Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Dry Reforming of Methane on Bimetallic Pt-Ni@CeO$_2$ Catalyst: A *in situ* DRIFTS-MS Mechanistic Study

Electronic Supplementary Information (ESI)

1. Charaterisation of as-prepared catalysts

In this work, the actual metal loading in all catalysts were measured by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Analytik Jena PlasmaQuant PQ 9000 Elite), and the results were listed in Table S1. Prior to ICP-OES analysis, the catalyst (~25 mg) was mixed with 12 mL aqua regia and digested in a Milestone ETHOS UP microwave digestion system for 20 min at 220 °C.

Table S1. ICP-OES analysis of the as-synthesised catalysts.

Catalyst	Actual Pt content (wt.%)	Actual Ni content (wt.%)
Ni@CeO$_2$	-	1.43
Pt@CeO$_2$	1.52	-
Pt-Ni@CeO$_2$	0.85	0.84

The pulse H_2 (for Ni@CeO$_2$ catalyst) and CO chemisorption experiments were performed using the Micromeritics AutoChem II 2920 instrument. The catalyst sample (~200 mg) was pre-treated under He (50 ml min^{-1}) at 200 °C for 30 min and cooled to 50 °C. Then it was heated to 600 °C (10 °C min^{-1}) and held for 1 h in a mixture of 10 vol.% H_2 in Ar (total flowrate at 50 ml min^{-1}), and cooled down in He (50 ml min^{-1}) for degassing before pulsing 10 vol.% H_2 or CO in He (590 μL loop). The amount of chemisorbed H_2 or CO was used to estimate the number of metal active sites on the catalyst with the assumption of H_2 or CO/metal ratio being 1:1. The metal dispersion and metallic surface area of the catalysts were presented in Table S2.

Table S2. Metal dispersion and metallic surface area of the catalysts by H_2 (for Ni@CeO$_2$ catalyst) and CO pulse chemisorption.

Catalysts	Metal dispersion [%]	Metallic surface area [$m^2\ g_{metal}^{-1}$]
Ni@CeO$_2$	0.9	5.9
Pt@CeO$_2$	13.3	32.8
Pt-Ni@CeO$_2$	37.6	92.9

HRTEM images were collected with an FEI Tecnai G2 F20 electron microscope operated at 200 kV. The sample was prepared by dispersion of the powder catalysts in ethanol with the assistance of sonication, and a drop of the suspension was spread onto a TEM carbon grid. The results were presented in Fig. S1, showing that the size of the metallic phases in the three catalysts are comparable

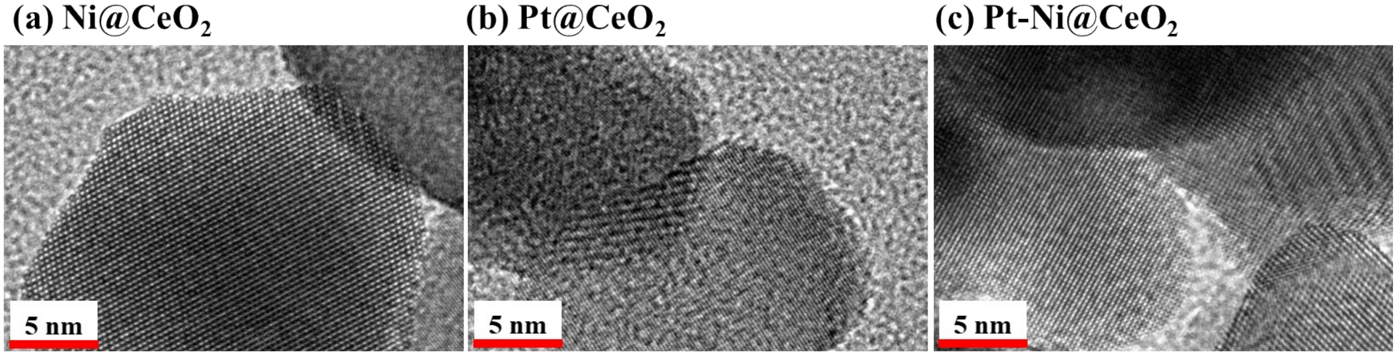


Fig. S1. TEM images of the as-prepared catalysts: (a) Ni@CeO$_2$, (b) Pt@CeO$_2$, and (c) Pt-Ni@CeO$_2$

In H_2 temperature programmed reduction (TPR) measurements, ~50 mg sample was pre-treated at 250 °C for 30 min under helium (He) flow to remove any adsorbed or chemisorbed H_2O and CO_2, and then cooled down to room temperature (RT). H_2-TPR was carried out under a gas mixture flow of 5%H_2/He and at temperatures of 30–900 °C with a heating rate of 10 °C min^{-1}. The H_2 consumption was continuously monitored by a thermal conductivity detector (TCD). The H_2-TPR profiles of developed catalysts were presented in Fig. S1. Results clearly indicate that the Pt-Ni bimetallic catalyst is much easier to be reduced than Pt or Ni monometallic catalysts. Regarding the reduction peak at >600 °C, it was due to the reduction of ceria support[1].

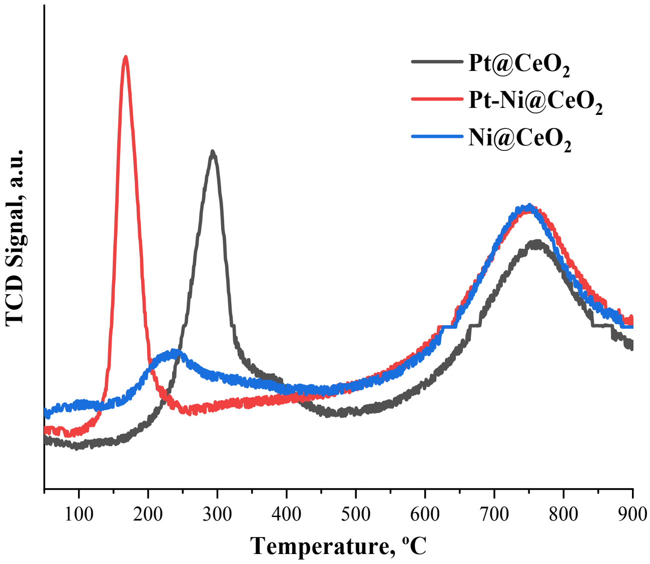


Fig. S2. H_2-TPR profiles of the as-prepared catalysts.

2. Activity and Long-term stability of the developed catalyst

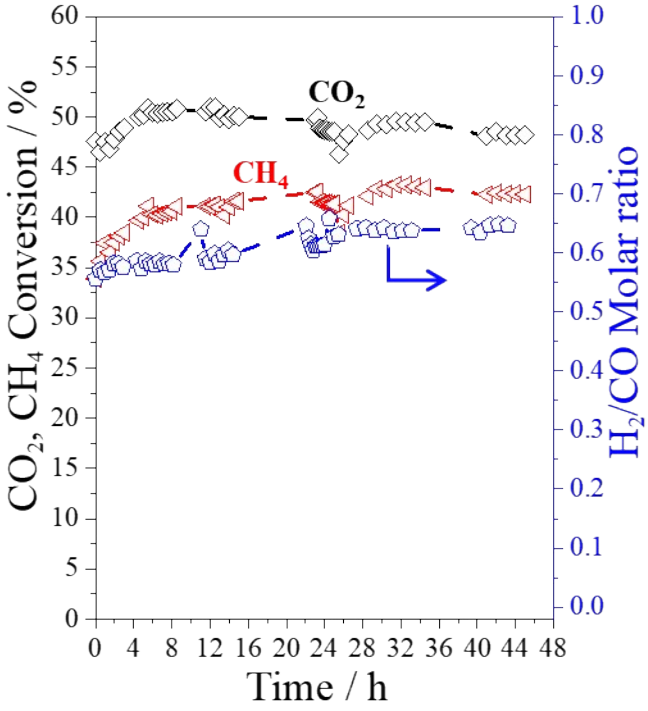


Fig. S3. Long-term stability of the Pt-Ni@CeO_2 catalyst regarding the CO_2/CH_4 conversions and H_2/CO molar ratio as a function of ToS. (Experimental conditions: feed gas = 45 vol.%CO_2/45 vol.%CH_4/10 vol.%Ar, total flow rate = 60 mL (STP) min^{-1}, temperature = 650 °C)

Table S3. Comparison with other catalysts on CeO_2 support for dry reforming of methane reported in the literatures.

