

## **Electronic Supplementary Information (ESI)**

### **Emergent Ni catalysts induced by nitride-to-oxide transformation for coking and sintering resistant dry reforming of methane**

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## Catalyst preparation

First, 0.404 g nickel chloride hexahydrate ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ) was thoroughly mixed with 24 mL glycol and 1 mL deionized water. After the solution was fully stirred, 0.38 g polyvinyl pyrrolidone (PVP) was slowly added, then continue to stir until PVP is completely dissolved. 0.9 g Zirconium nitride (ZrN) carrier was added to the above solvent and then heated to 80 °C. In this way, 5 mL of hydrazine hydrate glycol solution and 10 mL of sodium hydroxide glycol solution were added and stirred at 80 °C for 1 h. The solution was cooled to room temperature and washed with ethylene glycol and ethanol three times each and dried in the 80 °C oven overnight. Finally, the powder was heated to 550 °C at a ramp rate of 2 °C/min in an air atmosphere and calcined for 6 hours. Then, the calcined catalysts were reduced under 10%  $\text{H}_2/\text{N}_2$  atmosphere at 750 °C for 1 h to get the Ni/ZrO<sub>2</sub>-i catalyst. The preparation method of the Ni/ZrO<sub>2</sub> catalyst is similar to that of Ni/ZrO<sub>2</sub>-i catalyst except that the ZrN was replaced by ZrO<sub>2</sub>.

## **Characterization**

### **X-ray diffraction (XRD)**

XRD was carried out by using a Bruker D8 Advances X-ray diffractometer (3 Kw, Cu  $K_{\alpha}$  as the radiation source) for  $2\theta = 10-90^{\circ}$  with a scan speed of  $10^{\circ}\text{C}/\text{min}$ .

### **H<sub>2</sub>-temperature programmed reduction (H<sub>2</sub>-TPR)**

H<sub>2</sub>-TPR measurements were carried out on Micromeritics AutoChem II 2920. Firstly, the 0.08 g calcined sample was pre-treated at  $300^{\circ}\text{C}$  under He flow ( $30\text{ mL}/\text{min}$ ) for 30 min, then cooled to room temperature. The catalysts were heated from  $25^{\circ}\text{C}$  to  $800^{\circ}\text{C}$  ( $10^{\circ}\text{C}/\text{min}$ ) after switching to 10% H<sub>2</sub>/He mixture gas ( $30\text{ mL}/\text{min}$ ) and recorded the TCD signal.

### **X-ray photoelectron spectroscopy (XPS)**

XPS analysis performed using a RBD upgraded PHI 5000C ESCA system, which was carried out to investigate the surface electrical detection of catalysts. The XPS spectra of O 1s, C 1s, Zr 3d, Ni 2p regions were measured.

### **Thermogravimetric analysis (TG)**

The deposited coke amount of spent catalyst can be measured by NETZSCH STA 449 F1 with 10 mg of sample. The sample was heated from  $25^{\circ}\text{C}$  to  $800^{\circ}\text{C}$  with a rate of  $10^{\circ}\text{C}/\text{min}$  in an air atmosphere.

### **CO<sub>2</sub> temperature programmed desorption with mass spectrum (CO<sub>2</sub>-TPD-MS)**

The adsorb-ability of the catalyst to CO<sub>2</sub> can be performed by CO<sub>2</sub>-TPD-MS using a Micromeritics AutoChem II 2920 instrument with on-line mass spectrum (MS, Pfeiffer Omnistar). The 0.05g reduced catalysts were placed in a quartz tube of U-type and

preconditioned at 300 °C in He flow (30 mL/min) for 30 min. When cooled to 50 °C, the gas was switched to 10% CO<sub>2</sub>/He for pre-adsorption for 1 h. After purging with He, the reactor was heated to 800 °C (10 °C/min) for CO<sub>2</sub> desorption and the spectra were recorded by using TCD and online MS.

#### **CH<sub>4</sub> temperature-programmed surface reactions with mass spectrum (CH<sub>4</sub>-TPSR-MS)**

The methane-decomposition ability of the catalyst can be performed by CH<sub>4</sub>-TPSR-MS using the same instrument as CO<sub>2</sub>-TPD-MS. The test samples were first treated in 300 °C He atmosphere (30 mL/min) for 30 min, then cooled to 50 °C. Pure methane was introduced into the reactor and heated up to 800 °C at a rate of 10 °C/min for the measurement. Simultaneously, the spectrum of CO, CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub> were recorded by using online MS.

#### **HRTEM and TEM**

High-resolution Transmission Electron Microscopy and Transmission Electron Microscopy (HRTEM and TEM) images were collected on JEM-2010F and JEM-2100F. The energy dispersive spectroscopy (EDS) was implemented via OXFORD-315LM00022.

