Ni_{0.66}$-($Fe_{0.33}Ce_{0.50}O_x$)-900, E) $Ni_{0.50}$-($Fe_{0.50}Ce_{0.50}O_x$)-900, and F) $Ni_{0.34}$-($Fe_{0.67}Ce_{0.50}O_x$)-900 after cycled at 900°C. Red solid lines are for samples in the CH_4-reduced state from the 3rd CLDRM cycle, and blue solid lines are for in the CO_2-oxidized state from the 3rd CLDRM cycle. Three Ce references, CeO_2 (dashed purple), Ce_2O_3 (solid black) and $CeFeO_3$ (dashed navy) were utilized for the analysis.

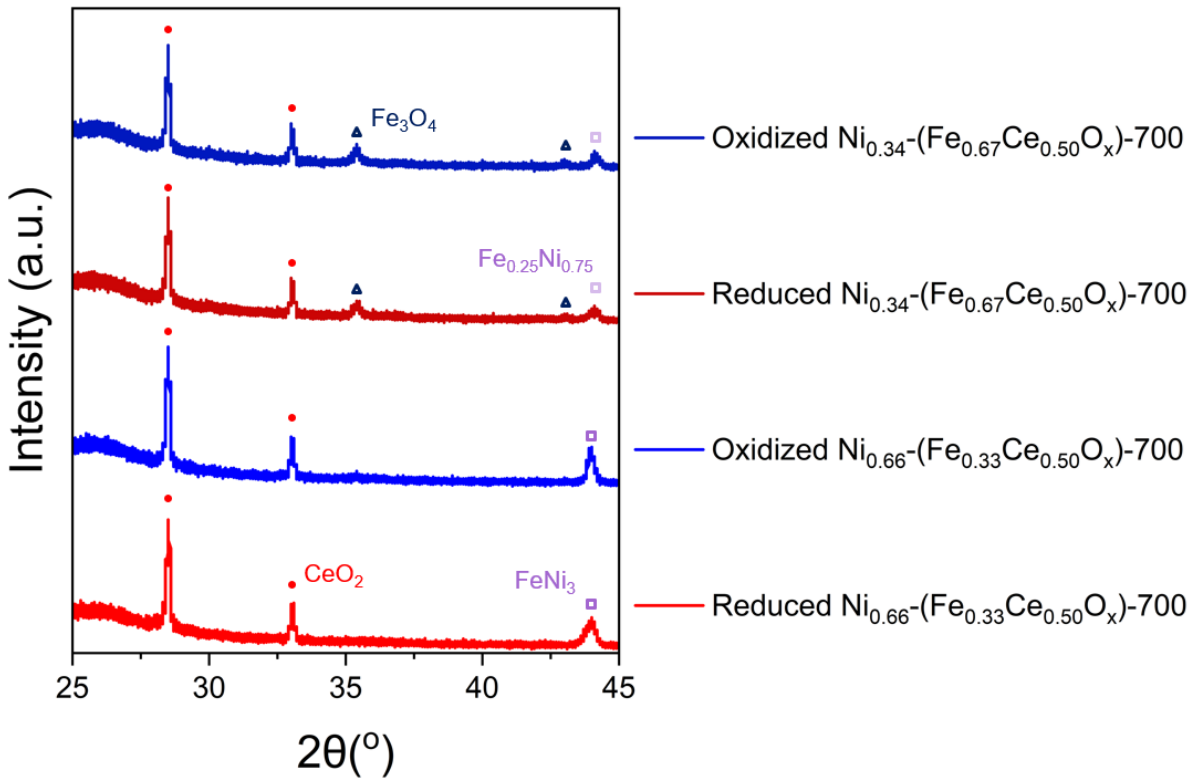

Figure S12: XRD results of $Ni_{0.66}$-($Fe_{0.33}Ce_{0.50}O_x$)-700 and $Ni_{0.34}$-($Fe_{0.67}Ce_{0.50}O_x$)-700 cycled at 700°C. The samples went through 2 complete CLDRM cycles and stopped in the 3rd cycle after CH_4 step and after CO_2 step to study reduced (red tones) and oxidized (blue tones) states. Circular shape symbols represent different types of cerium oxides. : $FeNi_3$ (PDF#: 010745840), : $Fe_{0.25}Ni_{0.75}$ (PDF#: 010889591), : Fe_3O_4 (PDF#: 010751372), : CeO_2 (PDF#: 010758371)

