**Supplementary Information for**

**Reaction-induced Ni-based interstitial carbon atoms for coke-free dry reforming of methane**

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Supplementary References

**Supplementary Note**

**Thermodynamic study.** The Gibbs free energy change of the reaction (Ni3Zn + 0.7CH4 → Ni3ZnC0.7 + 1.4H2, Equation 1) was calculated in the temperature range from 27 to 627℃. The general gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional[1, 2] were performed for the structure optimization of H2, CH4, Ni3Zn and Ni3ZnC0.7. To better describe the structure of Ni3Zn and Ni3ZnC0.7, a crystal model of Ni60Zn20 and Ni60Zn20C14 were selected. The projected-augmented wave (PAW)[3] pseudopotential was employed to treat the electron-ion interaction with cut-off energy of 500 eV and the k-points meshes were sampled as 3×3×3. The density functional dispersion correction (DFT-D3)[4] was used to consider the van der Waals interactions. All the above calculations were carried out in Vienna Ab initio Simulation Package (VASP)[[5, 6](#_ENREF_36" \o "Kresse, 1996 #87)]. The convergence criteria of total energy and force were 1×10-6 eV and 0.01 eV/Å, respectively. In the temperature range from 27 to 627℃, all of the thermodynamic data of Ni60Zn20 and Ni60Zn20C14 were obtained by Phonopy package[7], and the thermodynamic data of H2 and CH4 were obtained by Vaspkit code[8]. The Gibbs free energy change of the reaction (Equation 1) was obtained by following formula:

where represents the Gibbs free energy change of the reaction (Equation 1), represents the Gibbs free energy of Ni60Zn20C14, Ni60Zn20, CH4 and H2.

**Supplementary Table 1**. The Gibbs free energy of Ni60Zn20C14, Ni60Zn20, CH4, H2 and the Gibbs free energy change of the reaction between Ni3Zn and CH4.

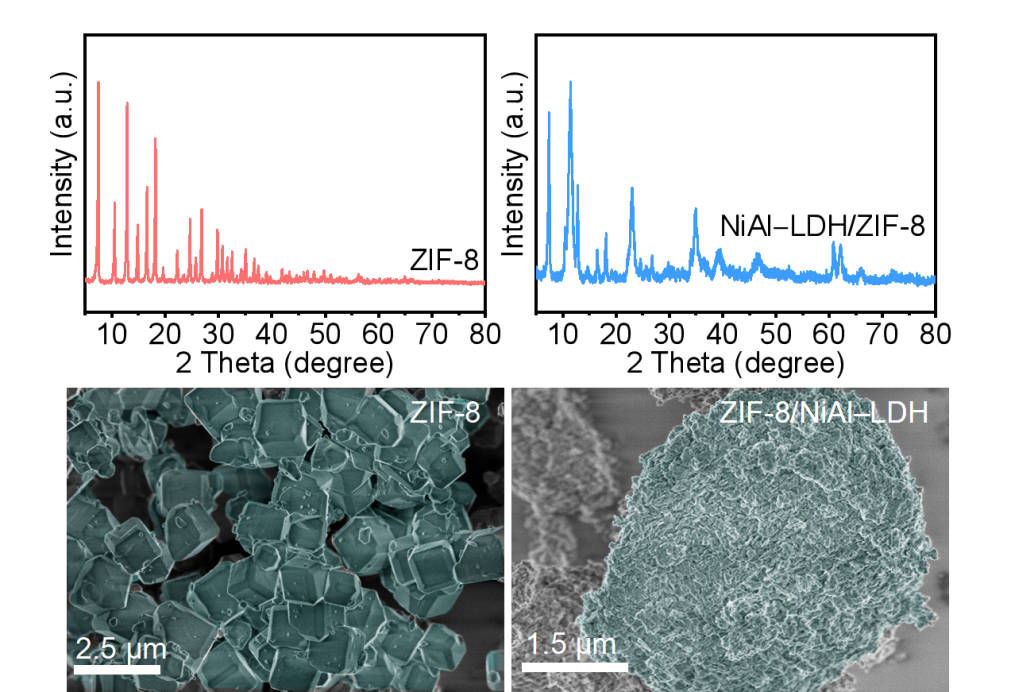
|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Temperature (℃) | Ni60Zn20C14  (kJ/mol) | Ni60Zn20  (kJ/mol) | CH4  (kJ/mol) | H2  (kJ/mol) | ΔrG  (kJ/mol) |
| 27 | -55787.22 | -37921.96814 | -2241.339513 | -603.699744 | -169.5046482 |
| 77 | -55917.74 | -38038.25826 | -2250.762105 | -610.136832 | -172.6323159 |
| 127 | -56061.80 | -38168.14782 | -2260.456665 | -616.781472 | -175.857069 |
| 177 | -56217.85 | -38310.30438 | -2270.405625 | -623.607552 | -179.1438428 |
| 227 | -56384.64 | -38463.61519 | -2280.596793 | -630.594912 | -182.4664086 |
| 277 | -56561.16 | -38627.1401 | -2291.020569 | -637.727136 | -185.8046586 |
| 327 | -56746.56 | -38800.07635 | -2301.669177 | -644.991264 | -189.1437547 |
| 377 | -56940.14 | -38981.73196 | -2312.535609 | -652.376064 | -192.4718276 |
| 427 | -57141.27 | -39171.50522 | -2323.613721 | -659.872416 | -195.7800542 |
| 477 | -57349.44 | -39368.86884 | -2334.897849 | -667.472256 | -199.0611963 |
| 527 | -57564.19 | -39573.35741 | -2346.382809 | -675.168672 | -202.3095723 |
| 577 | -57785.11 | -39784.55747 | -2358.063609 | -682.955616 | -205.5207485 |
| 627 | -58011.84 | -40002.09955 | -2369.935545 | -690.827904 | -208.6914027 |