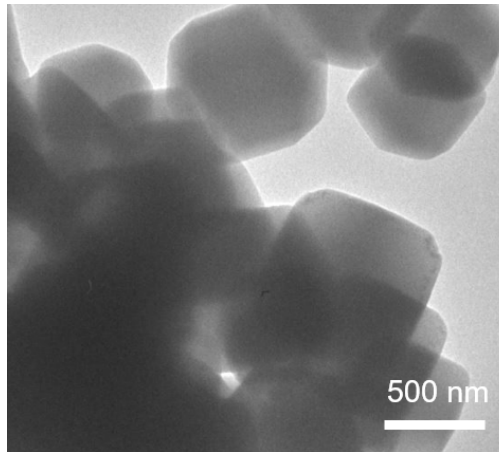
#### **SEM and SEM-EDS**

Scanning electron microscopy (SEM) was carried out over ZEISS sigma-300. The energy dispersive spectroscopy (EDS) was conducted at OXFORD AZTEC XMAX50.

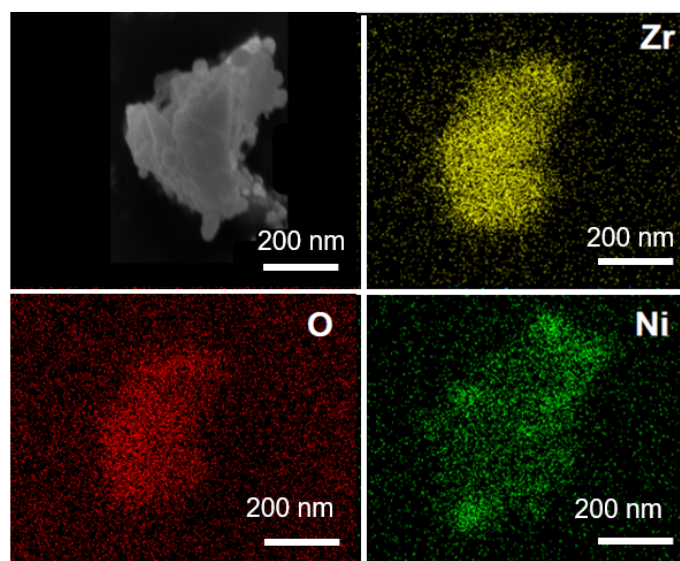
#### **Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)**

The American Perkin Elmer Optima 7300DV inductively coupled Plasma spectrometer

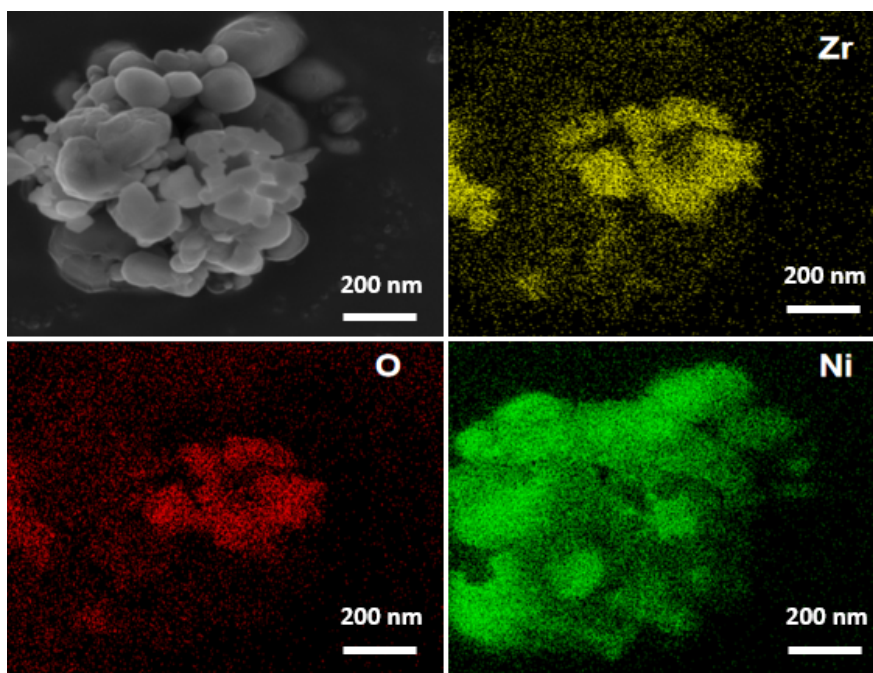
was used to analyze the actual metal content of the elements in the catalyst.



