

Supplementary information

Visible light suppresses carbon formation on Ni/CeO₂ catalyst in methane dry reforming reaction

Kristijan Lorber¹, Vasyl Shvalya², Damjan Vengust², Janez Zavašnik^{2,3}, Matej Huš^{1,4}, Blaž Likozar¹,

Matjaž Mazaj¹ and Petar Djinović^{1,5*}

¹National Institute of Chemistry, Hajdrihova ulica 19, SI-1000, Ljubljana, Slovenia

²Institute Jožef Stefan, Jamova ulica 39, SI-1000, Ljubljana, Slovenia

³Max-Planck-Institut für Nachhaltige Materialien, Max-Planck-Straße 1, 40237 Düsseldorf

⁴Association for Technical Culture of Slovenia (ZOTKS), Zaloška cesta 65, SI-1000 Ljubljana

⁵University of Nova Gorica, Vipavska 13, Nova Gorica, Slovenia

*Corresponding author e-mail: petar.djinovic@ki.si

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Mears criterion for estimation of mass transport limitations

$$\frac{r_{obs} * R_p}{k_c * C_{ab}} < 0.15$$

The r_{obs} is the CO₂ rate per catalyst volume at 600 °C (93 mol CO₂/(m³ s¹) for the light-assisted conditions), R_p is the particle radius (estimated from SEM visualization as 1*10⁻⁵ m), k_c is the mass transfer coefficient of the reactant (m/s) and C_{ab} is the concentration of the reactants in the bulk gas phase (estimated for CH₄ and CO₂ at 600 °C as 14 mol/m³). $D_{CO_2-H_2}$ is the diffusion coefficient of CO₂ in H₂ which is estimated as 5.5*10⁻⁵ m²/s.

$$k_c \sim \frac{D_{CO_2-H_2}}{R_p} = \frac{0.000055 \text{ m}^2 \text{ s}^{-1}}{0.00001 \text{ m}} = 5.5 \text{ m/s}$$

$$\frac{r_{obs} * R_p}{k_c * C_{ab}} = \frac{93 * 1 * 10^{-5}}{5.5 * 14} = 1.2 * 10^{-5} < 0.15$$

Experimental conditions satisfy the Mears criterion for the absence of external mass transfer limitations.

Calculation of reaction rates and H₂/CO ratio

All experiments were performed with CH₄ and CO₂ conversions well below 10 %, resulting in differential reactor operation. Absence of mass transfer limitations was verified above and ensures the integrity of obtained catalytic data. Considering the low conversions of methane and CO₂, the calculation of their reaction rates was not derived directly from GC data of methane and CO₂ concentrations, but rather recalculated from CO and H₂ concentrations, which are initially not present and are thus much more accurate. Reaction rates were calculated by considering conversion (X_A), mass of catalyst ($m_{cat.}$), flow rate (F_A) as well as constant of molar volume of gas (0.0446 mol/L) according to Eq.1:

$$r_A = \frac{X_A * F_A * 0.0446}{m_{cat.}}, \quad \left[\frac{\text{mmol}}{\text{g} * \text{min}} \right] \quad (1)$$

Reaction rates for CH₄ and CO₂



By combining (H_2) = 2x - y, (CO) = 2x + y and (H_2O) = y, we can calculate the individual rates as:

$$r(CH_4) = \frac{r(H_2) + r(CO)}{4} \quad (4)$$

$$r(CO_2) = \frac{3r(CO) - r(H_2)}{4} \quad (5)$$

$$r(H_2O) = \frac{r(CO) - r(H_2)}{2} \quad (6)$$

The H₂ selectivity is expressed as H₂/CO ratio and was calculated as a ratio between rates of H₂ and CO as shown in Eq.7:

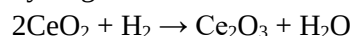
$$\frac{H_2}{CO} = \frac{r_{H_2}}{r_{CO}} \quad (7)$$