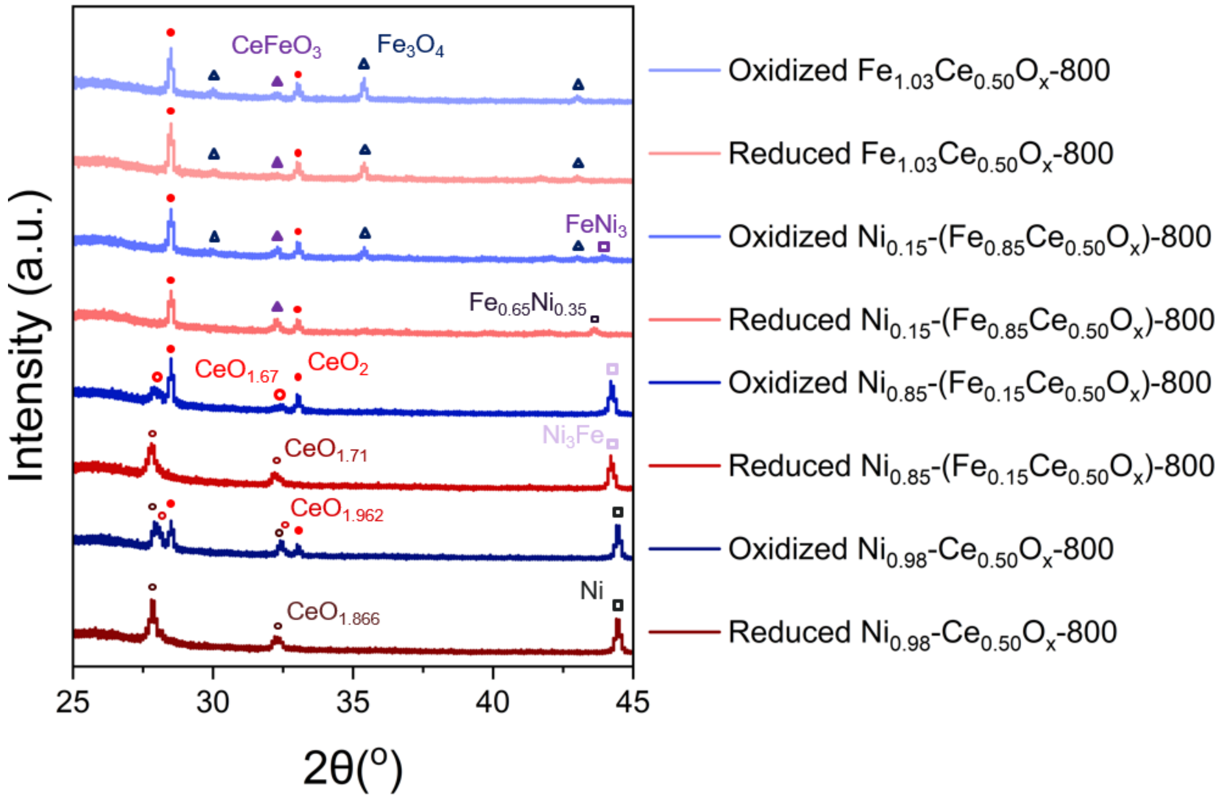

Figure S13: XRD results of four different materials cycled at 800°C. The samples went through 2 complete CLDRM cycles and stopped in the 3rd cycle after CH_4 and after CO_2 steps to study reduced (red tones) and oxidized (blue tones) states. Circular shape symbols represent different types of cerium oxides. ◘ : Ni (PDF#: 010885736), ◘ : Ni_3Fe (PDF#: 010881715), ◘ : $Fe_{0.65}Ni_{0.35}$ (PDF#: 010777970), ◘ : $FeNi_3$ (PDF#: 010745840), △ : Fe_3O_4 (PDF#: 010751372), ▲ : $CeFeO_3$ (PDF#: 000220166), ○ : Ce_3O_5 (PDF#: 010814450), ○ : Ce_7O_{12} (PDF#: 010898432), ○ : $CeO_{1.962}$ (PDF#: 010786853), ○ : $CeO_{1.866}$ (PDF#: 010786854), ● : CeO_2 (PDF#: 010758371)