**Supplementary Table 2**. Reaction rate and rate constant with different partial pressure of CH4 at 390, 400, 410 and 420℃ during DRM.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Temperature (℃) | Partial pressure of reactant  (kPa) | | Reaction rate  (mol gcat-1·s-1） | | k1 |
| CH4 | CO2 | CH4 | CO2 |
| 390 | 19.50 | 48.59 | 6.01×10-7 | 4.40×10-6 | 0.172 |
| 29.60 | 49.19 | 1.05×10-6 | 4.48×10-6 |
| 39.05 | 48.46 | 1.70×10-6 | 3.94×10-6 |
| 48.50 | 48.45 | 2.06×10-6 | 4.33×10-6 |
| 400 | 19.34 | 48.18 | 8.39×10-7 | 5.97×10-6 | 0.233 |
| 29.58 | 49.10 | 1.46×10-6 | 5.86×10-6 |
| 39.18 | 48.53 | 2.18×10-6 | 5.06×10-6 |
| 48.71 | 48.58 | 2.74×10-6 | 5.34×10-6 |
| 410 | 19.14 | 47.74 | 9.81×10-7 | 6.62×10-6 | 0.324 |
| 29.01 | 48.12 | 2.23×10-6 | 8.18×10-6 |
| 38.80 | 47.92 | 2.99×10-6 | 6.94×10-6 |
| 48.13 | 47.84 | 3.47×10-6 | 6.79×10-6 |
| 420 | 19.09 | 47.67 | 1.36×10-6 | 8.71×10-6 | 0.413 |
| 28.80 | 47.76 | 2.48×10-6 | 8.94×10-6 |
| 38.50 | 47.52 | 3.42×10-6 | 7.73×10-6 |
| 47.64 | 47.22 | 4.88×10-6 | 8.85×10-6 |

**Supplementary Table 3**. Reaction rate and rate constant with different partial pressure of CO2 at 390, 400, 410 and 420℃ during DRM.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Temperature (℃) | Partial pressure of reactant  (kPa) | | Reaction rate  (mol gcat-1·s-1） | | k2 |
| CH4 | CO2 | CH4 | CO2 |
| 390 | 48.82 | 19.41 | 4.28×10-6 | 1.48×10-6 | 0.460 |
| 49.02 | 29.27 | 2.92×10-6 | 2.18×10-6 |
| 48.60 | 38.93 | 2.93×10-6 | 3.59×10-6 |
| 48.68 | 48.60 | 4.98×10-6 | 6.54×10-6 |
| 400 | 49.18 | 19.44 | 3.48×10-6 | 1.55×10-6 | 0.519 |
| 48.87 | 29.07 | 3.40×10-6 | 2.65×10-6 |
| 48.36 | 38.62 | 3.49×10-6 | 4.35×10-6 |
| 48.77 | 48.54 | 4.71×10-6 | 6.90×10-6 |
| 410 | 49.02 | 19.25 | 4.42×10-6 | 1.93×10-6 | 0.621 |
| 49.25 | 29.18 | 3.90×10-6 | 3.10×10-6 |
| 48.60 | 38.71 | 3.92×10-6 | 4.99×10-6 |
| 48.66 | 48.34 | 5.75×10-6 | 8.36×10-6 |
| 420 | 49.30 | 19.24 | 3.74×10-6 | 2.03×10-6 | 0.684 |
| 48.99 | 28.88 | 4.04×10-6 | 3.55×10-6 |
| 48.43 | 38.44 | 4.45×10-6 | 5.81×10-6 |
| 48.83 | 48.37 | 5.48×10-6 | 8.66×10-6 |



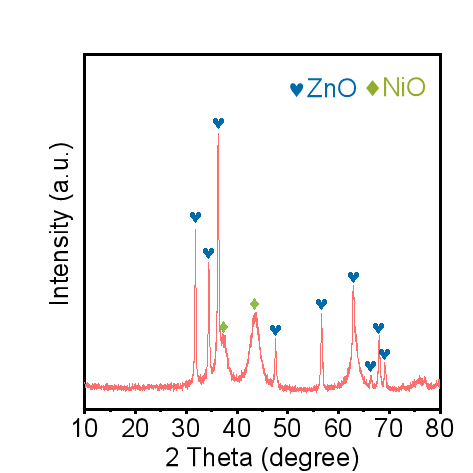
a

b

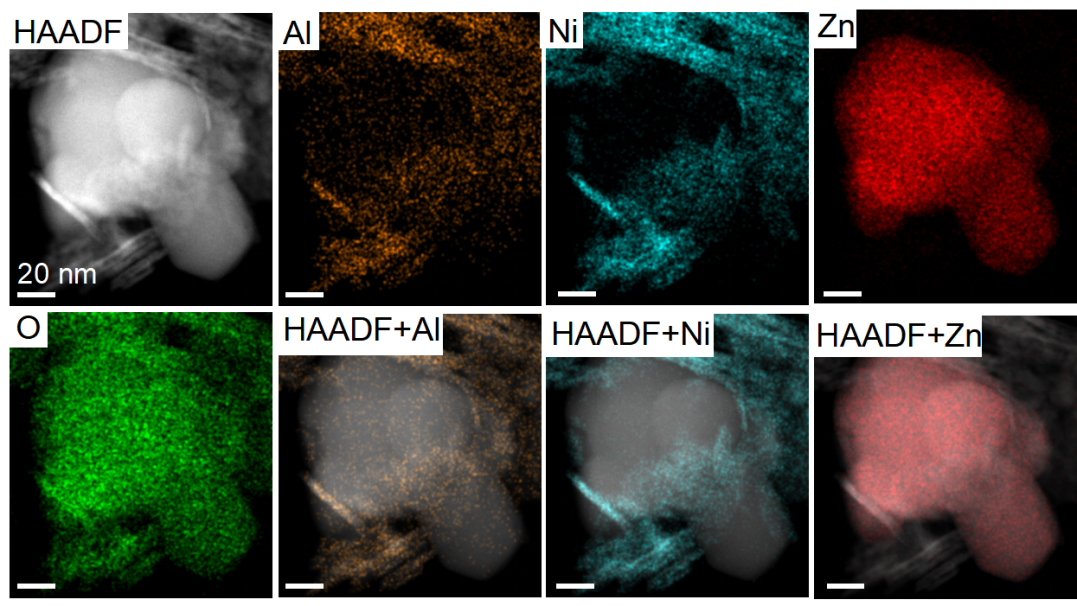
c

d

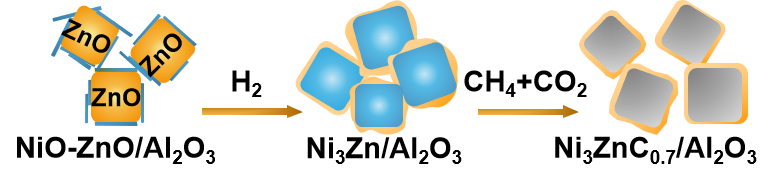
**Supplementary Figure 1. a**, **b**,XRD patterns and **c**, **d**, SEM images of (a, c) ZIF-8 and (b, d) ZIF-8/NiAl−LDH composite.