**Fig. S1** TEM image of ZrN

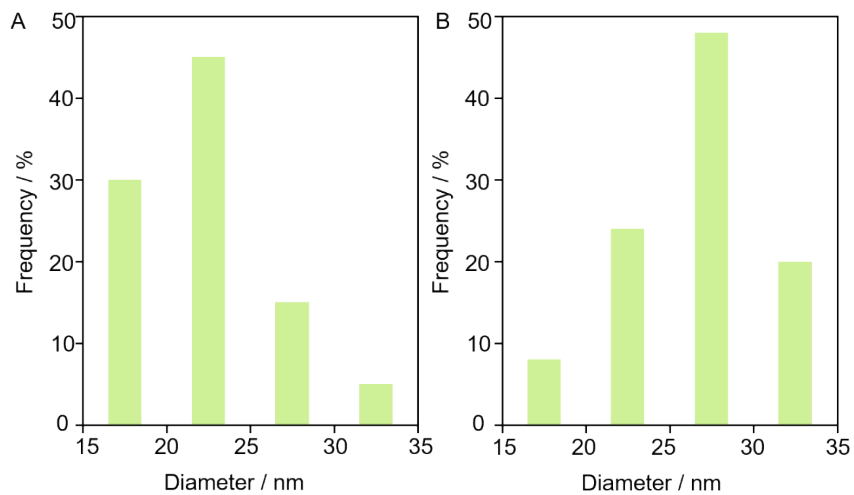


**Fig. S2** SEM image of Ni/ZrO<sub>2</sub>-i and corresponding elemental mapping images.

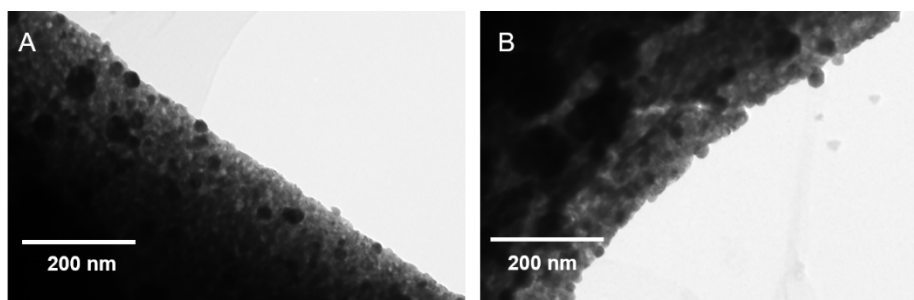


**Fig. S3** SEM image of Ni/ZrO<sub>2</sub> and corresponding elemental mapping images.

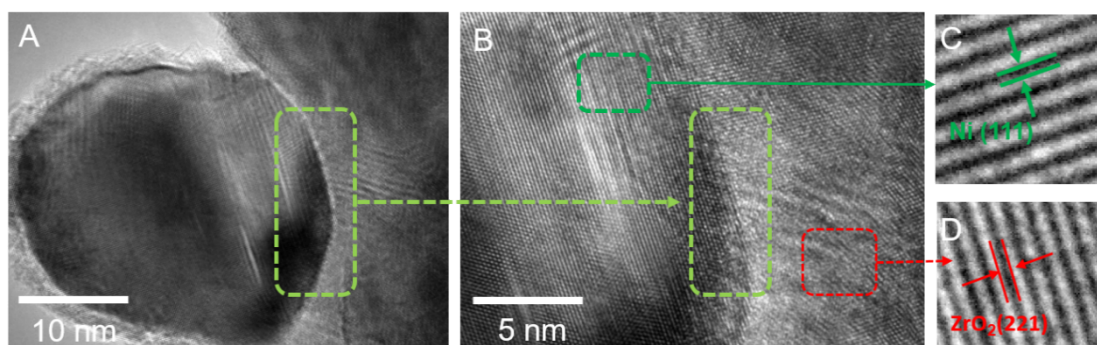




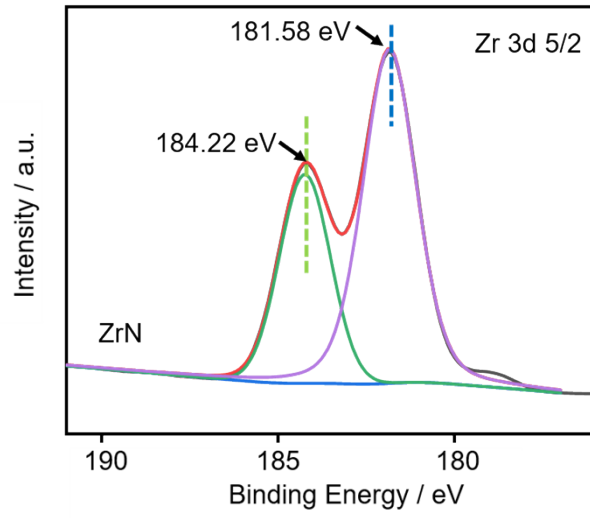
**Fig. S4** Statistical plots from TEM image for the size of Ni nanoparticles over (A) Ni/ZrO<sub>2</sub>-i and (B) Ni/ZrO<sub>2</sub>.



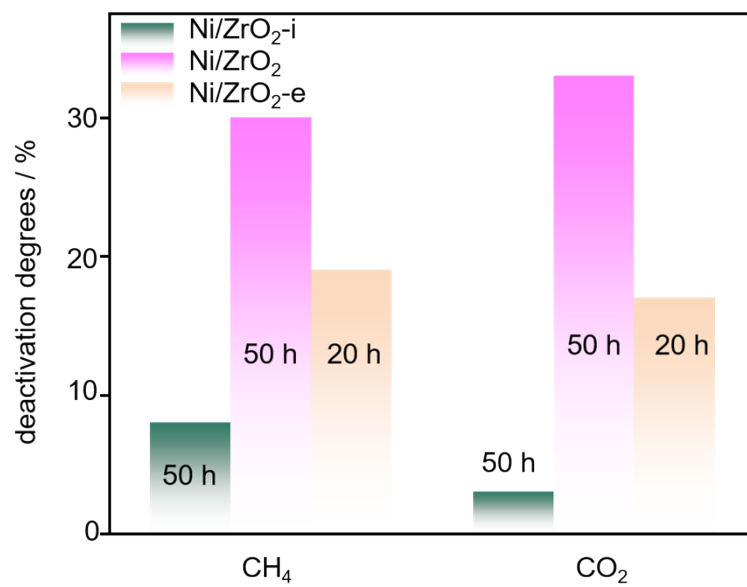
**Fig. S5** The embedding structure of Ni particles in fresh catalyst Ni/ZrO<sub>2</sub>-i