Catalyst	Total flow rate (mL (STP) min^{-1})	Temperature (°C)	CO_2 Conversion (%)	CH_4 Selectivity (%)	H_2/CO molar ratio (-)	Ref.
PtCo/CeO_2	80	600	25.5	14.3	-	[2]
PtNi/CeO_2	90	650	55	50	0.7	[3]
Pt-Ni@CeO_2	60	650	48	40	0.6	This work

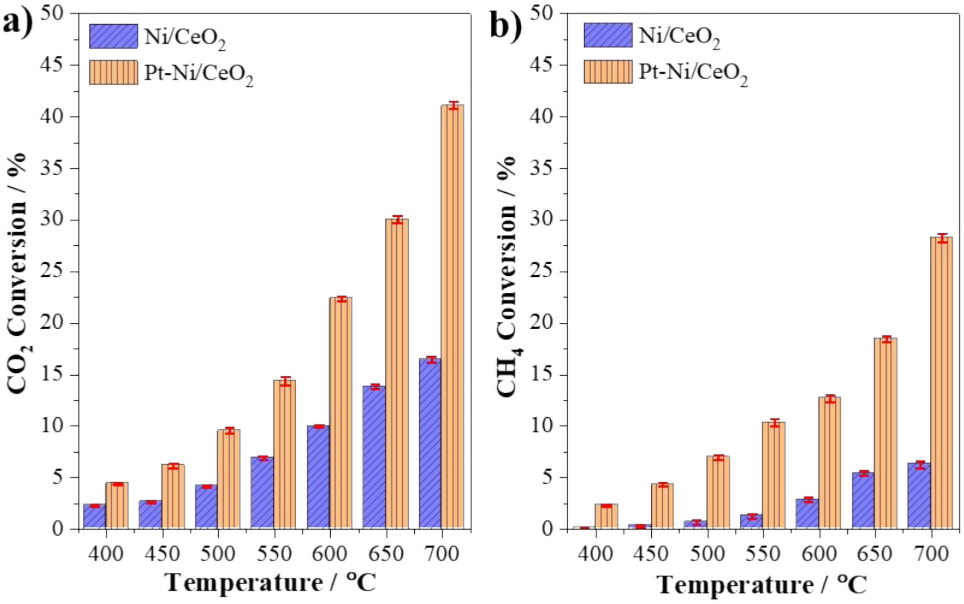


Fig. S4. Catalytic performances of developed Ni/CeO_2 and Pt-Ni/CeO_2 catalysts for DRM reaction.

3. *Temperature-ramping in situ DRIFTS-MS studies*

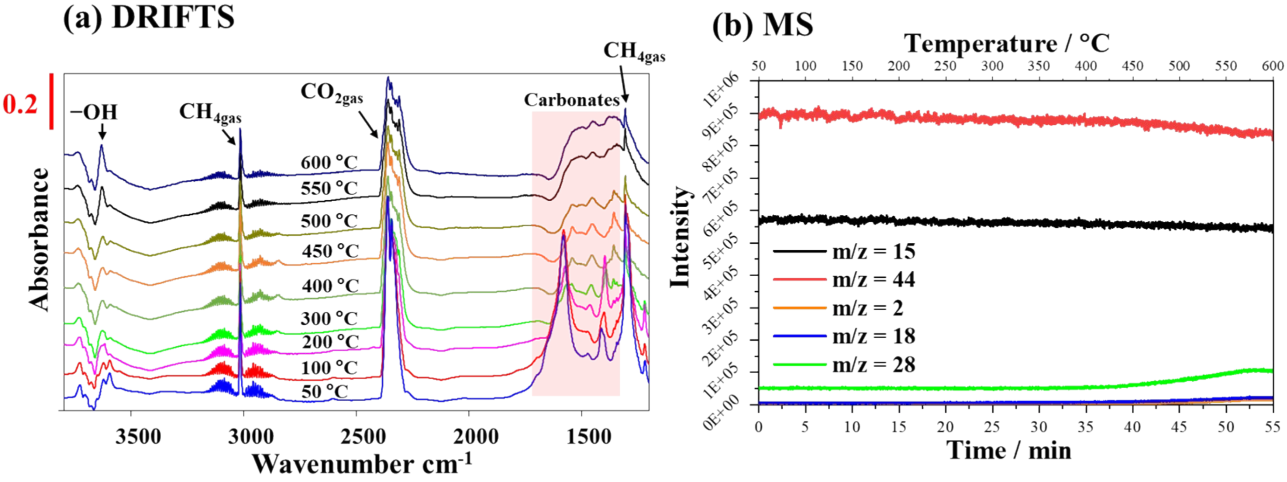


Figure S5. (a) *In situ* DRIFTS spectra of DRM over the bare CeO_2 support, and (b) corresponding MS signals collected at the exit of the DRIFTS cell during DRM in a temperature range of 50 to 600 °C. (Experimental conditions: feed gas = 10 vol.%CO_2/10 vol.%CH_4/80 vol.%Ar, total flow rate = 50 mL (STP) min^{-1})

4. Steady-state in situ DRIFTS-MS studies

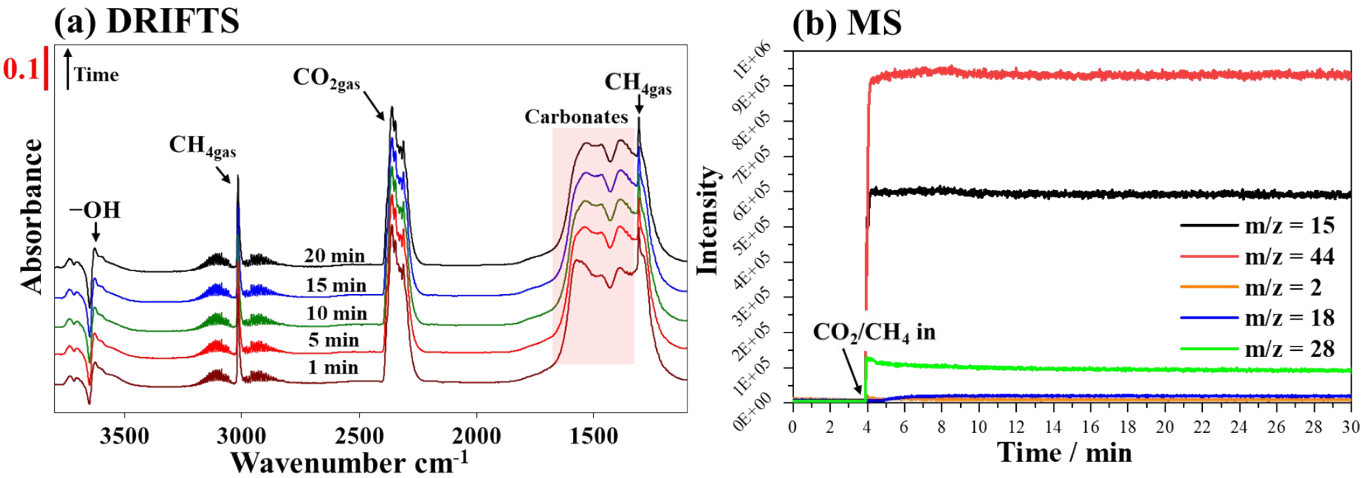
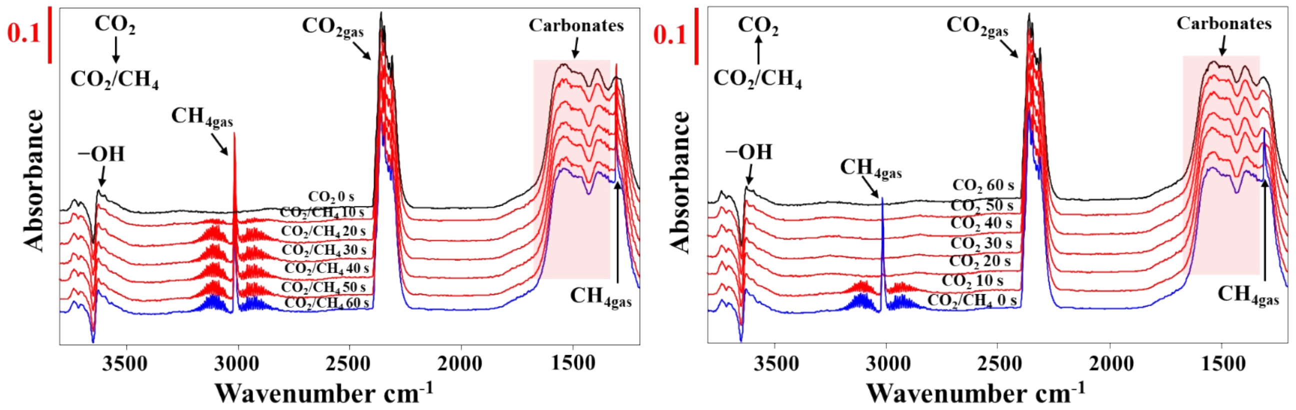


Figure S6. (a) *In situ* DRIFTS spectra of DRM over the bare CeO_2 support, and (b) corresponding MS signals collected at the exit of the DRIFTS cell as a function of ToS during DRM at 550 °C. (Experimental conditions: feed gas = 10 vol.%CO_2/10 vol.%CH_4/80 vol.%Ar, total flow rate = 50 mL (STP) min^{-1})