H₂-TPR analysis and the methodology for Ce³⁺ fraction estimation

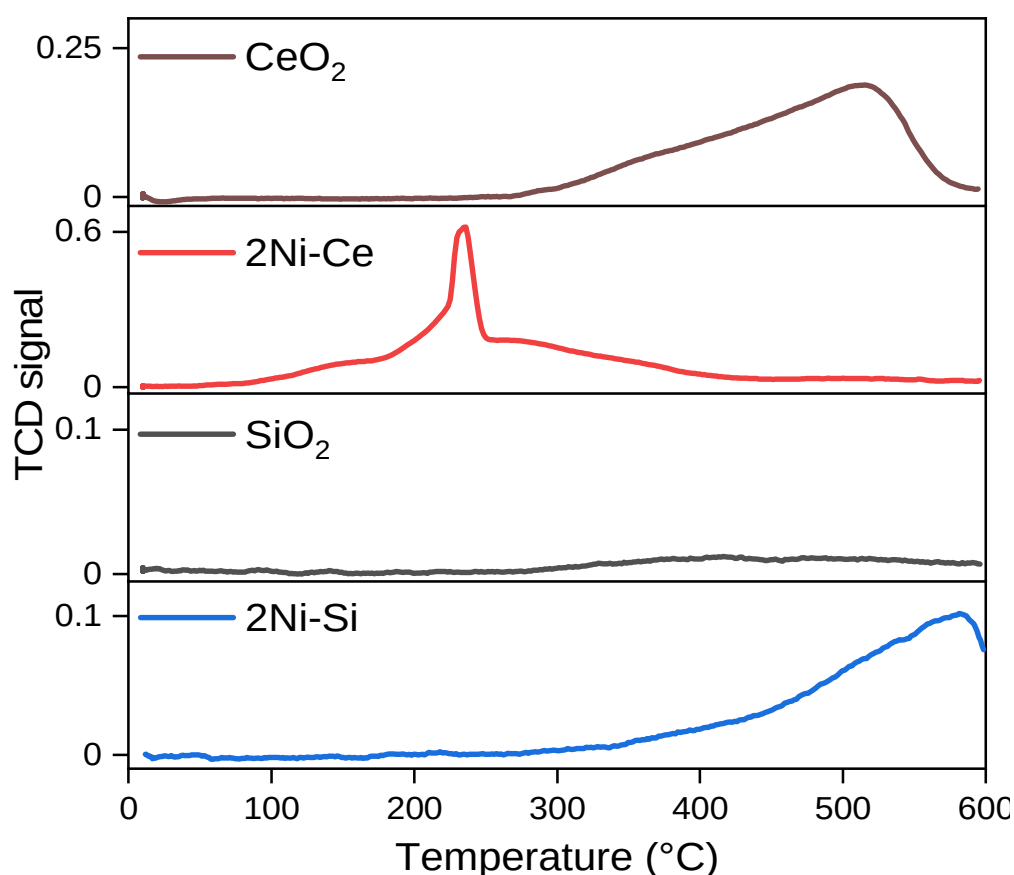
The total amount H₂ (ml/g) is obtained from the integration of the H₂-TPR signal using a suitable calibration. Total H₂ consumption contains contributions from reduction of NiO to Ni and partial reduction of CeO₂ to Ce₂O₃ which occur in the investigated temperature range.

The sample mass during the H₂-TPR analysis is known, the measured Ni content is 1.8 wt.%. We calculated the required amount of H₂ for complete nickel oxide reduction to metallic nickel, according to our previous work.¹ For bare CeO₂ samples, the H₂ consumption for Ni is zero.

The difference between total H₂ consumption and H₂ consumption estimated for Ni is the amount of hydrogen that remains for reduction of ceria. The ceria reduction stoichiometry is the following:



As a result, the amount of oxygen removed from ceria can be calculated, and thus the fraction of Ce³⁺ can be estimated.



Supplementary Figure 1. Temperature programmed reduction of catalysts and bare supports. H₂-TPR profiles for bare CeO₂ and SiO₂ supports and 2Ni-Ce and 2Ni-Si catalysts.

H₂-TPR analysis was employed to assess lattice oxygen reactivity. The reduction of bare CeO₂ begins around 260 °C and gradually intensifies until ~520 °C (Supplementary Fig. 1). Holding the sample at 600 °C for 30 min ensures a quasi-steady state reduction extent is reached. The fraction of reduced Ce³⁺ (determined from H₂ consumption between 10 and 600 °C) in bare CeO₂ was calculated as 18 %.

Reduction of the 2Ni-Ce catalyst commences at ~60 °C and extends through multiple overlapping peaks up to ~450 °C, which are induced by nickel reduction alongside surface and partial bulk ceria reduction.^{2,3} For the bare SiO₂ support, no H₂ consumption was observed, signifying absence of reduction while for the 2Ni-Si catalyst, reduction initiates around 270 °C and progresses up to 580 °C.

CO chemisorption

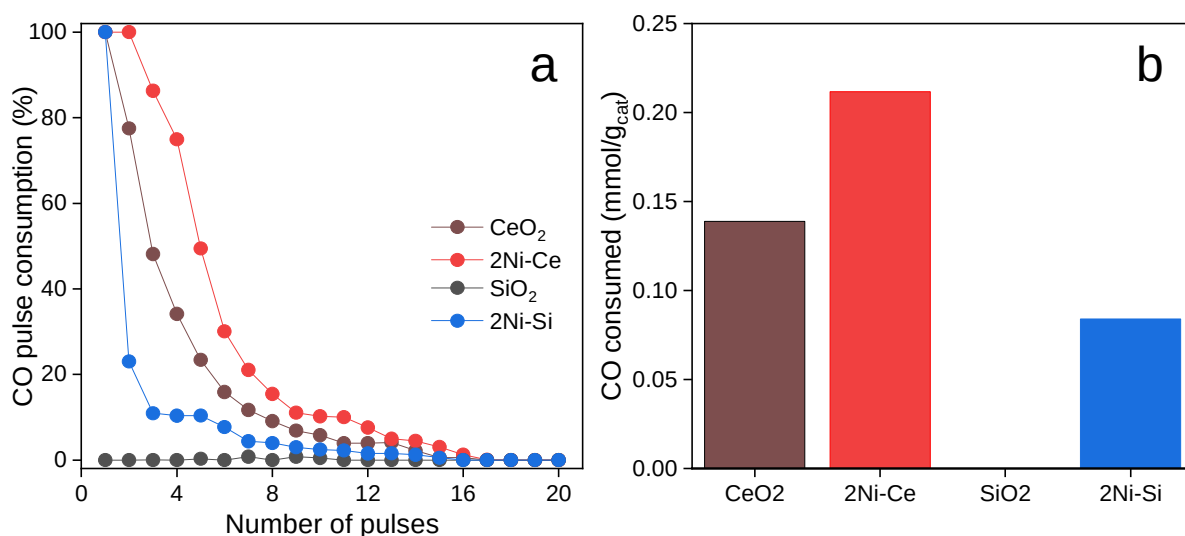
Nickel dispersion was quantified using pulse CO chemisorption at -10°C, a stoichiometry of CO/Ni_{surface} = 1 : 1 was assumed. Ni dispersion ($D_{Ni} = Ni_{surface}/Ni_{total}$) was determined according to Eq. 8:

$$D_{Ni}(\%) = \frac{1 \cdot n(CO)}{n(Ni_{total})} * 100\% \quad (8)$$

Where 1 presents the 1 : 1 stoichiometry of CO/Ni_{surface}, $n(CO, \text{mmol/g}_{cat})$ is the amount of consumed CO during pulse experiment and $n(Ni, \text{mmol/g}_{cat})$ is the total amount of Ni in the catalyst. The average size of Ni (d_{Ni}) was calculated according to Eq. 9, assuming spherical nickel nanoparticles:

$$d_{Ni} = \frac{C1}{D_{Ni}} \quad (9)$$

C1 is the constant for Ni = 97, adopted from earlier work of Bartholomew and Farrauto and D_{Ni} is Ni dispersion (%), as estimated by Eq. 8.^{4,5}



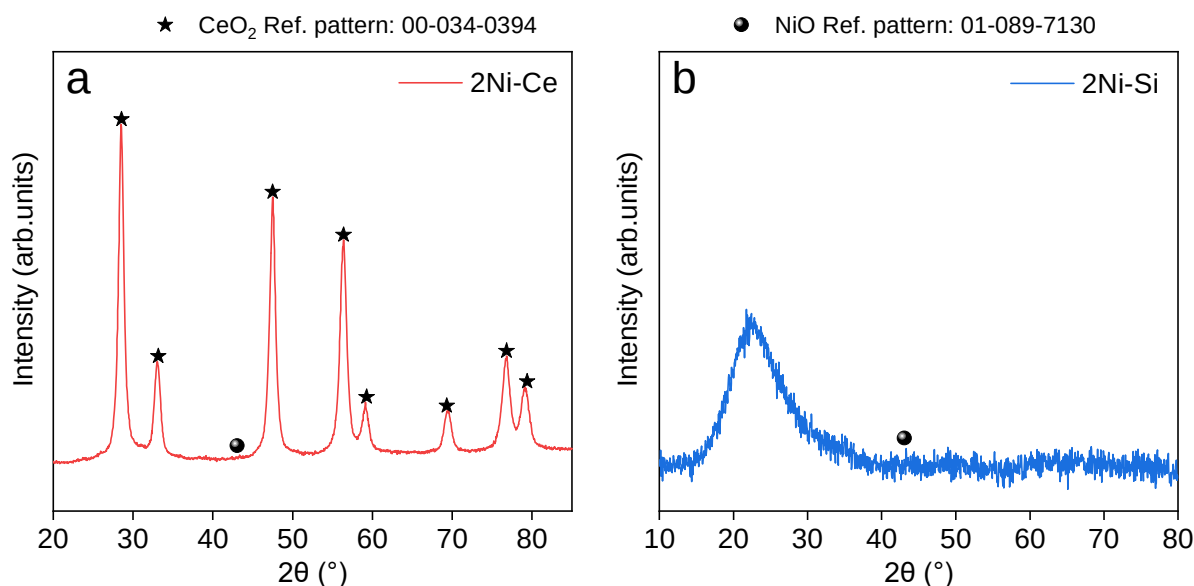
Supplementary Figure 2. Pulse CO chemisorption analysis. (a) Percentage of CO chemisorbed during consecutive pulses and (b) total amount of chemisorbed CO on CeO₂, 2Ni-Ce, SiO₂ and 2Ni-Si materials.

Supplementary Table 1. Fraction of Ce³⁺ attained during H₂-TPR, nickel dispersion and the average Ni size estimated from CO dispersion and TEM analysis.