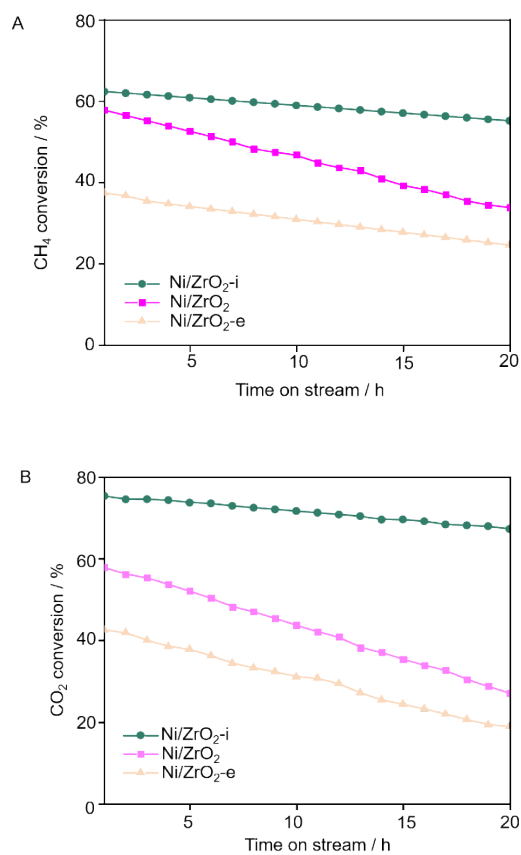
**Fig. S6** HRTEM image of Ni/ZrO<sub>2</sub>-i catalyst (A) and lattice fringe at the interface (B), (C and D) inverse FFT pattern of the selected HRTEM image in **Fig. S6** (A)



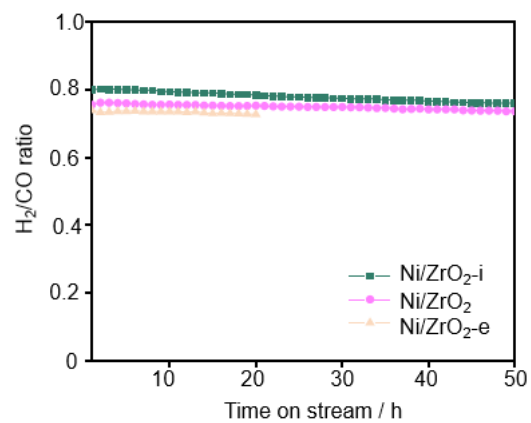
**Fig. S7** XPS spectra for Zr 3d over the ZrN.



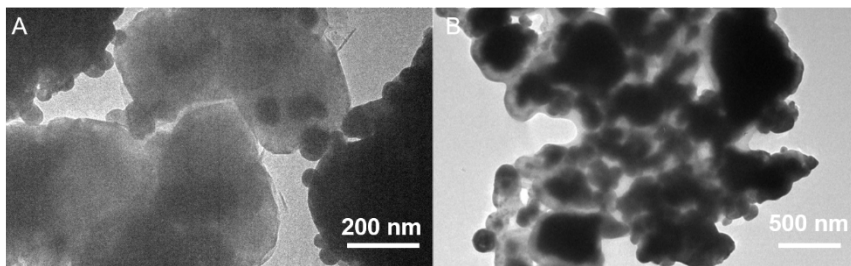
**Fig. S8** The deactivation degrees of Ni/ZrO<sub>2</sub>-i and Ni/ZrO<sub>2</sub>, and Ni/ZrO<sub>2</sub>-e after DRM reaction.



**Fig. S9** (A) CH<sub>4</sub> and (B) CO<sub>2</sub> conversion of catalysts obtained at the repeated test.

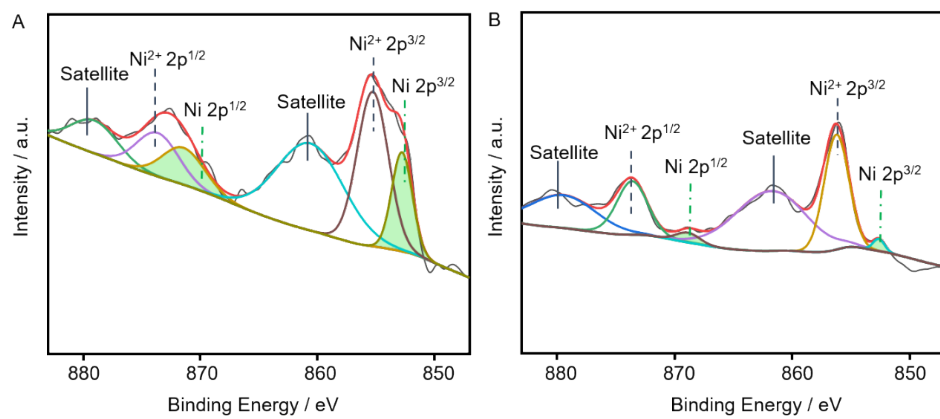


**Fig. S10** H<sub>2</sub>/CO ratio as a function of reaction time on Ni/ZrO<sub>2</sub>-i and Ni/ZrO<sub>2</sub> catalysts.