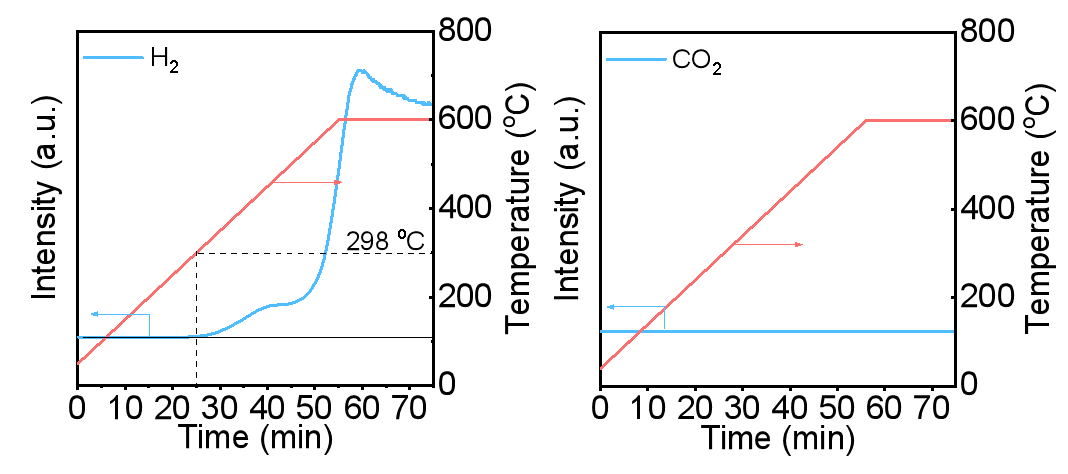
**Supplementary Figure 2.** XRD pattern of NiO−ZnO/Al2O3.



**Supplementary Figure 3.** STEM−HAADF images with elemental mapping of NiO−ZnO/Al2O3.



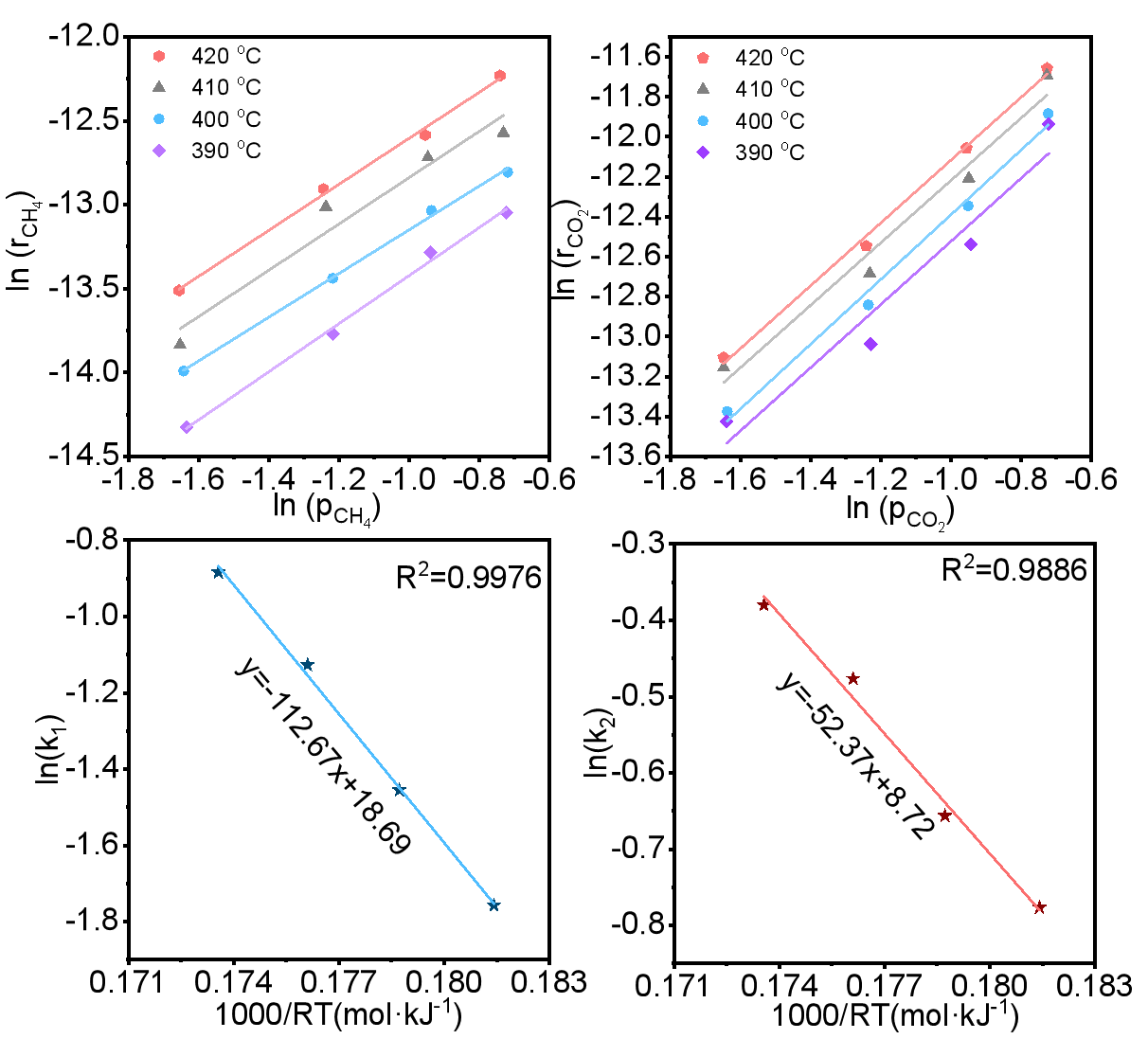
**Supplementary Figure 4.** Schematic illustration of the process of the changes from NiO−ZnO/Al2O3 to Ni3Zn/Al2O3 under H2 reduction and further to Ni3ZnC0.7/Al2O3 during DRM.