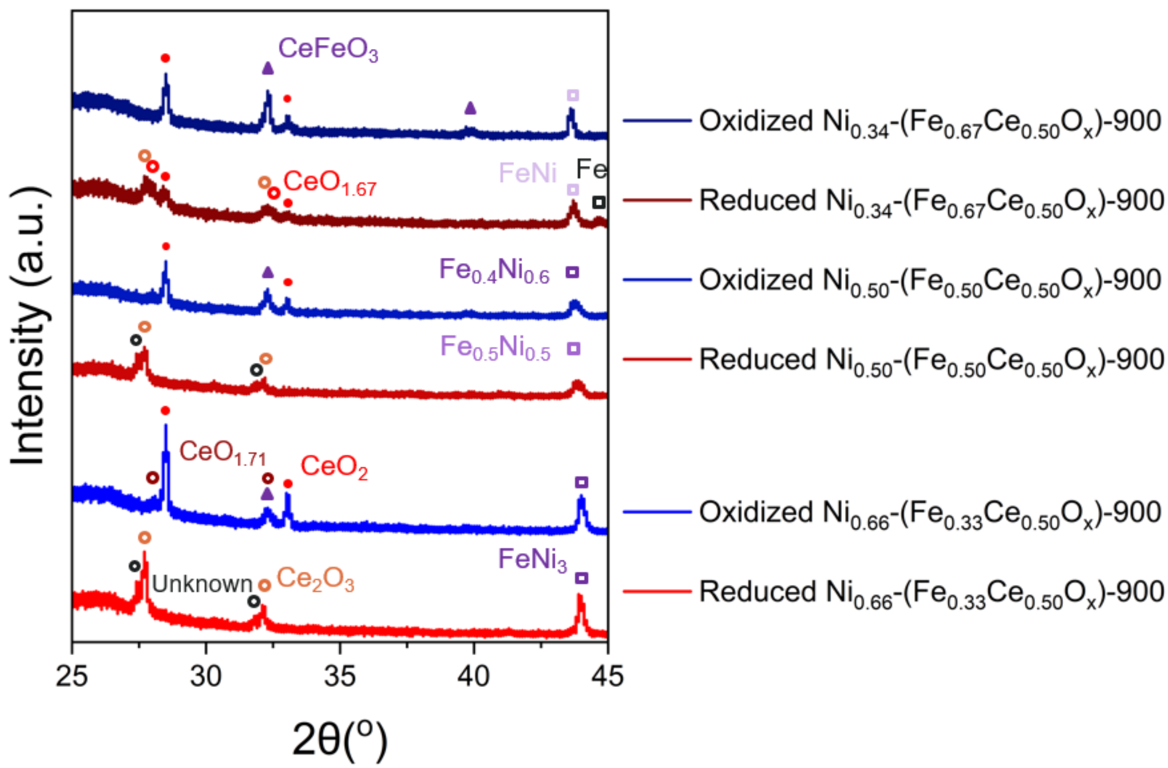

Figure S14: XRD results of Ni$_{0.66}$-(Fe$_{0.33}$Ce$_{0.50}$O$_x$)-900, Ni$_{0.50}$-(Fe$_{0.50}$Ce$_{0.50}$O$_x$)-900, and Ni$_{0.34}$-(Fe$_{0.67}$Ce$_{0.50}$O$_x$)-900 cycled at 900°C. The samples went through 2 complete CLDRM cycles and stopped in the 3rd cycle after CH_4 and after CO_2 steps to study reduced (red tones) and oxidized (blue tones) states. Circular shape symbols represent different types of cerium oxides. : FeNi$_3$ (PDF#: 010745840), : Fe$_{0.4}$Ni$_{0.6}$ (PDF#: 010777972), : FeNi (PDF#: 010718321), : Fe$_{0.50}$Ni$_{0.50}$ (PDF#: 010889593), : Fe (PDF#: 010714409), : CeFeO$_3$ (PDF#: 000220166), : Ce$_2$O$_3$ (PDF#: 010825921), : Ce$_3$O$_5$ (PDF#: 010814450), : Ce$_7$O$_{12}$ (PDF#: 010898432), : CeO$_2$ (PDF#: 010758371), : Reduced ceria not in XRD database.