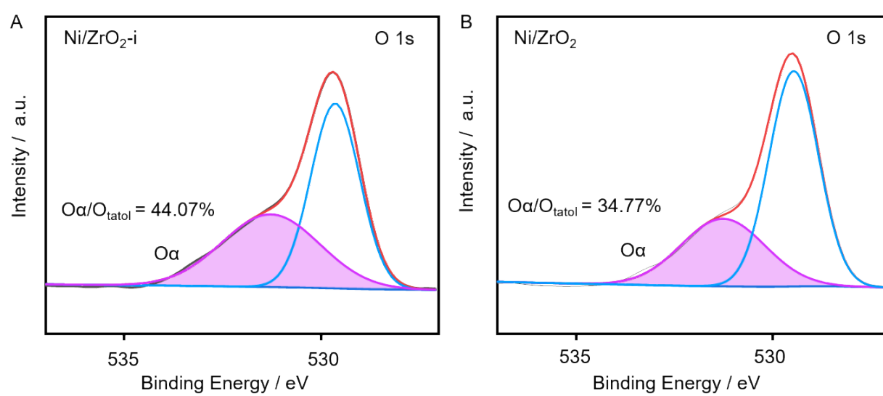


**Fig. S11** TEM image of spent catalysts (A)Ni/ZrO<sub>2</sub>-i and (B) Ni/ZrO<sub>2</sub>.

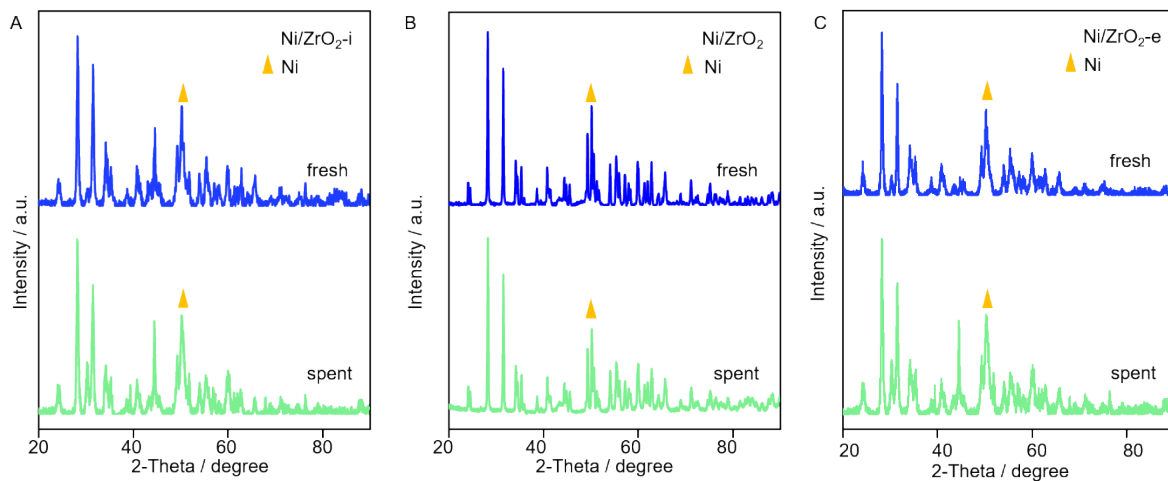




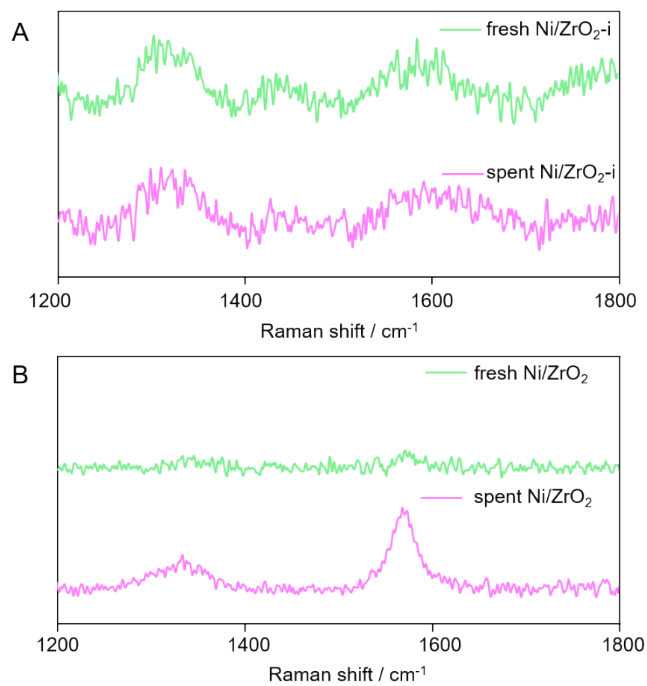
**Fig. S12** Ni 2p XPS spectra over (A) spent Ni/ZrO<sub>2</sub>-i and spent (B) Ni/ZrO<sub>2</sub> after DRM reaction.