a

b

**Supplementary Figure 5.** TPSR−MS results of Ni3Zn/Al2O3 at elevated temperatures under (a) CH4 and (b) CO atmosphere.



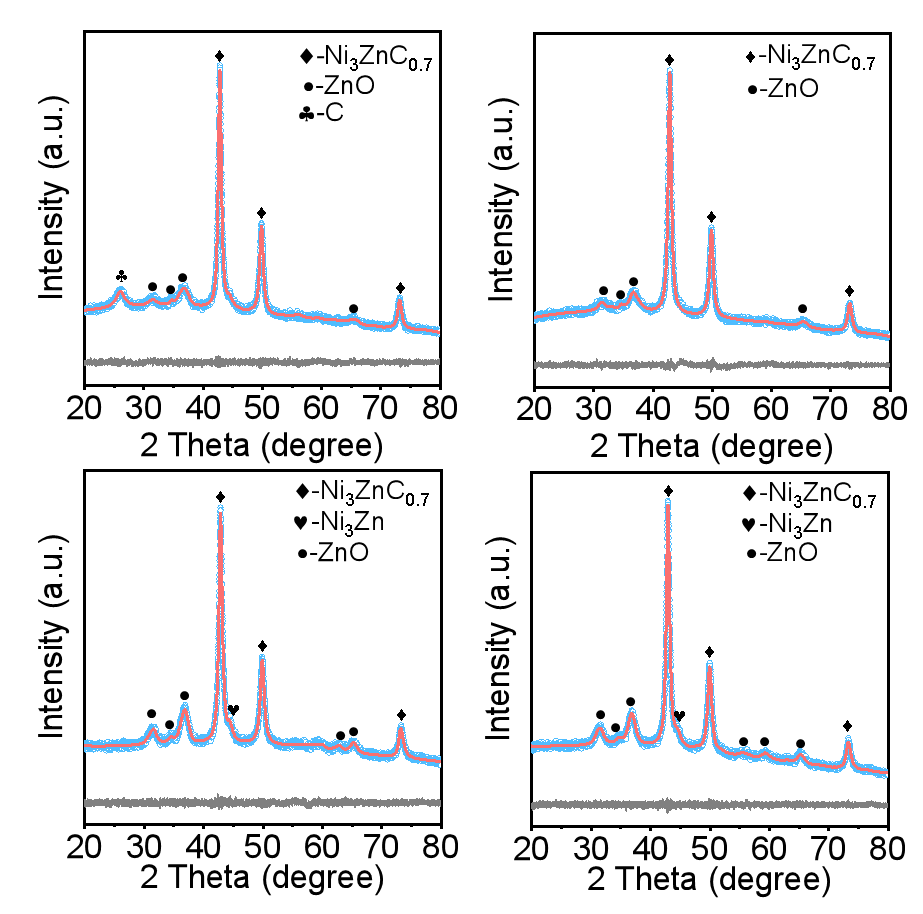
a

b

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d

**Supplementary Figure 6.** (a, b) Changes of reaction rates as the partial concentration of reactants changes and the corresponding Arrhenius plots for (c) CH4 and (d) CO2 activation energies over Ni3ZnC0.7/Al2O3.