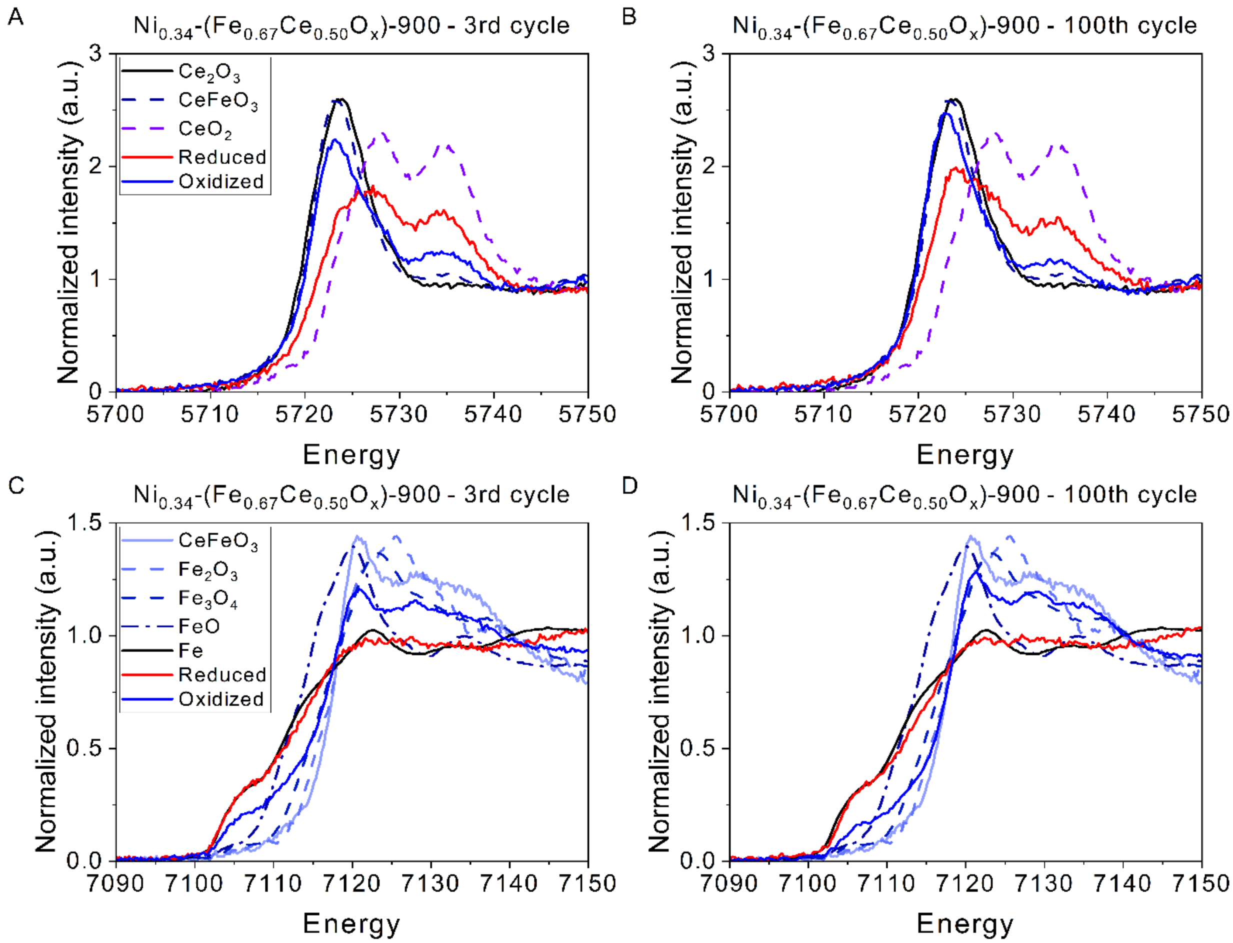

Figure S15: Ce L III edge XANES spectra of reduced and oxidized A) $Ni_{0.34}$-($Fe_{0.67}Ce_{0.50}O_x$)-900 at 3rd cycle, B) $Ni_{0.34}$-($Fe_{0.67}Ce_{0.50}O_x$)-900 at 100th cycle. Three Ce references, CeO_2 (dashed purple), Ce_2O_3 (solid black) and $CeFeO_3$ (dashed navy) were utilized for the analysis. Fe K edge XANES spectra of reduced and oxidized C) $Ni_{0.34}$-($Fe_{0.67}Ce_{0.50}O_x$)-900 at 3rd cycle, D) $Ni_{0.34}$-($Fe_{0.67}Ce_{0.50}O_x$)-900 at 100th cycle. Five different reference materials were used to help analyze the oxidation state of iron: cerium orthoferrites (solid pale blue), hematite (long dashed light blue), magnetite (short dashed dark blue), rock salt phase iron oxide (dashed-dotted navy), and metal Fe (solid black). Red solid lines are for samples in the CH_4-reduced state, and blue solid lines are for in the CO_2-oxidized state.