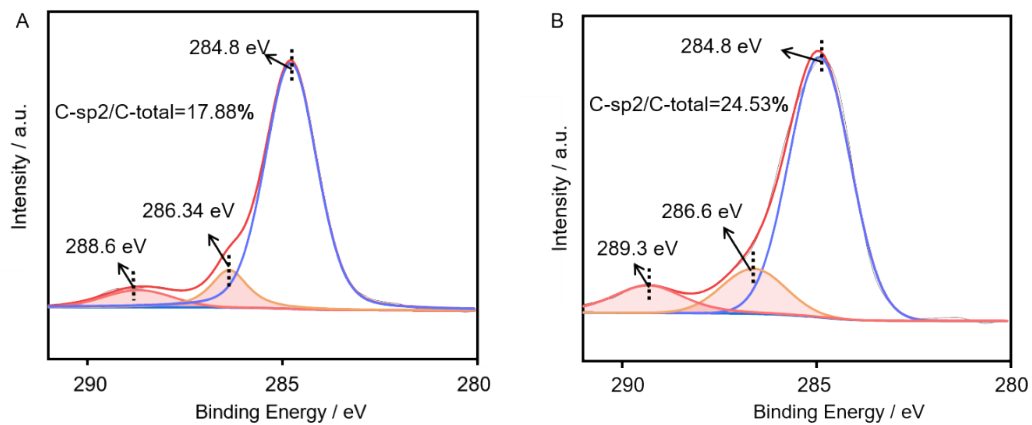
**Fig. S13** O 1s XPS spectra over (A) spent Ni/ZrO<sub>2</sub>-i and (B) spent Ni/ZrO<sub>2</sub> after DRM reaction.



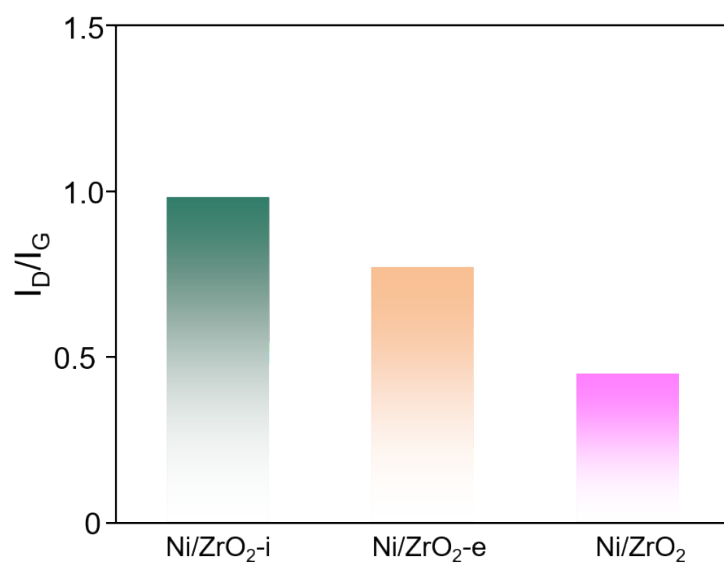
**Fig. S14** XRD patterns of the fresh and spent catalysts of (A) Ni/ZrO<sub>2</sub>-i, (B) Ni/ZrO<sub>2</sub> and (C) Ni/ZrO<sub>2</sub>-e. Wherein, the marked Ni peak is the peak used by the Scherrer.



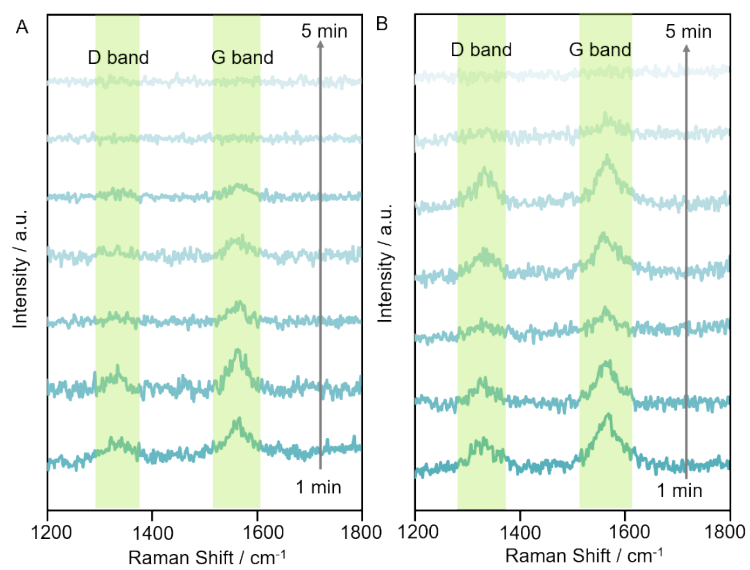
**Fig. S15** Raman spectra of fresh catalyst and spent (A) Ni/ZrO<sub>2</sub>-i and (B) Ni/ZrO<sub>2</sub> catalysts.