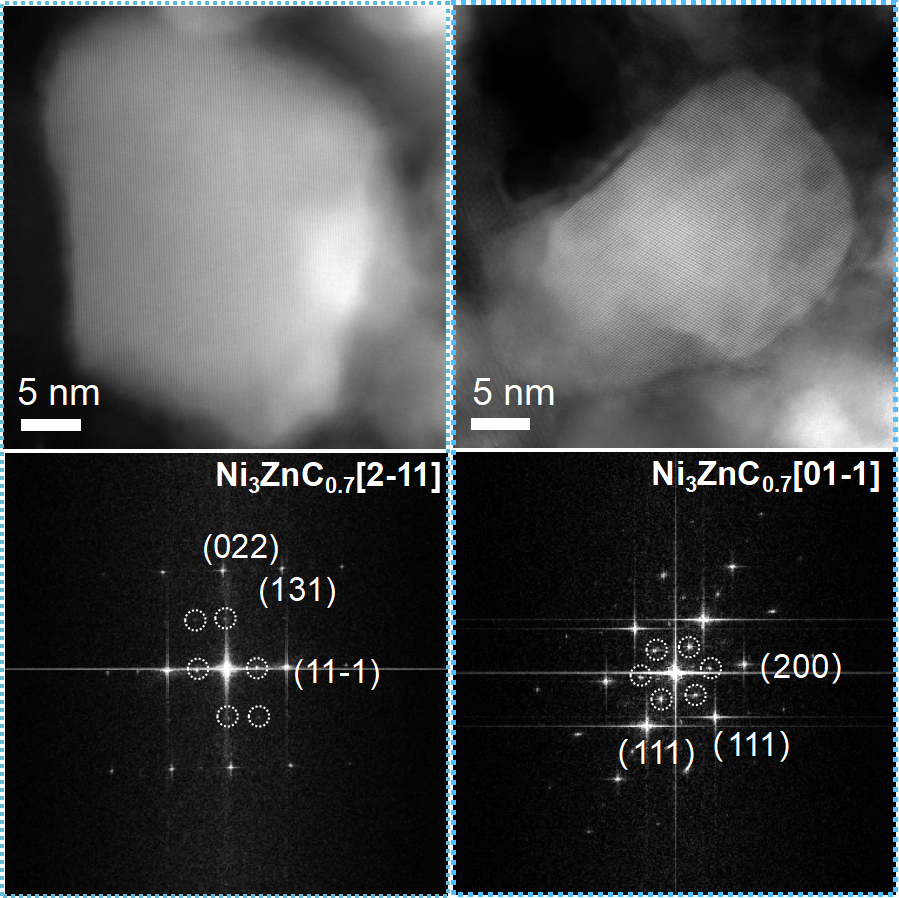
a

b

c

d

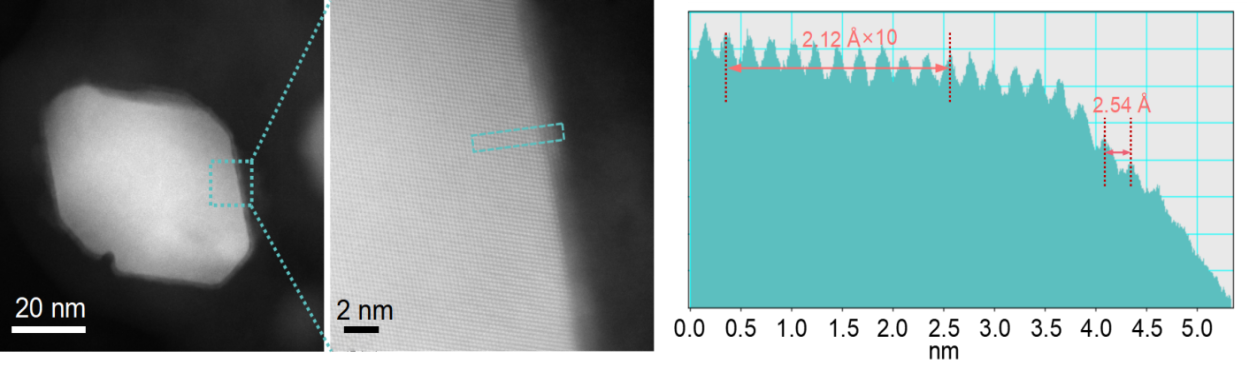
**Supplementary Figure 7.** Refined XRD patterns of Ni3ZnC0.7/Al2O3 after 100 h DMR at 500℃ with CH4/CO2 ratio of (a) 4/1, (b) 2/1, (c) 1/2 and (d) 1/4.



a

b

**Supplementary Figure 8.** HRTEM images and SAED patterns of Ni3ZnC0.7/Al2O3 after 100 h reaction with CH4/CO2 ratio of 1/1 in different regions and different crystal axis directions.

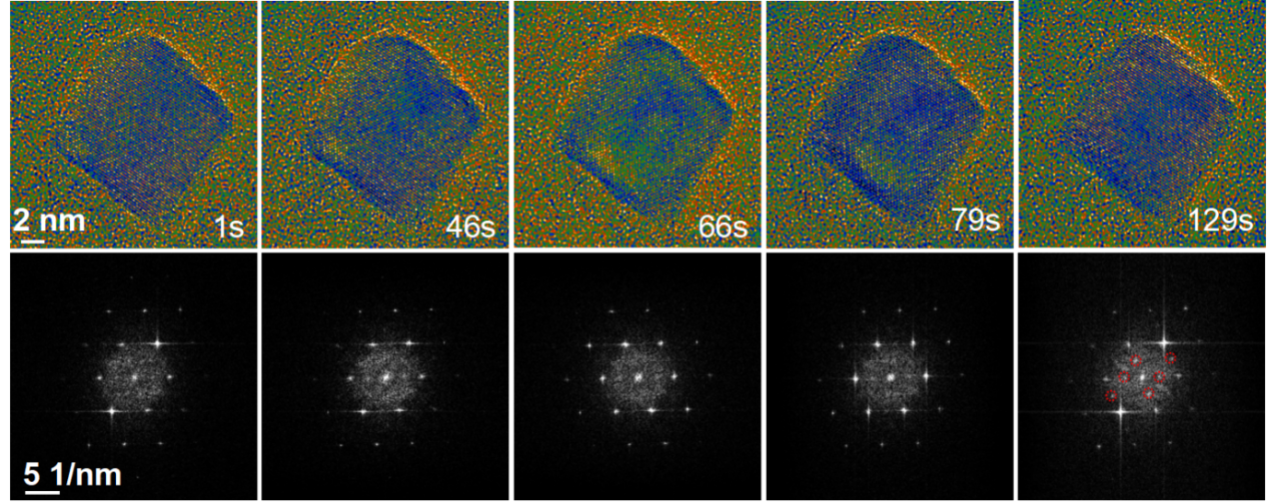


a

b

c

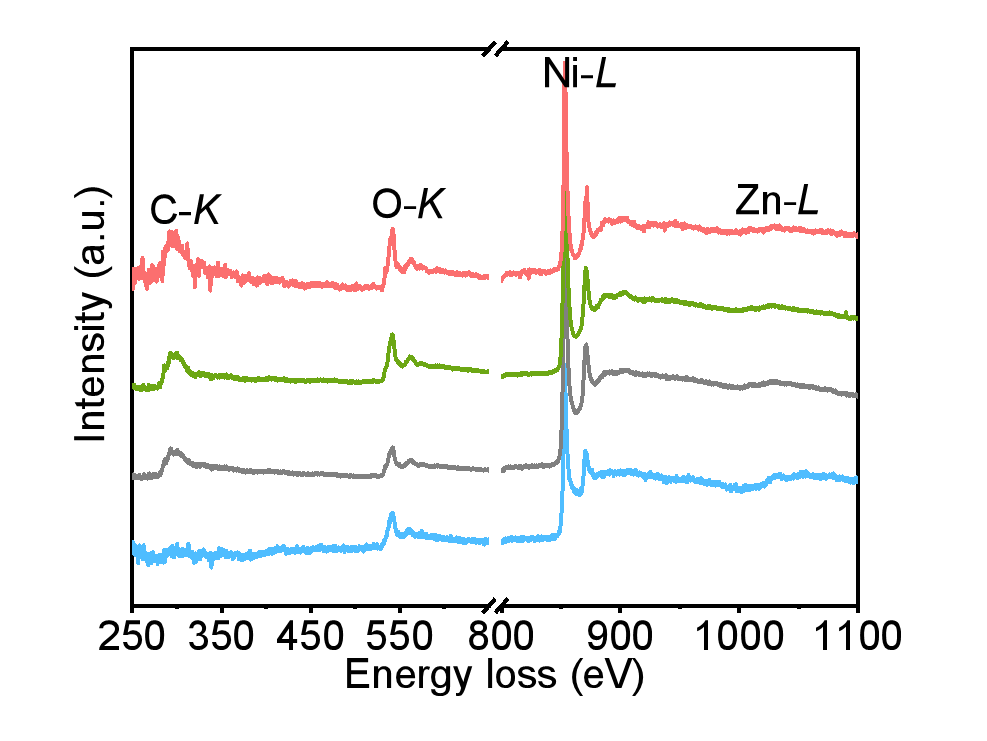
**Supplementary Figure 9.** (a) TEM, (b) HRTEM images, and (c) corresponding profile of the Ni3ZnC0.7/Al2O3.