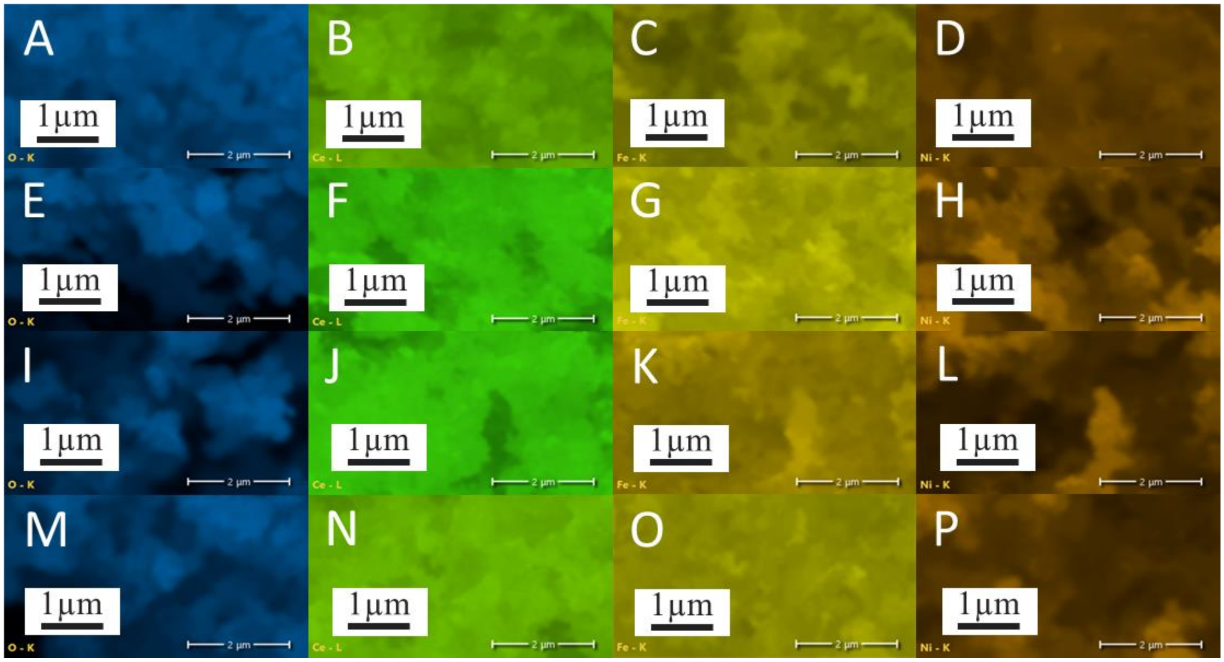

Figure S16: EDS elemental distribution of fresh and cycled $Ni_{0.34}$-($Fe_{0.67}Ce_{0.50}O_x$)-900. Four major elements, O (blue), Ce (Green), Fe (yellow), and Ni (orange) were observed. A, B, C, and D) Fresh, E, F, G, and H) CH_4-reduced in 3rd cycle, I, J, K and L) CO_2-oxidized in 3rd cycle, M, N, O, and P) CH_4-reduced in 100th cycle are presented.

Table S1: Linear combination fitting results of fractions of every metal oxidation state by XANES spectra for cycled samples at 800°C. Samples were collected from the 3rd CLDRM cycle. Three different oxidation states of Fe, Fe_3O_4, and $CeFeO_3$ and two oxidation states of cerium, Ce_2O_3 and CeO_2 and Ni and NiO were used for the analysis. The numbers in parenthesis are error bars.

	Fe+0	**Fe+2**	**Fe+3**	**Ce+3**	**Ce+4**	**Ni+0**	**Ni+2**
Reduced $Ni_{0.66}$-($Fe_{0.33}Ce_{0.50}O_x$)-800	0.99 (0.0122)	0	0.01 (0.0122)	0.615 (0.0179)	0.385 (0.0194)	1 (0.0133)	0 (0.0133)