5. Fast cycling transient in situ DRIFTS-MS studies

5.1 Feed switch between CO_2 and CO_2/CH_4

(a) 1st cycle



(b) 2nd cycle

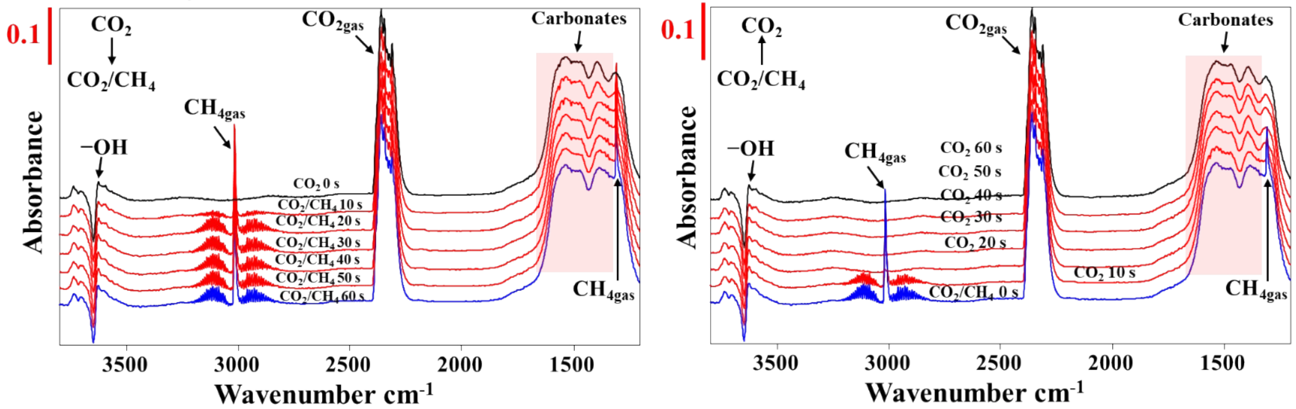


Figure S7. *In situ* DRIFTS spectra over the bare CeO_2 support as a function of ToS during DRM switching between CO_2 and CO_2/CH_4 feeds at 550 °C: (a) 1st cycle, and (b) 2nd cycle. (Experimental conditions: feed gas = 10 vol.%CO_2/90 vol.%Ar and feed gas = 10 vol.%CO_2/10 vol.%CH_4/30 vol.%Kr/50 vol.%Ar, total flow rate = 50 mL (STP) min^{-1})

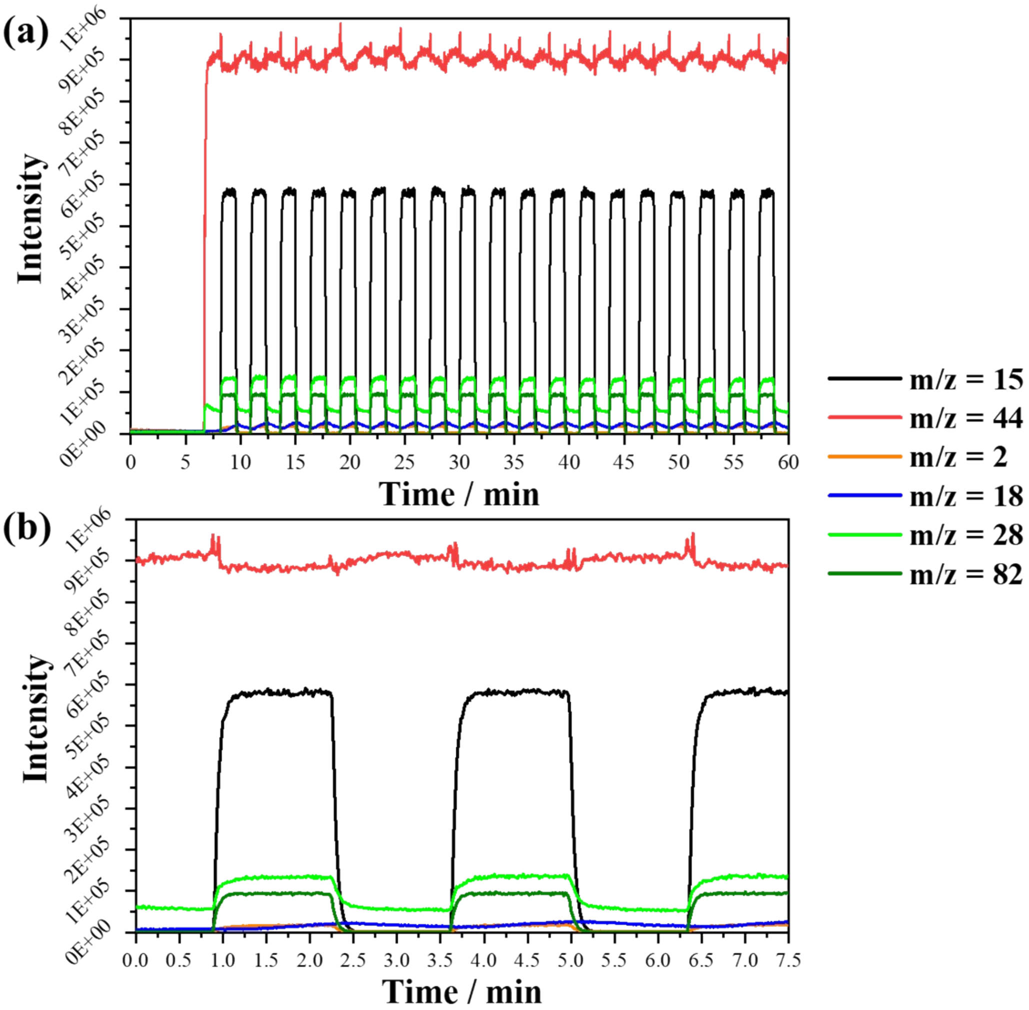
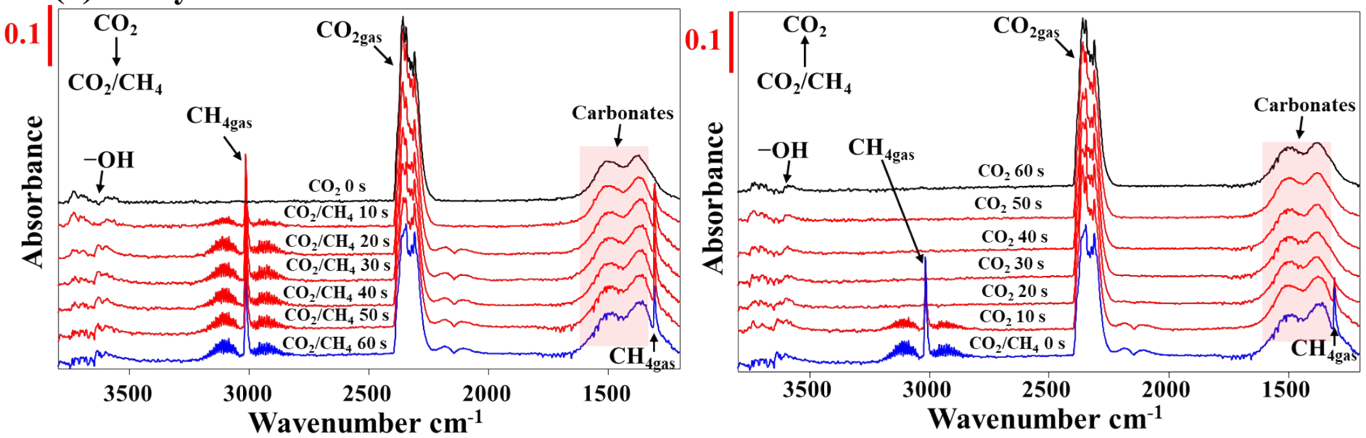
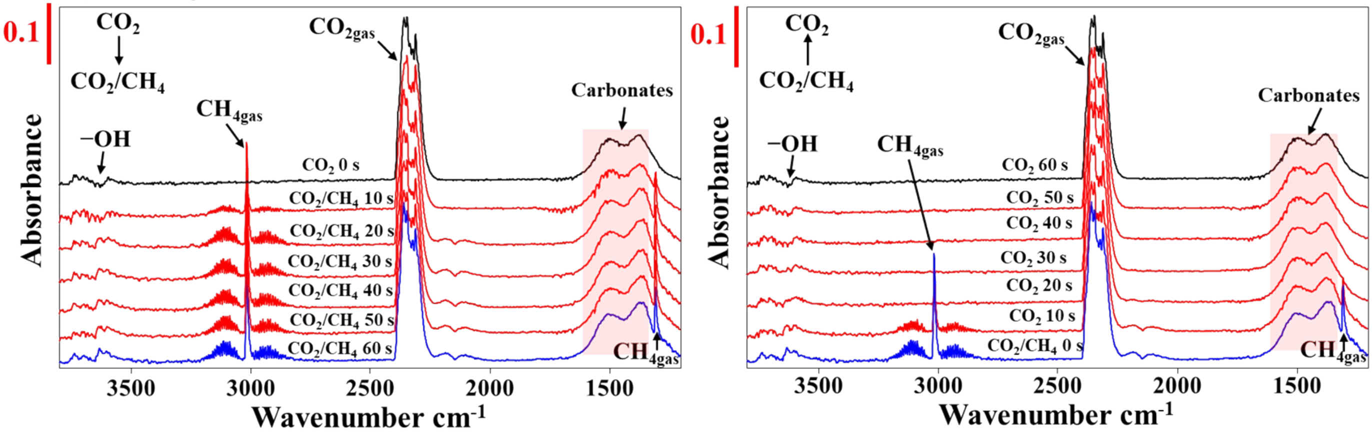


Figure S8. MS signals collected at the exit of the DRIFTS cell as a function of ToS during DRM switching between CO_2 and CO_2/CH_4 feeds over the bare CeO_2 support at 550 °C: (a) 20 cycles, and (b) 1^{st}–3^{rd} cycle. (Experimental conditions: feed gas = 10 vol.%CO_2/90 vol.%Ar and feed gas = 10 vol.%CO_2/10 vol.%CH_4/30 vol.%Kr/50 vol.%Ar, total flow rate = 50 mL (STP) min^{-1})