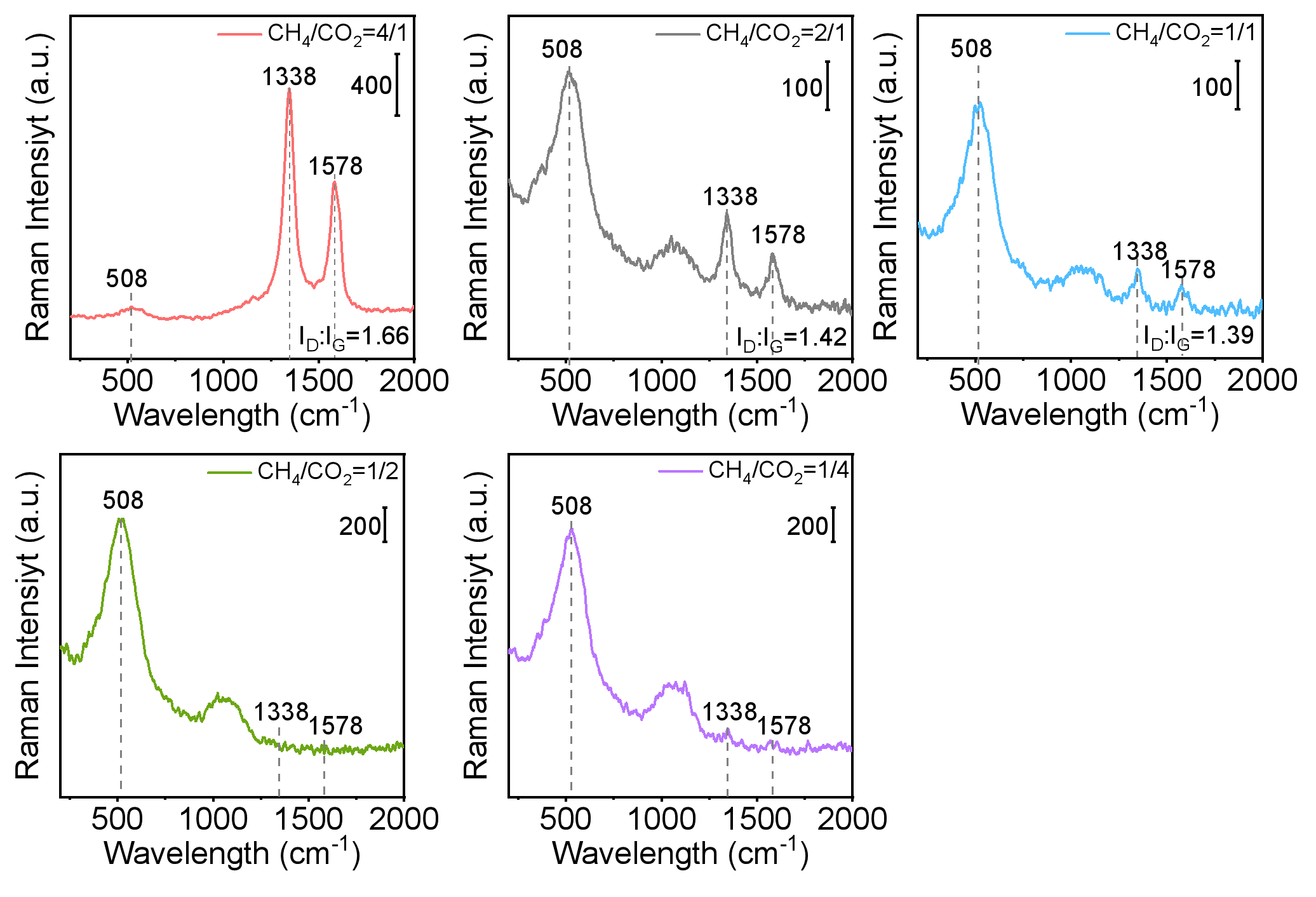
a

b

**Supplementary Figure 10.** (a) Color-coded in-situ HRTEM images on the evolution from Ni3Zn to Ni3ZnC0.7 during the DMR with CH4/CO2 ratio of 1/1 at 500℃ and (b) corresponding FFT images.



**Supplementary Figure 11.** In situ EEL spectra of Ni3Zn/Al2O3 during DRM with CH4/CO2 ratio of 1/1. The profile from bottom to up was obtained at room temperature, at 500℃ under CH4 and CO2, at 500℃ without reactants, and at room temperature after the reaction.