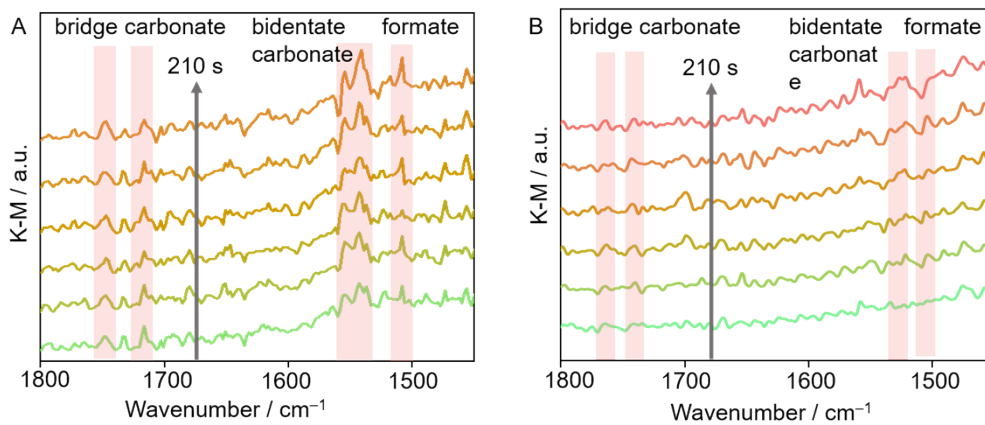
**Fig. S16** C 1s XPS spectra over (A) spent Ni/ZrO<sub>2</sub>-i and (B) spent Ni/ZrO<sub>2</sub> after DRM reaction.



**Fig. S17**  $I_D/I_G$  of the spent catalysts.

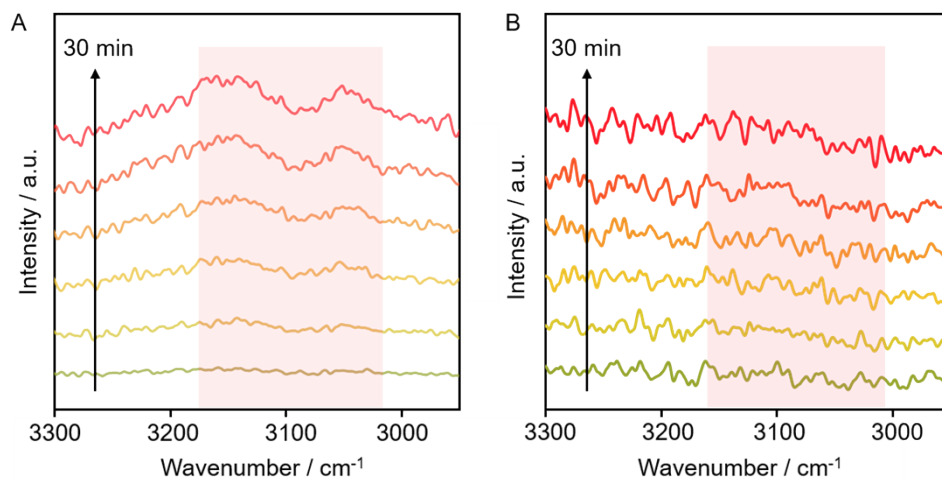


**Fig. S18** In situ Raman spectra collected during the oxidation of coking catalysts under the atmosphere of 15 mL/min 21vol% O<sub>2</sub>/N<sub>2</sub> on (A) Ni/ZrO<sub>2</sub>-i and (B) Ni/ZrO<sub>2</sub> catalysts.