Oxidized $Ni_{0.66}$-($Fe_{0.33}Ce_{0.50}O_x$)-800	0.962 (0.0100)	0	0.038 (0.0158)	0.186 (0.00739)	0.814 (0.00739)	1 (0.0116)	0 (0.116)
Reduced $Ni_{0.50}$-($Fe_{0.50}Ce_{0.50}O_x$)-800	1 (0)	0	0 (0.0122)	0.394 (0.0185)	0.606 (0.00486)	1 (0.0098)	0 (0.0098)
Oxidized $Ni_{0.50}$-($Fe_{0.50}Ce_{0.50}O_x$)-800	0.656 (0.0092)	0	0.344 (0.0092)	0.407 (0.0199)	0.593 (0.00868)	1 (0.016)	0 (0.016)
Reduced $Ni_{0.34}$-($Fe_{0.67}Ce_{0.50}O_x$)-800	0.748 (0.0275)	0	0.252 (0.0275)	0.213 (0.0192)	0.787 (0.00695)	1 (0.013)	0 (0.013)
Oxidized $Ni_{0.34}$-($Fe_{0.67}Ce_{0.50}O_x$)-800	0.407 (0.0252)	0.167 (0.174)	0.426 (0.115)	0.191 (0.0188)	0.809 (0.00595)	1 (0.0278)	0 (0.0278)

Table S2: Linear combination fitting results of fractions of every metal oxidation state by XANES spectra for cycled samples at 900°C. Samples were collected from the 3rd CLDRM cycle. Three different oxidation states of Fe, Fe_3O_4, and $CeFeO_3$ and two oxidation states of cerium, Ce_2O_3 and CeO_2 and Ni and NiO were used for the analysis. The numbers in parenthesis are error bars.