a

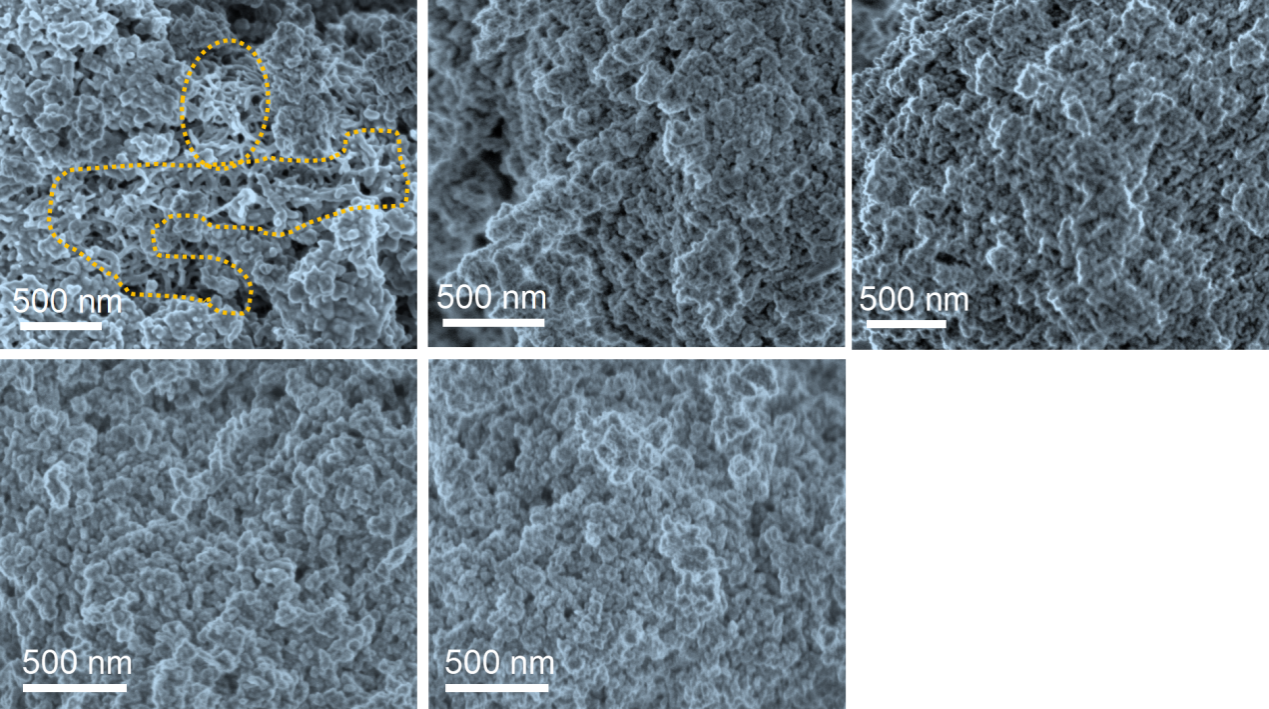
b

c

d

e

**Supplementary Figure 12.** Raman spectra of the catalysts after 100 h at 500℃ with CH4/CO2 ratio of (a) 4/1, (b) 2/1, (c) 1/1, (d) 1/2 and (e) 1/4.



a

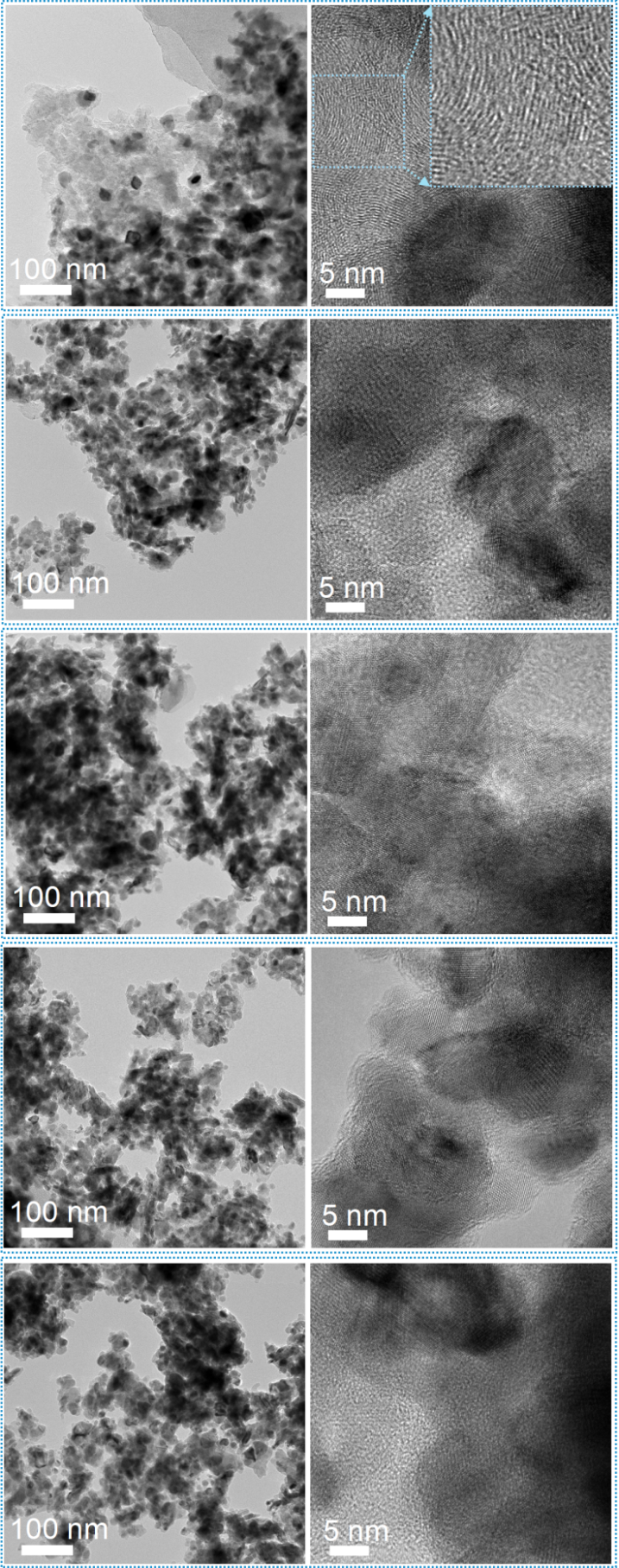
b

c

d

e

**Supplementary Figure 13.** SEM images of Ni3ZnC0.7/Al2O3 after 100 h period at 500℃ with CH4/CO2 ratio of (a) 4/1, (b) 2/1, (c) 1/1, (d) 1/2, and (e) 1/4.