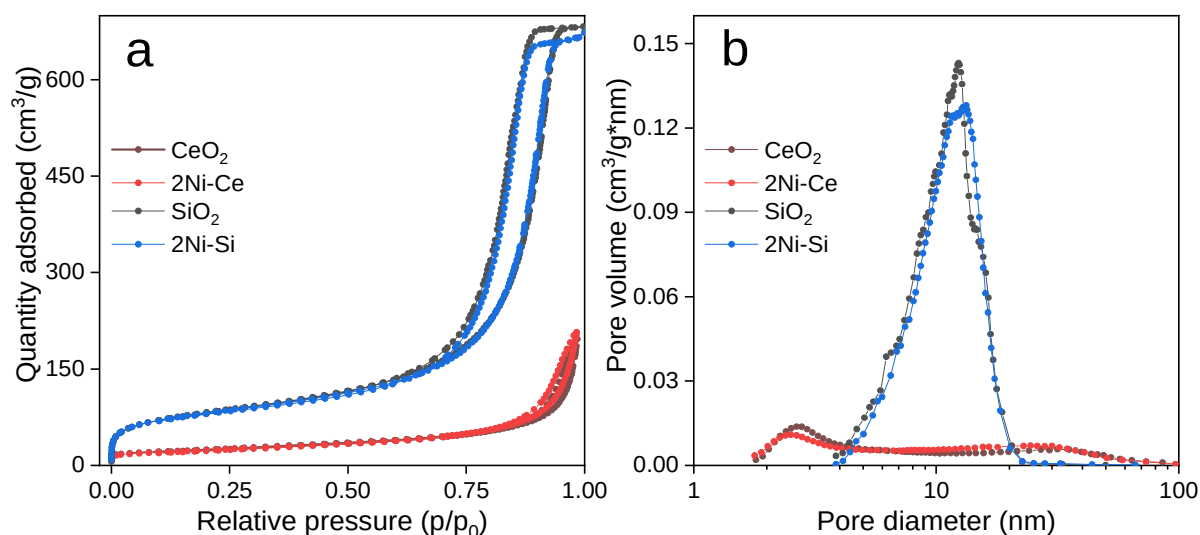
Sample	Fraction of Ce ³⁺ (%)	Ni dispersion (%)	Ni particle size (CO chemisorption) (nm)	Ni particle size (TEM analysis) (nm)
CeO ₂	18	/	/	/
2Ni-Ce	21	23.7	4.1	5.7
SiO ₂	/	/	/	/
2Ni-Si	/	24.6	3.9	5.1

XRD, N₂ physisorption and TEM analyses

XRD analysis showed only presence of *fcc* CeO₂ crystalline phase in the 2Ni-Ce catalyst. Amorphous SiO₂ is the only identifiable phase in the 2Ni-Si catalyst. Nickel containing crystalline phases could not be identified in any catalyst, due to low loading and high dispersion.



Supplementary Figure 3. X-ray diffraction analysis. XRD diffraction patterns of the (a) 2Ni-Ce and (b) 2Ni-Si catalyst. Star and sphere symbols show where most intense diffraction lines from CeO₂ and NiO are expected.