(a) 2nd cycle



(b) 10th cycle



(c) 20th cycle

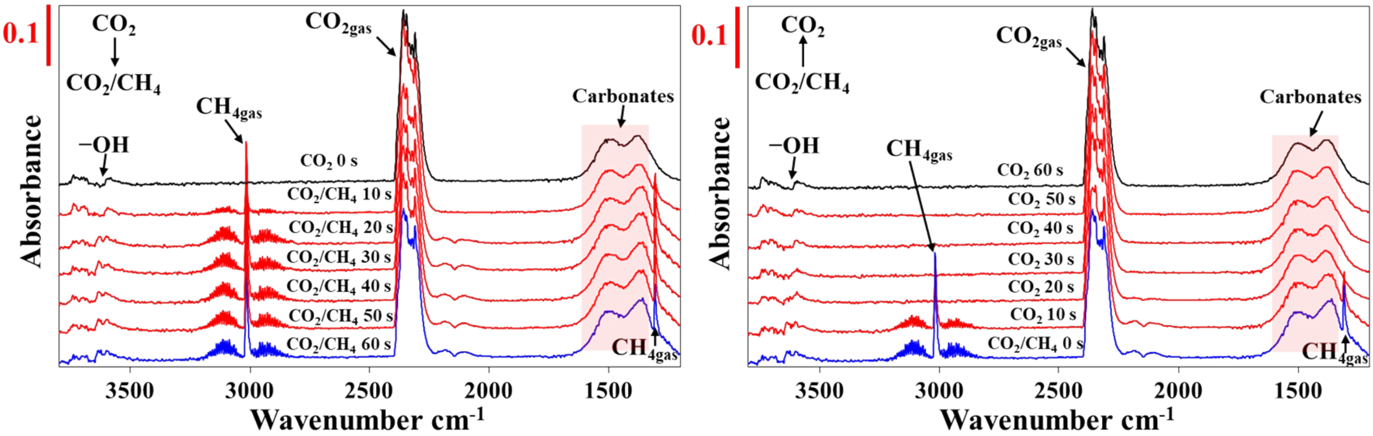


Figure S9. *In situ* DRIFTS spectra over the Ni@CeO_2 catalyst during the 1st cycle of DRM switching between CO_2 and CO_2/CH_4 feeds at 550 °C: (a) CO_2 to CO_2/CH_4, and (b) CO_2/CH_4 to CO_2. (Experimental conditions: feed gas = 10 vol.%CO_2/90 vol.%Ar and feed gas = 10 vol.%CO_2/10 vol.%CH_4/30 vol.%Kr/50 vol.%Ar, total flow rate = 50 mL (STP) min^{-1})

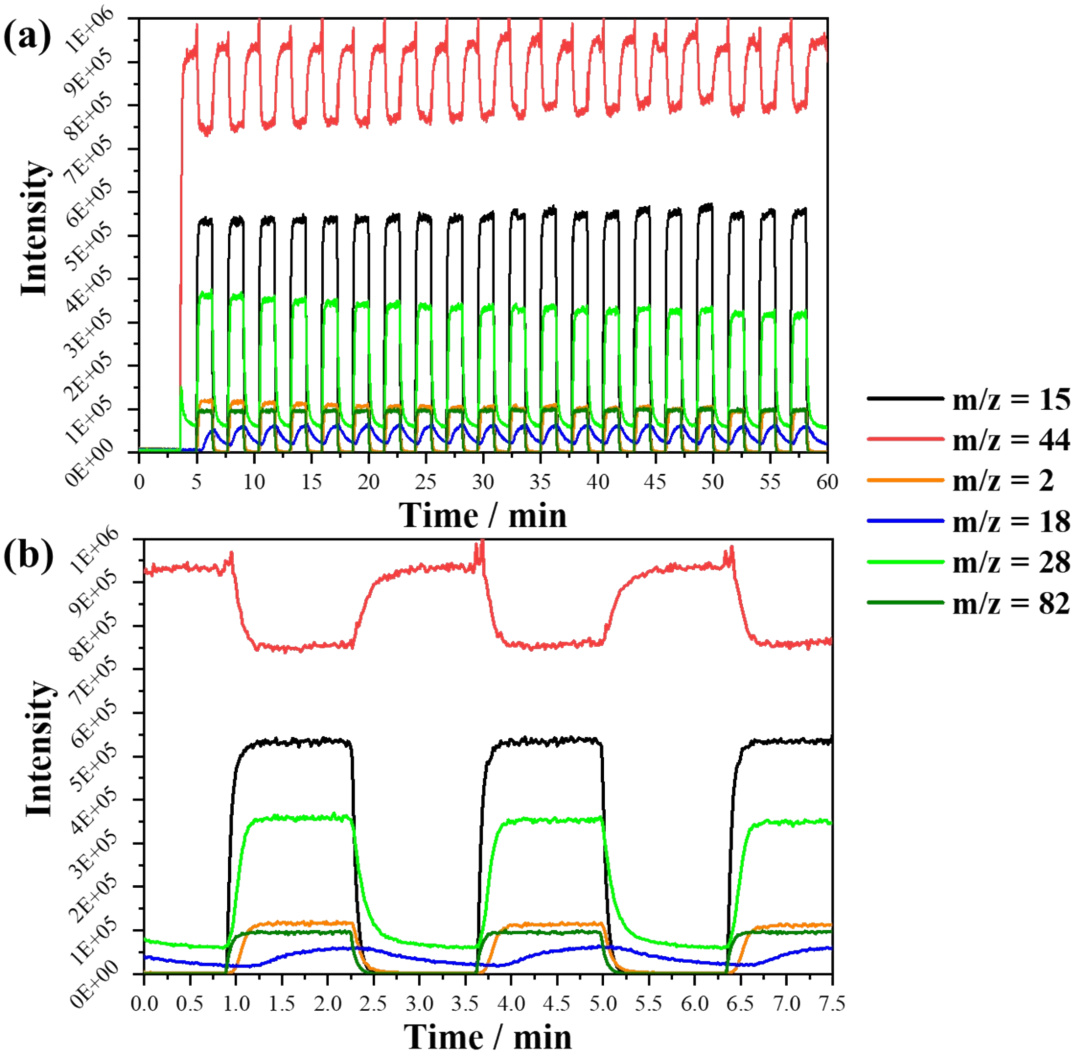
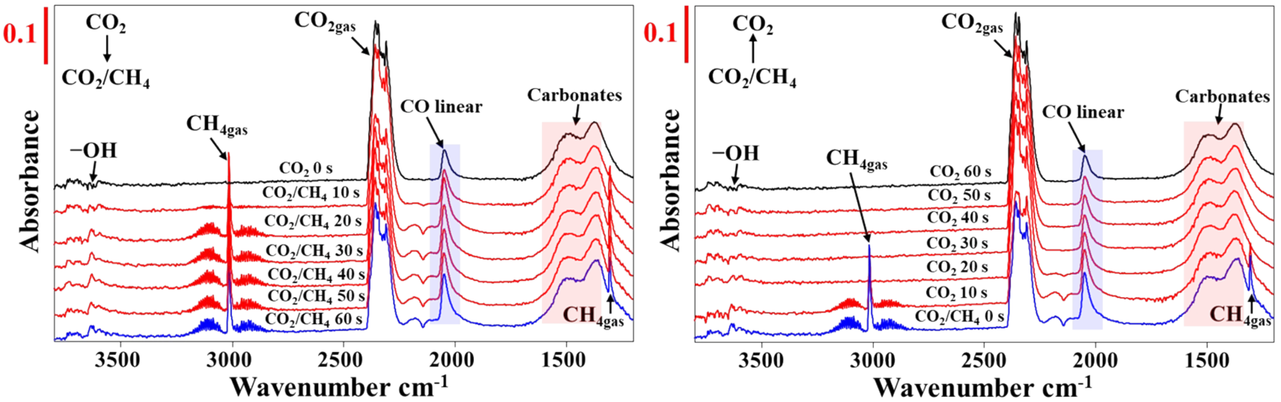
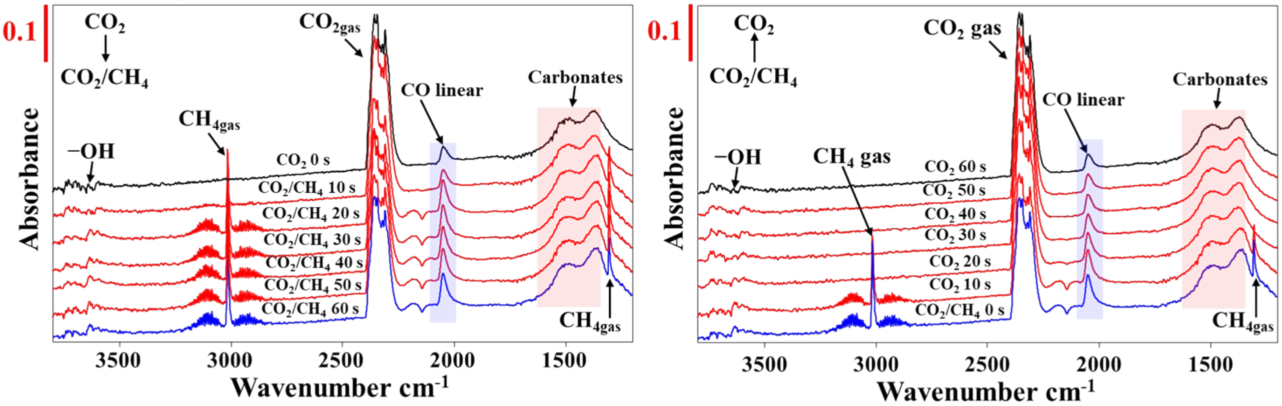