	Fe+0	**Fe+3**	**Ce+3**	**Ce+4**	**Ni+0**	**Ni+2**
Reduced $Ni_{0.66}$-($Fe_{0.33}Ce_{0.50}O_x$)-900	0.898 (0.018)	0.102 (0.022)	0.722 (0.0130)	0.278 (0.013)	1 (0.0104)	0 (0.0104)
Oxidized $Ni_{0.66}$-($Fe_{0.33}Ce_{0.50}O_x$)-900	0.811 (0.012)	0.189 (0.018)	0.238 (0.0137)	0.762 (0.00437)	0.9753 (0.0127)	0.0247 (0.0127)
Reduced $Ni_{0.50}$-($Fe_{0.50}Ce_{0.50}O_x$)-900	0.935 (0.020)	0.065 (0.009)	0.460 (0.0150)	0.540 (0.00737)	0.9658 (0.0226)	0.0342 (0.0226)
Oxidized $Ni_{0.50}$-($Fe_{0.50}Ce_{0.50}O_x$)-900	0.62 (0.009)	0.38 (0.013)	0.469 (0.00609)	0.531 (0.00609)	0.9732 (0.0191)	0.0268 (0.019)
Reduced $Ni_{0.34}$-($Fe_{0.67}Ce_{0.50}O_x$)-900	0.972 (0.012)	0.028 (0.008)	0.322 (0.00604)	0.678 (0.00604)	1 (0.0161)	0 (0.0161)
Oxidized $Ni_{0.34}$-($Fe_{0.67}Ce_{0.50}O_x$)-900	0.495 (0.00684)	0.505 (0.01)	0.745 (0.00956)	0.255 (0.0074)	1 (0.0279)	0 (0.0279)

Table S3: Comparison between oxygen gain by the solid material during CO_2 step calculated from reactor exhaust gas analysis vs. oxygen uptake of metal oxide by XANES linear combination fitting. The 1st column shows oxygen gain by the material calculated from CO formation amount and converted CO_2 amount in the CO_2 step of Cycle 3. The oxygen uptake of metal oxide in the 2nd column was calculated based on combined oxidation state changes of each element from XANES data of reduced and oxidized samples from the 3rd cycle.

	Oxygen uptake by the solid material during CO_2 step in Cycle 3 [mol per 0.5g fresh material]	Total oxygen uptake of metal oxide via XANES analysis of samples from Cycle 3 [mol per 0.5g fresh material]
$Ni_{0.66}$-($Fe_{0.33}Ce_{0.50}O_x$)-800	0.000575	0.000376
$Ni_{0.50}$-($Fe_{0.50}Ce_{0.50}O_x$)-800	0.001242	0.000787
$Ni_{0.34}$-($Fe_{0.67}Ce_{0.50}O_x$)-800	0.001159	0.000900
$Ni_{0.66}$-($Fe_{0.33}Ce_{0.50}O_x$)-900	0.000784	0.000560
$Ni_{0.50}$-($Fe_{0.50}Ce_{0.50}O_x$)-900	0.001070	0.000712
$Ni_{0.34}$-($Fe_{0.67}Ce_{0.50}O_x$)-900	0.001755	0.001152

References

1 A. More, S. Bhavsar and G. Veser, *Energy Technol.*, 2016, **4**, 1147–1157.
2 J. Zhang, V. Haribal and F. Li, *Sci. Adv.*, 2017, **3**, e1701184.
3 Y. Kim, H. S. Lim, M. Lee and J. W. Lee, *Catal. Today*, 2021, **368**, 86–95.
4 J. Zhang, T. Yang, Q. Rao, Z. Gai, P. Li, Y. Shen, M. Liu, Y. Pan and H. Jin, *Fuel*, 2024, **366**, 131344.