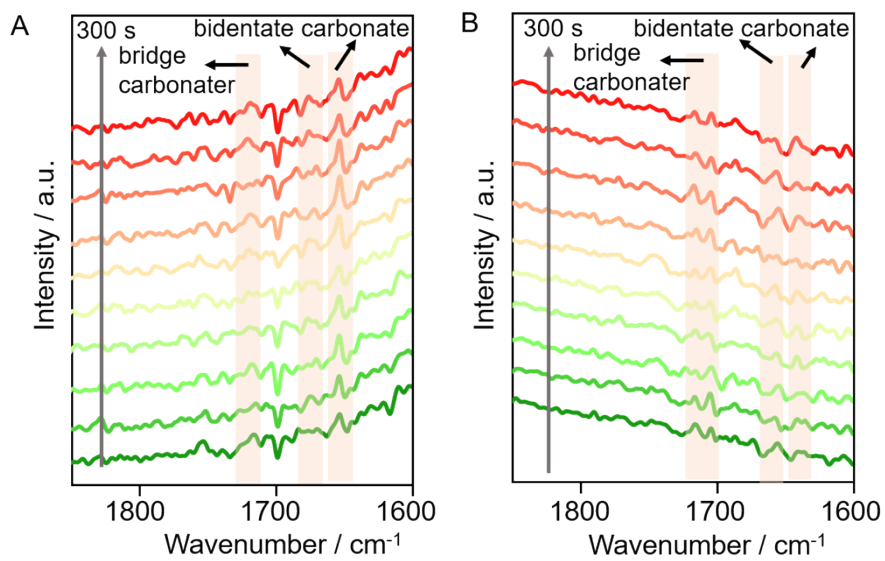


**Fig. S19** In situ DRIFTS obtained during DRM over (A) Ni/ZrO<sub>2</sub>-i and (B) Ni/ZrO<sub>2</sub> at 700 °C.





**Fig. S20** In situ DRIFTS over (A) Ni/ZrO<sub>2</sub>-i and (B) Ni/ZrO<sub>2</sub>.



**Fig. S21** The transient state experiment with pre-adsorption of CH<sub>4</sub> and followed by CO<sub>2</sub> over (A) Ni/ZrO<sub>2</sub>-i and (B) Ni/ZrO<sub>2</sub> at 650 °C.

**Table S1.** Structural information and TOF of catalysts.

Catalysts	Ni (%) <sup>a</sup>	Dispersion <sup>b</sup> (%)	H <sub>2</sub> consumption <sup>c</sup> (mmol/g)	TOF <sup>d</sup>		Particle size <sup>e</sup> (nm)	
				CH <sub>4</sub> (s <sup>-1</sup> )	CO <sub>2</sub> (s <sup>-1</sup> )	fresh	spent
Ni/ZrO <sub>2</sub> -i	9.5	1.54	0.025	3.6	5.3	22.2	26.9
Ni/ZrO <sub>2</sub>	10.2	1.21	0.029	2.3	3.1	28.5	34.8
Ni/ZrO <sub>2</sub> -e	9.1	0.73	0.005	2.1	2.8	27.6	34.4

<sup>a</sup> Ni loading was measured by ICP-OES.

<sup>b</sup> Ni dispersion was measured by H<sub>2</sub> pulse chemisorption.

<sup>c</sup> H<sub>2</sub> consumption was measured by H<sub>2</sub>-TPR.

<sup>d</sup> The value of TOF was tested at 650 °C with CH<sub>4</sub>/CO<sub>2</sub> flow rate of 50/50 mL/min.

<sup>e</sup> The Ni particle size was calculated based on XRD via Scherrer equation.

**Table S2.** Surface Ni, O<sub>α</sub> and Zr<sup>3+</sup> exposure from XPS.

Catalysts	Ni <sup>0</sup> /Ni <sub>total</sub>	O <sub>α</sub> /O <sub>total</sub>	Zr <sup>3+</sup> /(Zr <sup>3+</sup> + Zr <sup>4+</sup> )
Ni/ZrO <sub>2</sub> -i	34.3%	34.1%	33.3%
Ni/ZrO <sub>2</sub>	23.1%	33.0%	29.1%

**Table S3.** Selected DRM catalysts reported in the literature and their activity and durability.

catalysts	temperature (°C)	GHSV (mL·g <sub>cat</sub> <sup>-1</sup> ·h <sup>-1</sup> )	Test time (h)	Coke formation rate (mg <sub>c</sub> ·g <sub>cat</sub> <sup>-1</sup> ·h <sup>-1</sup> )	references
Ni/ZrO <sub>2</sub> -i	750	37500 CH <sub>4</sub> :CO <sub>2</sub> =1:1	50	-	
Ni/ZrO <sub>2</sub>	750	37500 CH <sub>4</sub> :CO <sub>2</sub> =1:1	50	8	this work
Ni/ZrO <sub>2</sub> -e	750	37500 CH <sub>4</sub> :CO <sub>2</sub> =1:1	20	3.4	
Ni/ZrO <sub>2</sub>	750	24000 CH <sub>4</sub> :CO <sub>2</sub> =1:1	5	6	1
Ni/ZSM-5	750	60000 CH <sub>4</sub> :CO <sub>2</sub> =1:1	20	18.9	2
Ni/AlN	800	50000 CH <sub>4</sub> :CO <sub>2</sub> :N <sub>2</sub> = 1:1:0.5	100	7.6	3
Ni/La <sub>2</sub> O <sub>3</sub>	650	24000 CH <sub>4</sub> :CO <sub>2</sub> :N <sub>2</sub> =3:3:14	50	3.5	4

## Reference:

1. J. Ren, F. Zeng, C. Mebrahtu and R. Palkovits, *J. Catal*, 2022, **405**, 385-390.
2. M. F. Bekheet, P. Delir Kheyrollahi Nezhad, N. Bonmassar, L. Schlicker, A. Gili, S. Praetz, A. Gurlo, A. Doran, Y. Gao, M. Heggen, A. Niaei, A. Farzi, S. Schwarz, J. Bernardi, B. Klotzer and S. Penner, *ACS Catal*, 2021, **11**, 43-59.
3. H. Wang, L. Wang, D. Lin, X. Feng, Y. Niu, B. Zhang and F.-S. Xiao, *Nat. Catal*, 2021, **4**, 418-424.
4. Y. Lou, M. Steib, Q. Zhang, K. Tiefenbacher, A. Horvath, A. Jentys, Y. Liu and J. A. Lercher, *J. Catal*, 2017, **356**, 147-156.