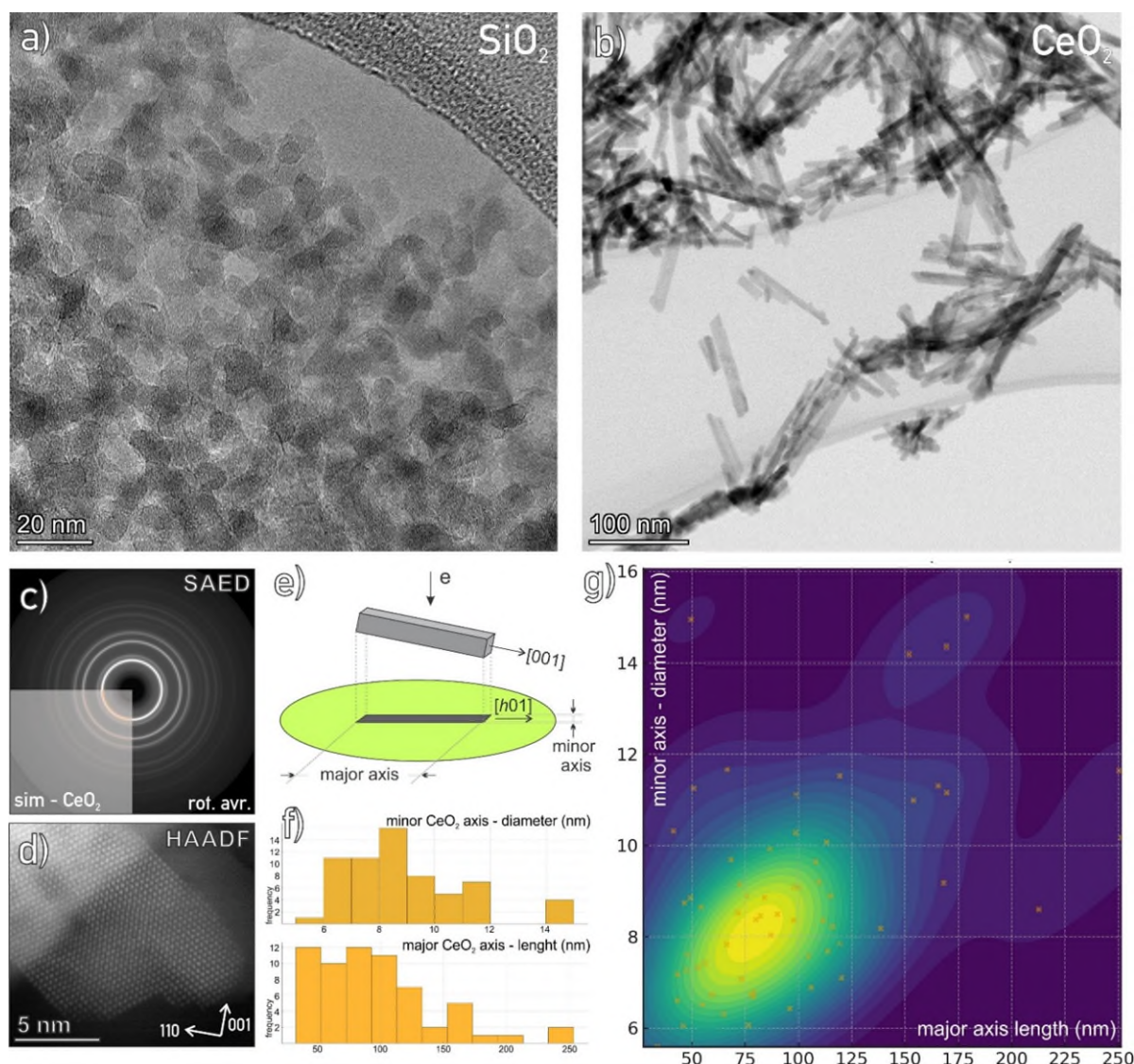


Supplementary Figure 4. N₂-physisorption analysis. (a) N₂ physisorption isotherms and (b) pore size distribution for bare CeO₂ and SiO₂ supports as well as 2Ni-Ce and 2Ni-Si catalysts.

Supplementary Table 2. Specific surface area and total pore volume values.

Sample	S _{BET} (m ² /g)	V _{pore} (cm ³ /g)
CeO ₂	85	/
2Ni-Ce	82	/
SiO ₂	287	1.06
2Ni-Si	282	1.03

TEM analysis



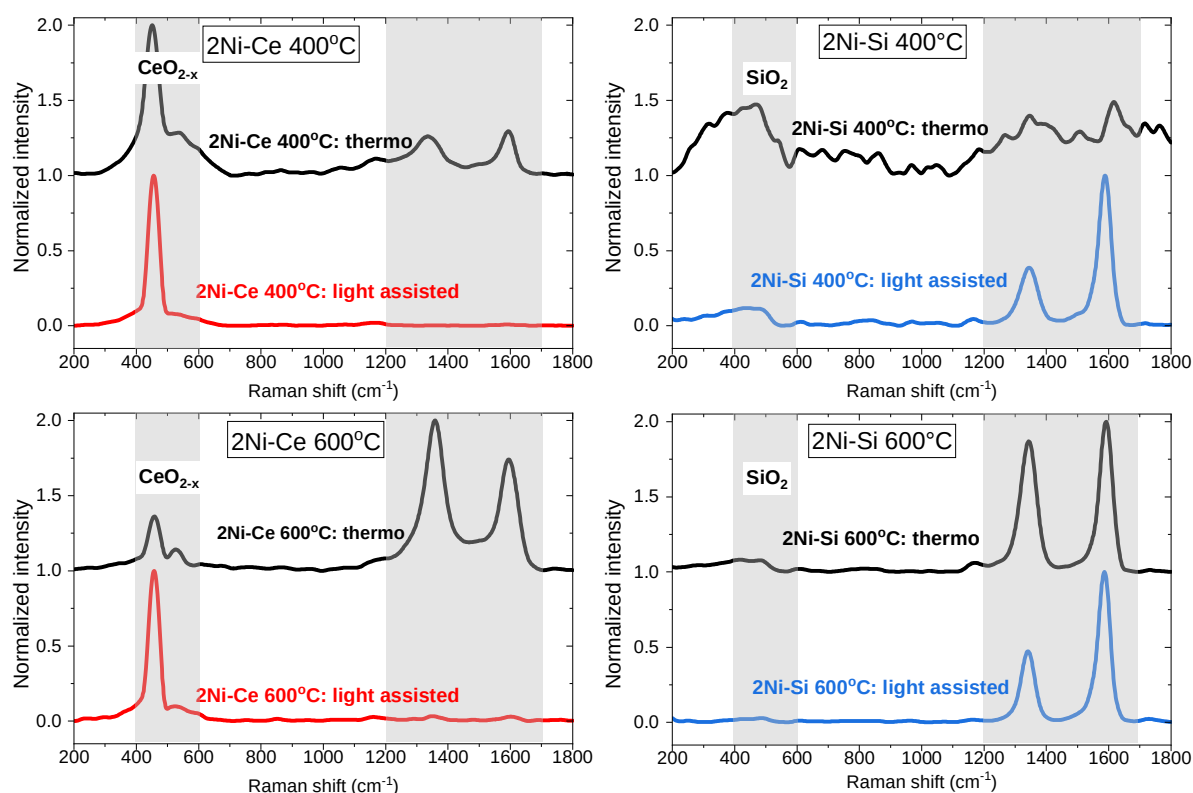
Supplementary Figure 5. TEM analysis and CeO₂ nanorod size distribution. STEM-BF micrograph showing (a) pure SiO₂ and (b) randomly oriented CeO₂ nanorods. (c) Phase composition confirmed by Selected Area Electron Diffraction (SAED), simulated CeO₂ pattern is shown in the inset. (d) High-Angle Annular Dark-Field STEM (HAADF-STEM) micrograph of a nanorod termination, with principal crystallographic planes indicated. (e) Schematic 2D projection of a CeO₂ nanorod, with marked measured minor and major axes. (f) Size distribution histograms of CeO₂ nanorod diameter (minor axis) and lengths (major axis) obtained from TEM projections. (g) Kernel density estimation (KDE) map of the joint distribution of major versus minor axes of CeO₂ nanorods.