a

c

e

g

i

b

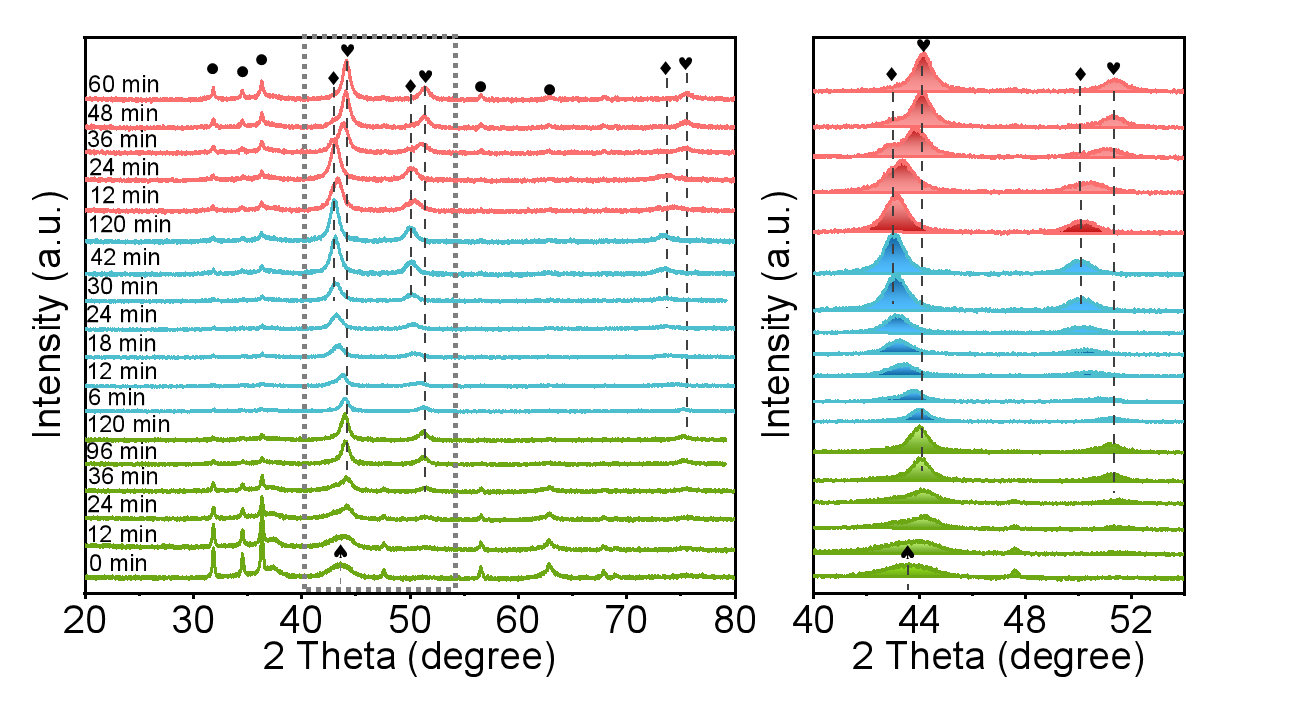
d

f

h

j

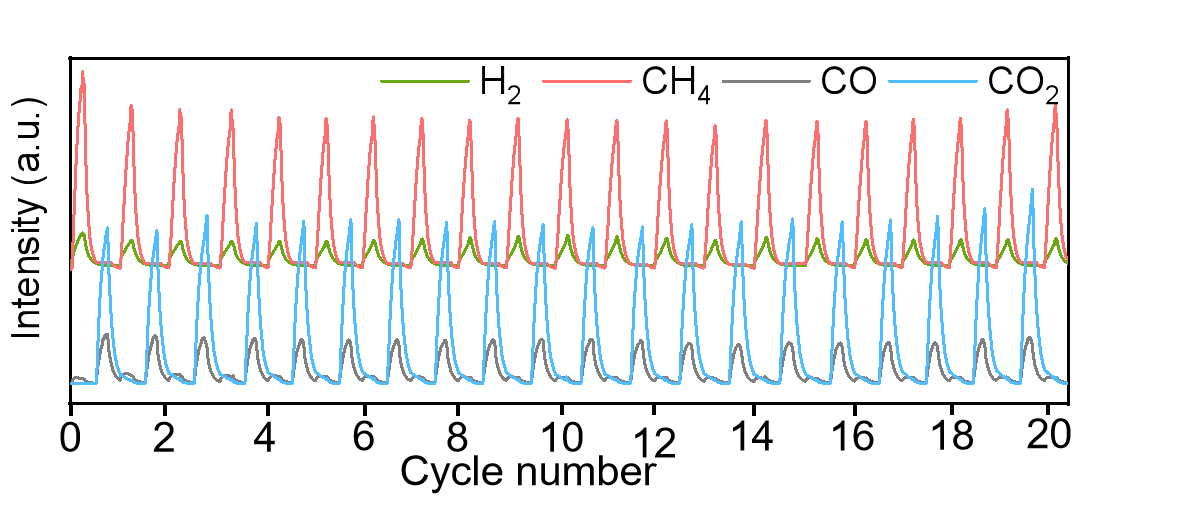
**Supplementary Figure 14.** TEM and HRTEM images of Ni3ZnC0.7/Al2O3 after 100 h period at 500℃ with CH4/CO2 ratio of (a, b) 4/1, (c, d) 2/1, (e, f) 1/1, (g, h) 1/2, and (i, j) 1/4.



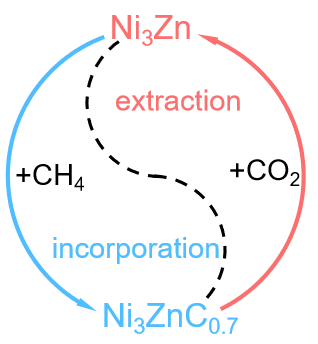
a

b

**Supplementary Figure 15.** **a,** In situ (a) XRD patterns and (b) cross sections of NiO−ZnO/Al2O3 under H2 reduction process at 550℃ (green curve), and then under DRM with CH4/CO2 ratio of 1/1 at 500℃ (blue curve), and further under CO2 at 500℃ (pink curve). ●, ♥, ♦ and ♠: ZnO, Ni3Zn, Ni3ZnC0.7 and NiO.



**Supplementary Figure 16.** Pulse experiment of CH4−Ar−CO2−Ar−CH4 cycles for the reduced catalyst at 600℃.



**Supplementary Figure 17.** Illustration of carbon cycle between Ni3Zn and Ni3ZnC0.7 during DRM.

**Supplementary References**

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