Figure S10. MS signals collected at the exit of the DRIFTS cell as a function of ToS during DRM switching between CO_2 and CO_2/CH_4 feeds over the Ni@CeO_2 catalyst at 550 °C: (a) 20 cycles, and (b) 1^{st}–3^{rd} cycle. (Experimental conditions: feed gas = 10 vol.%CO_2/90 vol.%Ar and feed gas = 10 vol.%CO_2/10 vol.%CH_4/30 vol.%Kr/50 vol.%Ar, total flow rate = 50 mL (STP) min^{-1})

(a) 2nd cycle



(b) 10th cycle



(c) 20th cycle

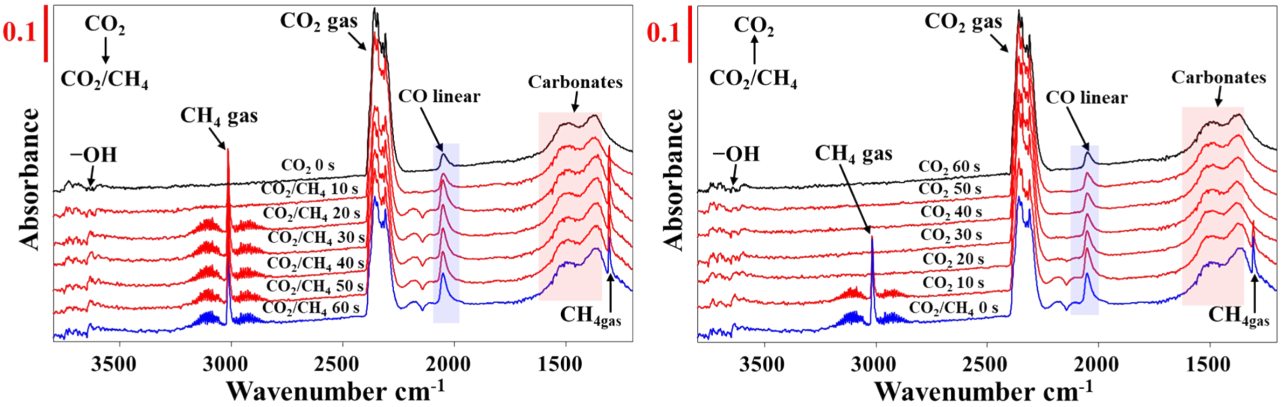


Figure S11. *In situ* DRIFTS spectra over the Pt-Ni@CeO_2 catalyst as a function of ToS during DRM switching between CO_2 and CO_2/CH_4 feeds at 550 °C: (a) 2nd cycle, (b) 10th cycle, and (c) 20th cycle. (Experimental conditions: feed gas = 10 vol.%CO_2/90 vol.%Ar and feed gas = 10 vol.%CO_2/10 vol.%CH_4/30 vol.%Kr/50 vol.%Ar, total flow rate = 50 mL (STP) min^{-1})

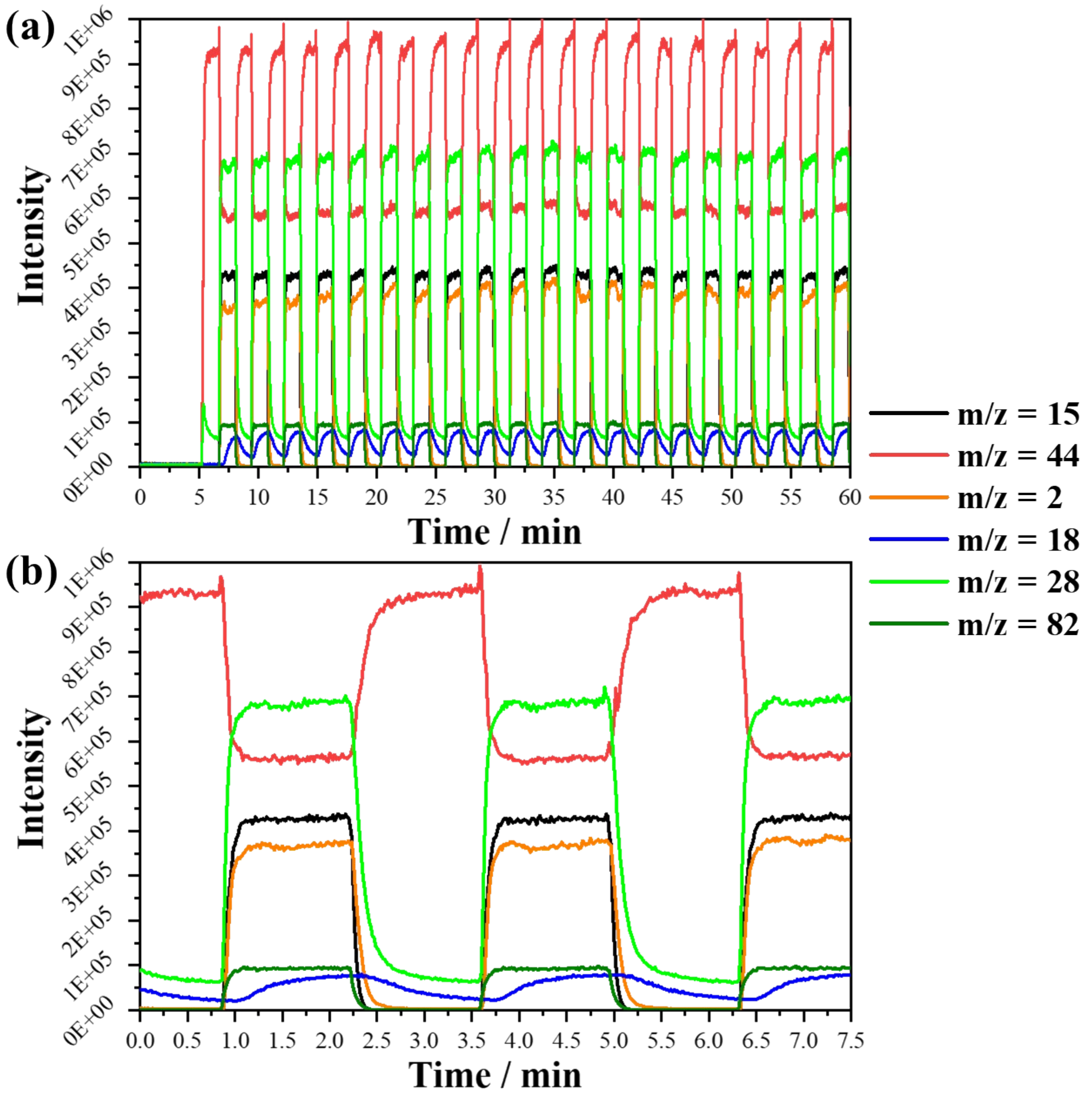
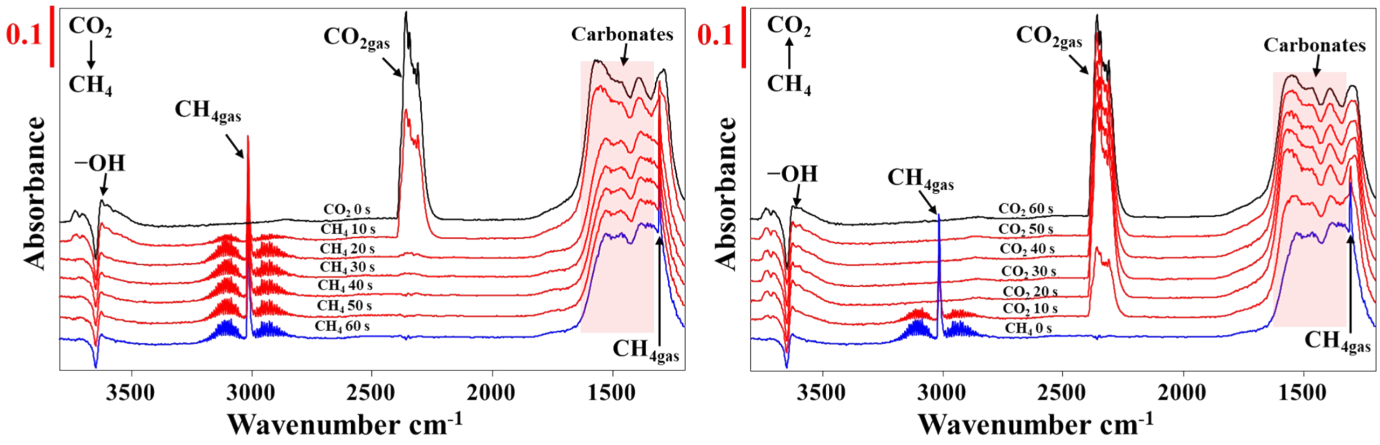