Bare SiO₂ sample is composed of highly amorphous particles of ~10 nm in size. The CeO₂ support comprises of crystalline, anisotropic, rod-like nanoparticles measuring about 8 nm in diameter and 50-150 nm in length.

For the purpose of DFT simulations, a detailed analysis of exposed surfaces of CeO₂ crystals was conducted. All investigated CeO₂ nanorods are crystalline, anisotropic, rod-like single-crystal nanoparticles with well-defined Wulff surfaces. The analysis by FFT, SAED patterns, and HAADF-STEM micrographs revealed that majority of exposed surfaces belong to {111} family of planes. The {100} and {110} are only present at the tips and edges of the nanorods.^{1,6}

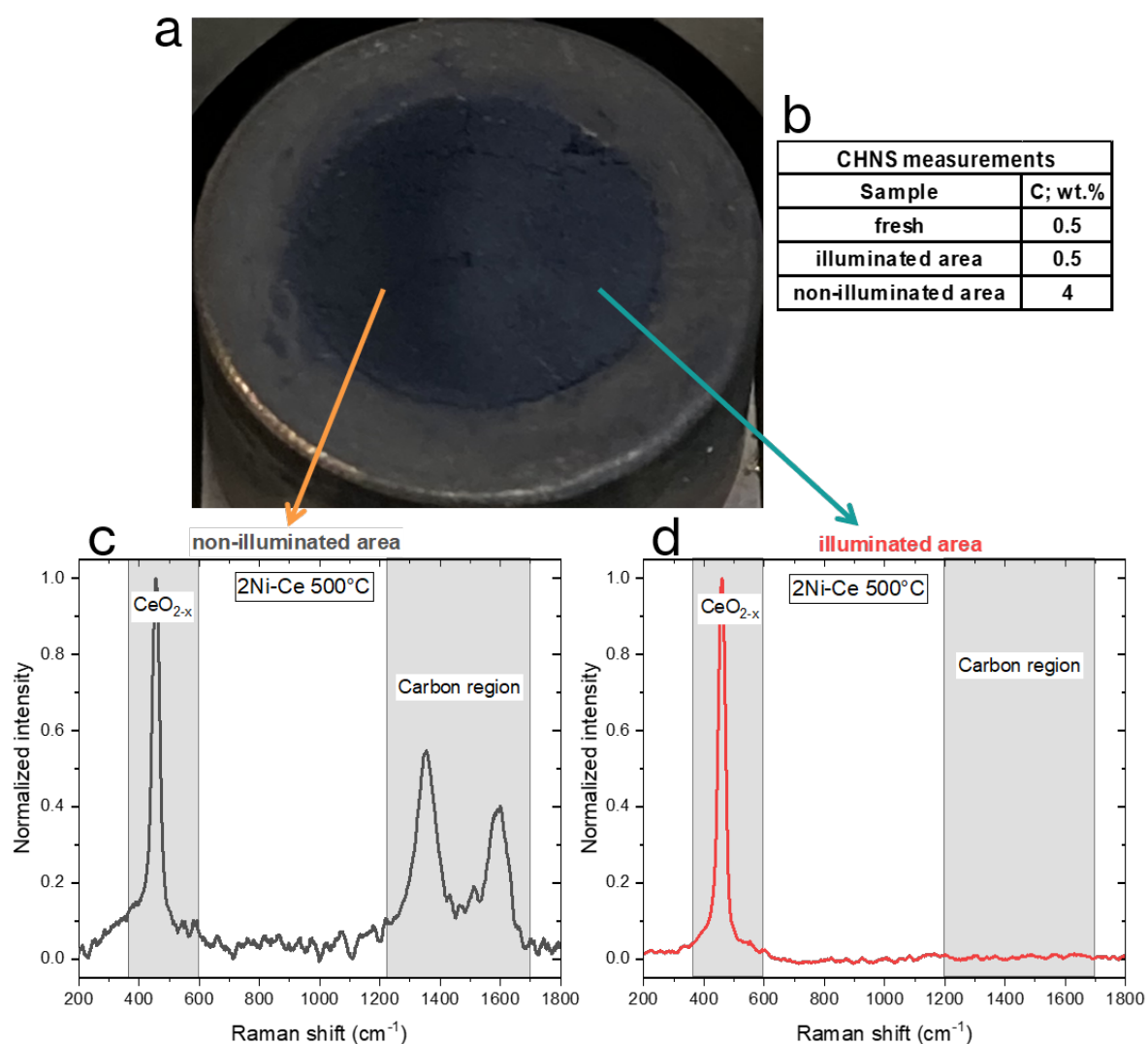
Carbon formation during DRM

The shaded region between 400 and 600 cm^{-1} marks the spectral range where Raman features of the catalyst are expected, whereas the shaded region between 1200 and 1700 cm^{-1} marks the characteristic D/G-band range of Raman-active carbonaceous