Figure S12. MS signals collected at the exit of the DRIFTS cell as a function of ToS during DRM switching between CO_2 and CO_2/CH_4 feeds over the Pt-Ni@CeO_2 catalyst at 550 °C: (a) 20 cycles, and (b) 1^{st}–3^{rd} cycle. (Experimental conditions: feed gas = 10 vol.%CO_2/90 vol.%Ar and feed gas = 10 vol.%CO_2/10 vol.%CH_4/30 vol.%Kr/50 vol.%Ar, total flow rate = 50 mL (STP) min^{-1})

5.2 Feed switching between CO_2 and CH_4

(a) 1^{st} cycle



(b) 2^{nd} cycle

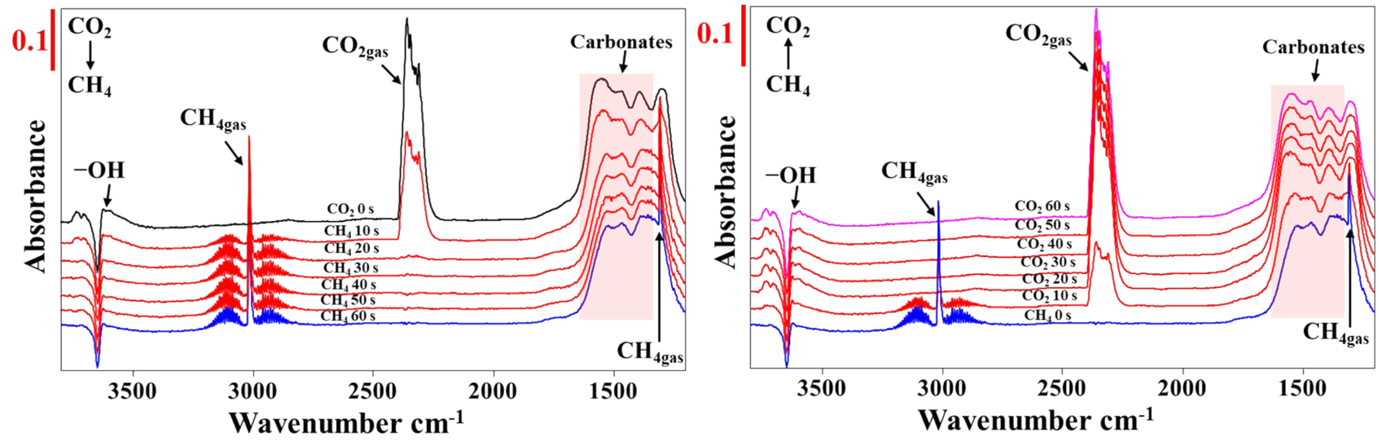


Figure S13. *In situ* DRIFTS spectra over the bare CeO_2 support as a function of ToS during DRM switching between CO_2 and CH_4 feeds at 550 °C: (a) 1st cycle, and (b) 2nd cycle. (Experimental conditions: feed gas = 10 vol.%CO_2/90 vol.%Ar and feed gas = 10 vol.%CH_4/30 vol.%Kr/60 vol.%Ar, total flow rate = 50 mL (STP) min^{-1})

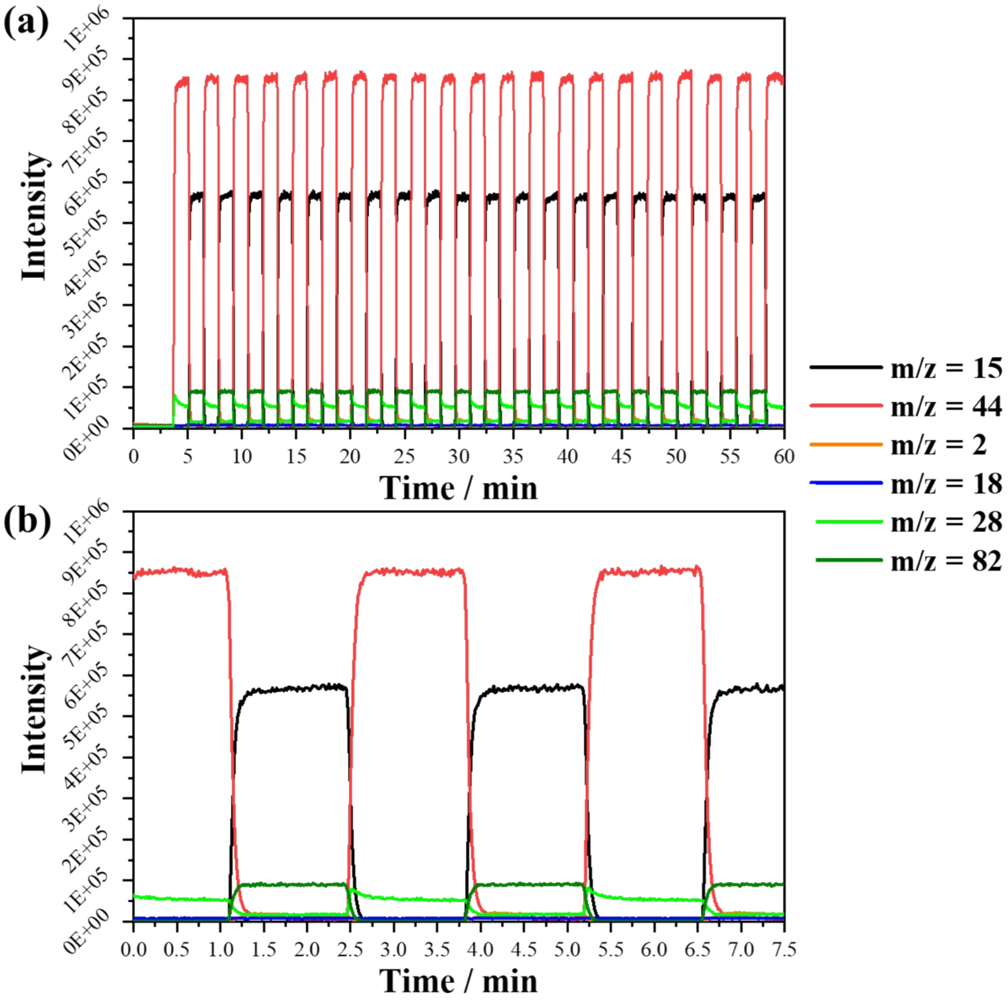
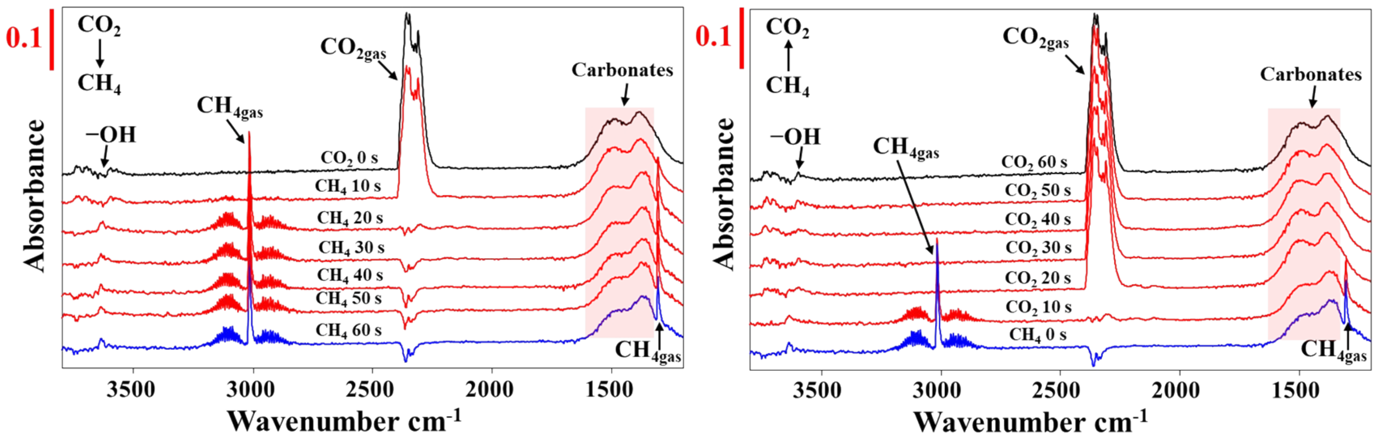
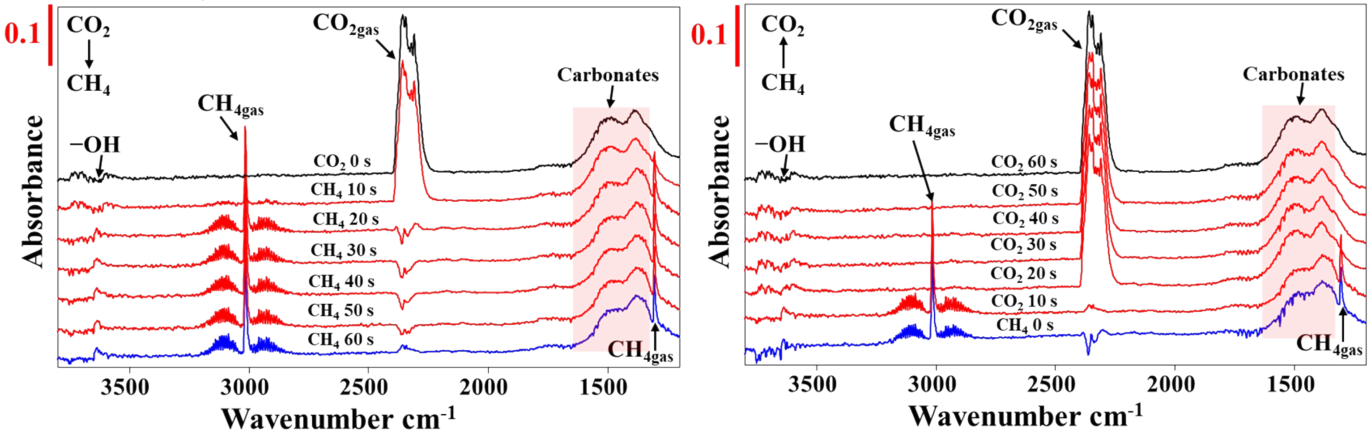


Figure S14. MS signals collected at the exit of the DRIFTS cell as a function of ToS during DRM switching between CO_2 and CH_4 feeds over the bare CeO_2 support at 550 °C: (a) 20 cycles, and (b) 1st–3rd cycle. (Experimental conditions: feed gas = 10 vol.%CO_2/90 vol.%Ar and feed gas = 10 vol.%CH_4/30 vol.%Kr/60 vol.%Ar, total flow rate = 50 mL (STP) min^{-1})

(a) 2nd cycle



(b) 10th cycle



(c) 20th cycle

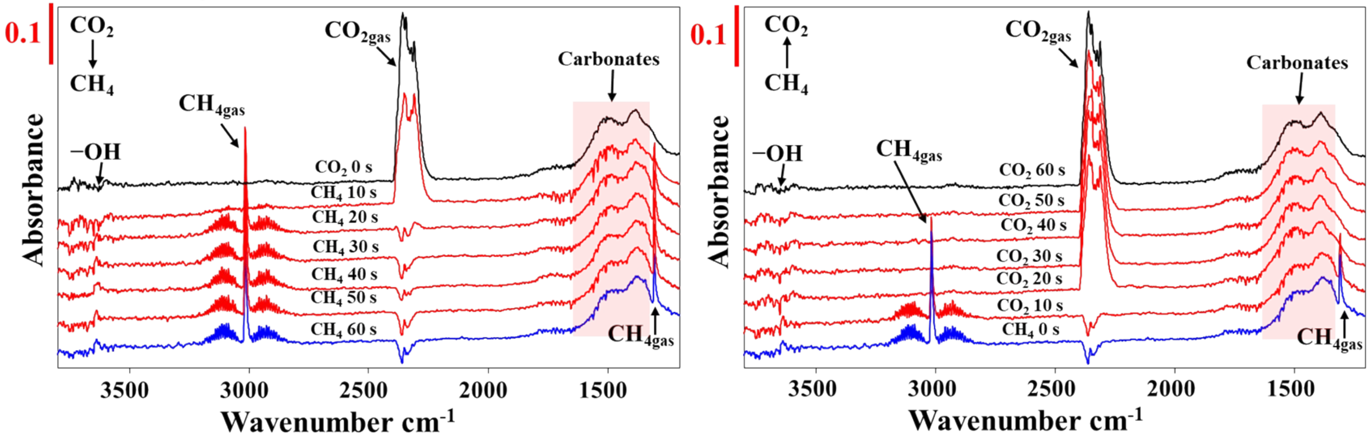


Figure S15. *In situ* DRIFTS spectra over the Ni@CeO$_2$ catalyst during the 1st cycle of DRM switching between CO$_2$ and CH$_4$ feeds at 550 °C: (a) CO$_2$ to CH$_4$, and (b) CH$_4$ to CO$_2$. (Experimental conditions: feed gas = 10 vol.%CO$_2$/90 vol.%Ar and feed gas = 10 vol.%CH$_4$/30 vol.%Kr/60 vol.%Ar, total flow rate = 50 mL (STP) min^{-1})

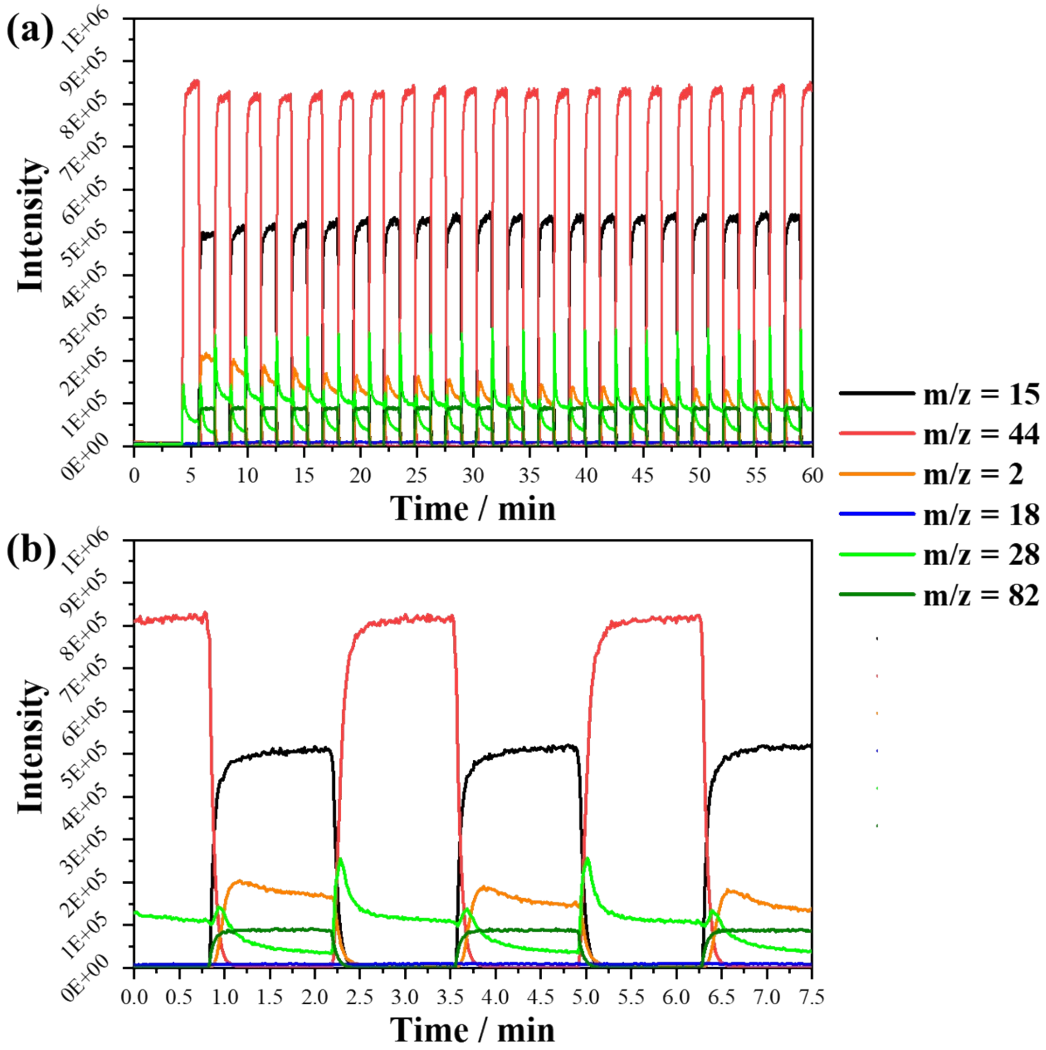
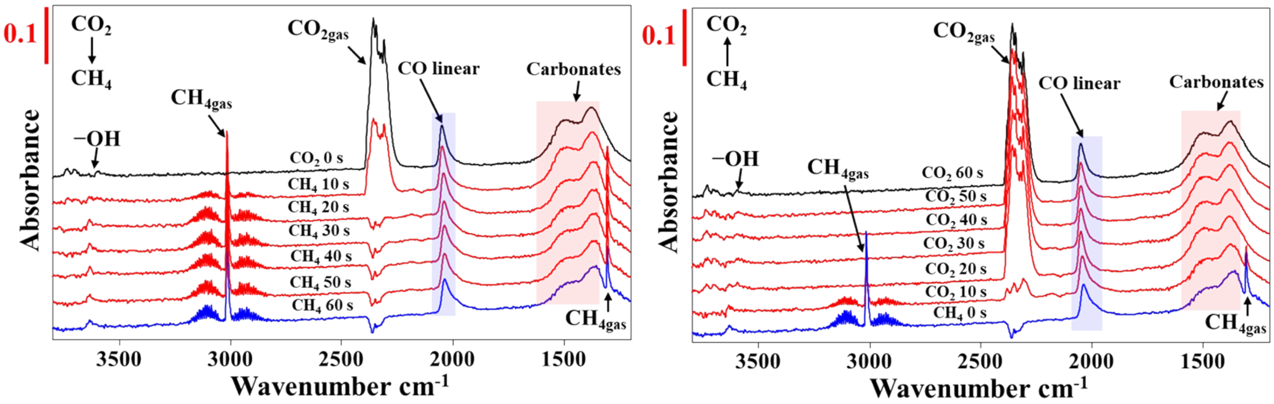
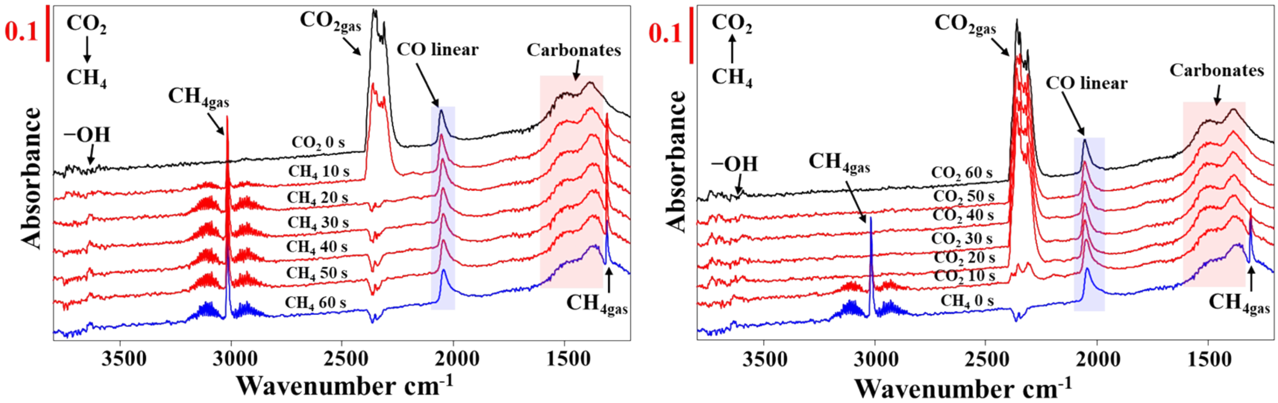