deposits. Raman D/G bands in this region are commonly used to identify disordered, graphitic, and nanostructured sp^2 -rich carbon. To reduce local sampling bias, Raman spectra were collected from three separate regions of the catalyst bed. At each region, spectra were recorded at the central position and at two neighboring positions displaced by approximately ± 100 μm , giving nine Raman sampling positions per catalyst/condition. All individual spectra were inspected for carbon D/G bands before averaging. The Raman results are therefore reported as the presence or absence of Raman-detectable carbon under the applied multi-position sampling protocol, rather than as bulk quantitative carbon content.



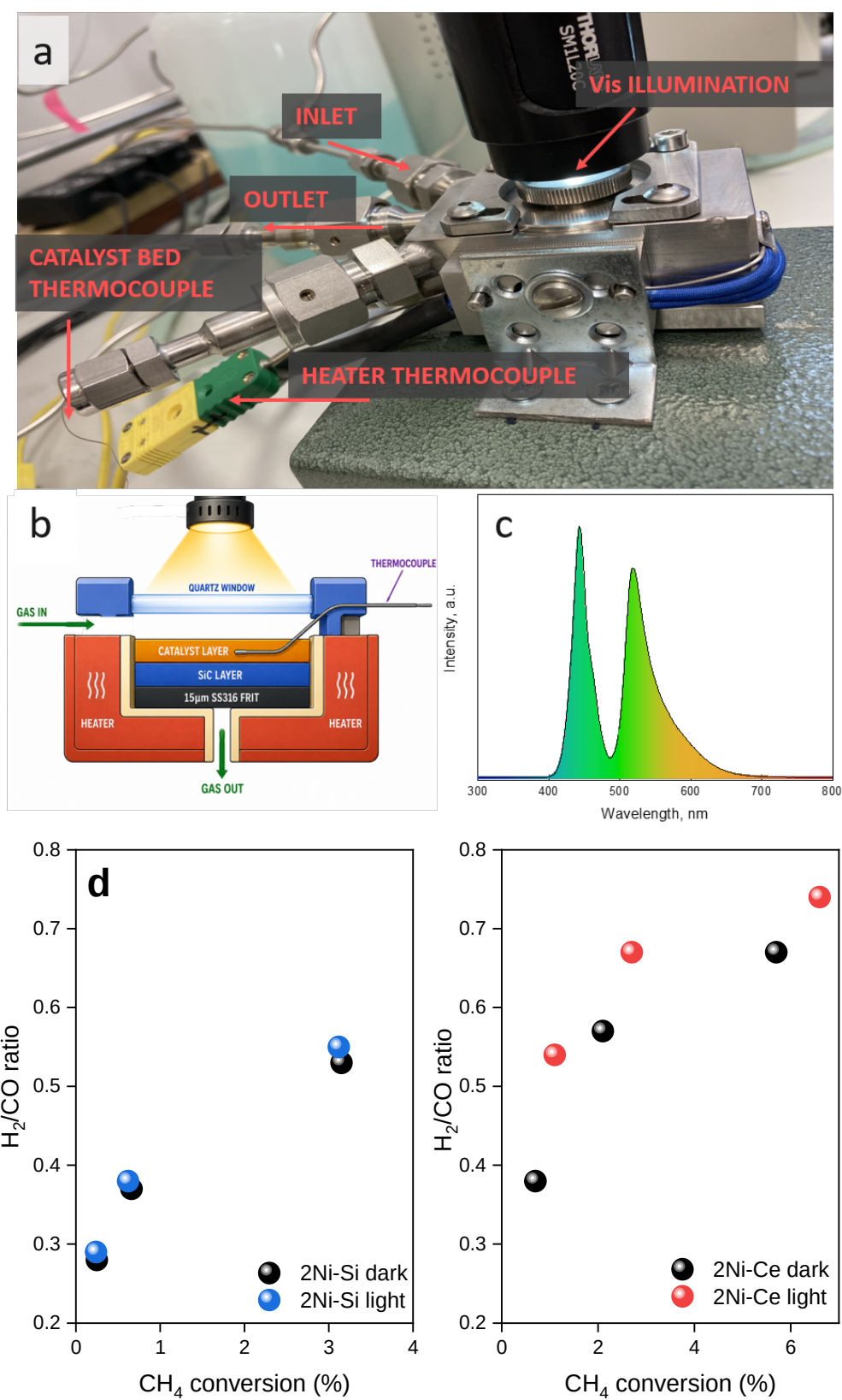
Supplementary Figure 7. Raman analysis for carbon presence after DRM reaction. Raman spectra used to evaluate carbon formation during DRM over 2Ni-Ce and 2Ni-Si catalysts under thermal and light-assisted conditions at 400 °C and 600 °C.