Figure S16. MS signals collected at the exit of the DRIFTS cell as a function of ToS during DRM switching between CO_2 and CH_4 feeds over the Ni@CeO_2 catalyst at 550 °C: (a) 20 cycles, and (b) 1st–3rd cycle. (Experimental conditions: feed gas = 10 vol.%CO_2/90 vol.%Ar and feed gas = 10 vol.%CH_4/30 vol.%Kr/60 vol.%Ar, total flow rate = 50 mL (STP) min^{-1})

(a) 2nd cycle



(b) 10th cycle



(c) 20th cycle

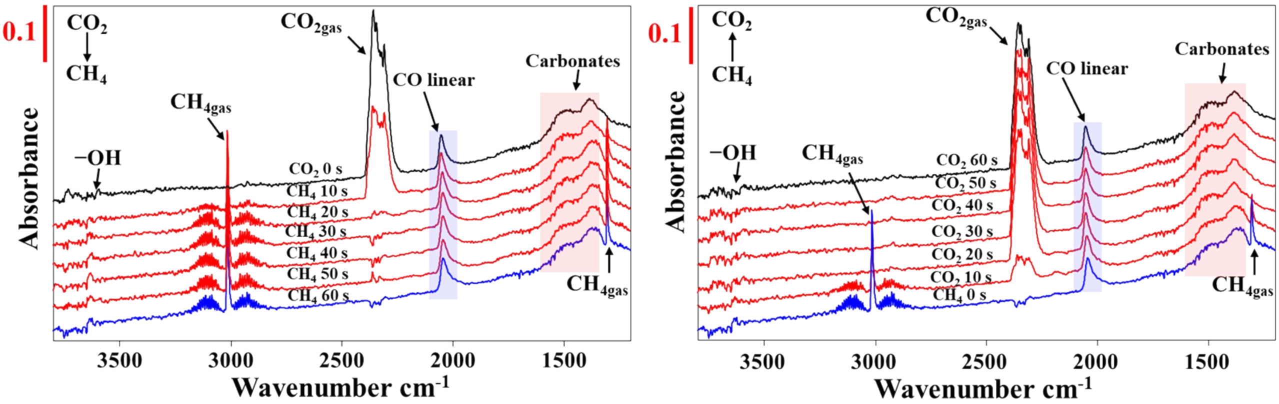


Figure S17. *In situ* DRIFTS spectra over the Pt-Ni@CeO_2 catalyst as a function of ToS during DRM switching between CO_2 and CH_4 feeds at 550 °C: (a) 2nd cycle, (b) 10th cycle, and (c) 20th cycle. (Experimental conditions: feed gas = 10 vol.%CO_2/90 vol.%Ar and feed gas = 10 vol.%CH_4/30 vol.%Kr/60 vol.%Ar, total flow rate = 50 mL (STP) min^{-1})

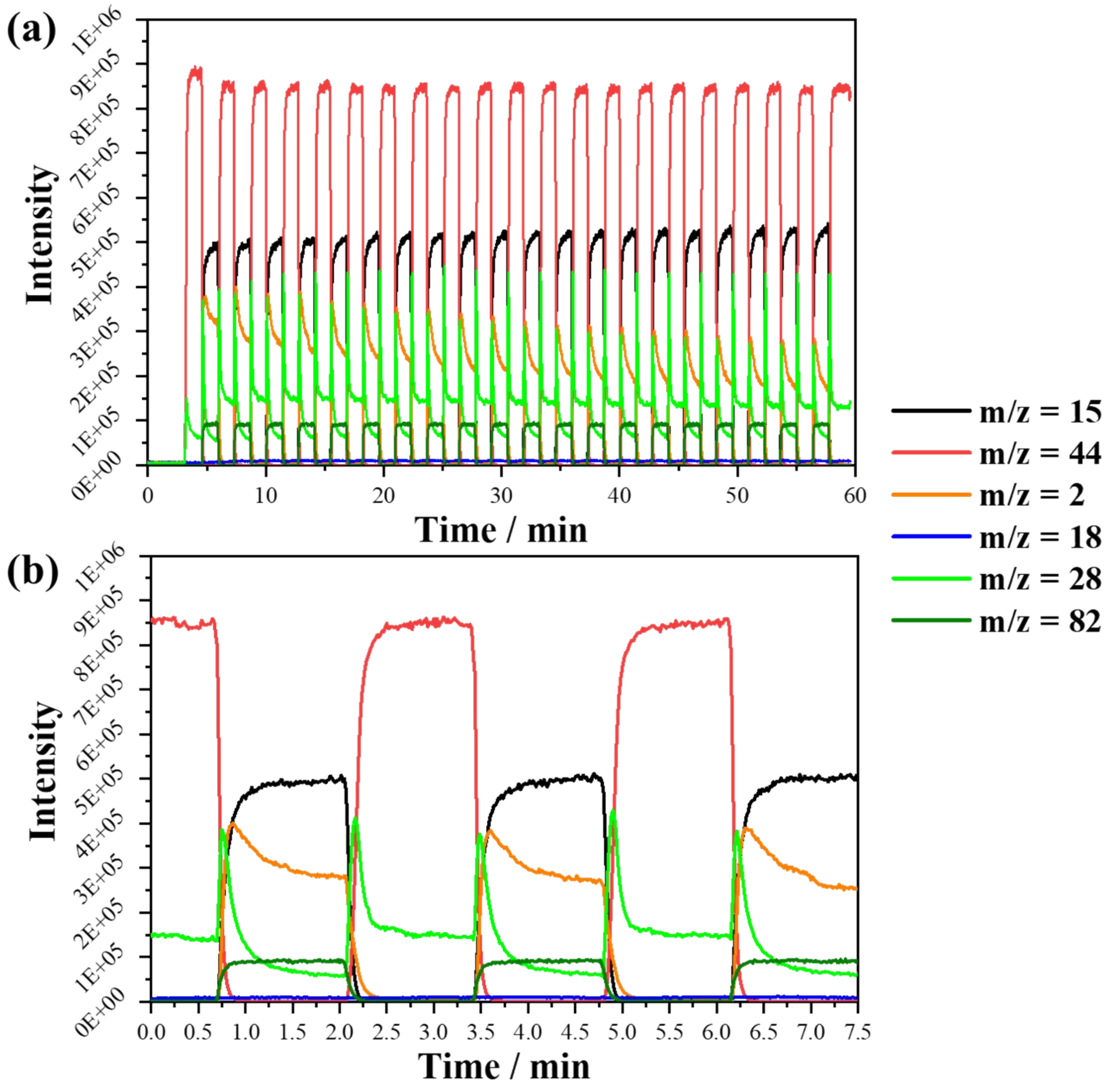


Figure S18. MS signals collected at the exit of the DRIFTS cell as a function of ToS during DRM switching between CO_2 and CH_4 feeds over the Pt-Ni@CeO_2 catalyst at 550 °C: (a) 20 cycles, and (b) 1^{st}–3^{rd} cycle. (Experimental conditions: feed gas = 10 vol.%CO_2/90 vol.%Ar and feed gas = 10 vol.%CH_4/30 vol.%Kr/60 vol.%Ar, total flow rate = 50 mL (STP) min^{-1})

Reference

[1] A. Laachir, V. Perrichon, A. Badri, J. Lamotte, E. Catherine, J.C. Lavalley, J. El Fallah, L. Hilaire, F. Le Normand, E. Quéméré, G.N. Sauvion, O. Touret, Reduction of CeO_2 by hydrogen. Magnetic susceptibility and Fourier-transform infrared, ultraviolet and X-ray photoelectron spectroscopy measurements, Journal of the Chemical Society, Faraday Transactions, 87 (1991) 1601-1609.