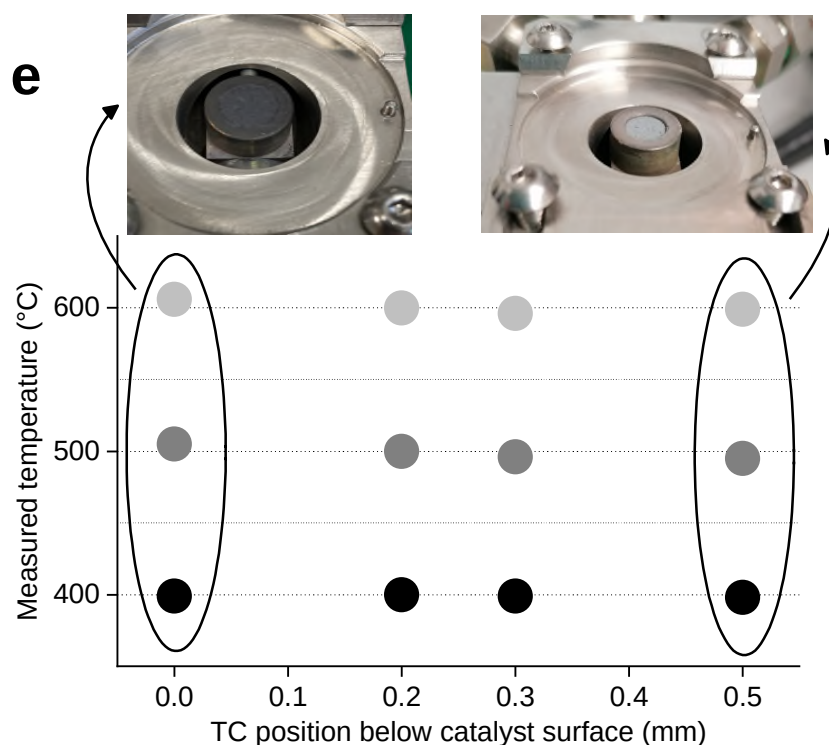
The 1200-1700 cm^{-1} region corresponds to the characteristic D/G-band range of carbonaceous deposits. Individual spectra were collected from nine Raman sampling positions per catalyst/condition and inspected for carbon D/G bands before averaging. To further verify the effect of visible light on preventing carbon formation, an additional experiment was performed in which only one half of the 2Ni-Ce catalyst bed was illuminated during the DRM reaction at 500 °C (Supplementary Fig. 8A). After 1 h of reaction, neither Raman spectroscopy nor elemental (CHNS) analysis detected carbon deposits on the illuminated region of the catalyst. In contrast, both Raman spectroscopy and CHNS analysis clearly confirmed carbon formation on the non-illuminated region, demonstrating that illumination effectively suppresses carbon deposition during the DRM reaction.



Supplementary Figure 8. Visualization of the spent 2Ni-Ce catalyst layer after DRM reaction, CHNS analysis for carbon quantification and Raman analysis of the dark and illuminated sections of the catalytic layer. (a) Picture of 2Ni-Ce catalyst where half of the sample area was illuminated with visible light (400-700 nm) and half remained in dark during DRM reaction at 500 °C. (b) Elemental analysis of the amount of carbon on fresh, illuminated and non-illuminated part of the 2Ni-Ce catalyst sample. (c) Raman spectra on non-illuminated and (d) illuminated part of the 2Ni-Ce sample after DRM reaction test at 500 °C.

Experimental setup and verification of correct temperature measurement





Supplementary Figure 9. Reaction chamber for light-assisted catalytic experiments, emission spectrum of the LED light source and control experiments for catalyst temperature heterogeneity verification. (a) Reaction chamber used for the catalytic and spectroscopic experiments. (b) Schematic side-view of the reaction chamber showing all crucial elements. (c) Emission spectrum of the LED light that was used for catalytic experiments. (d) H_2/CO ratio versus CH_4 conversion during DRM reaction under thermal and visible light assisted conditions for 2Ni-Si and 2Ni-Ce samples. (e) Temperature measured at different axial thermocouple positions (0= top of catalyst bed, 0.5 mm is touching the catalyst bed from below). Pictures in top left and top right corner emphasize the situation. Sample was irradiated by 610 mW/cm^2 of white light and reaction chamber was flushed with 20 ml/min of argon during temperature measurements.

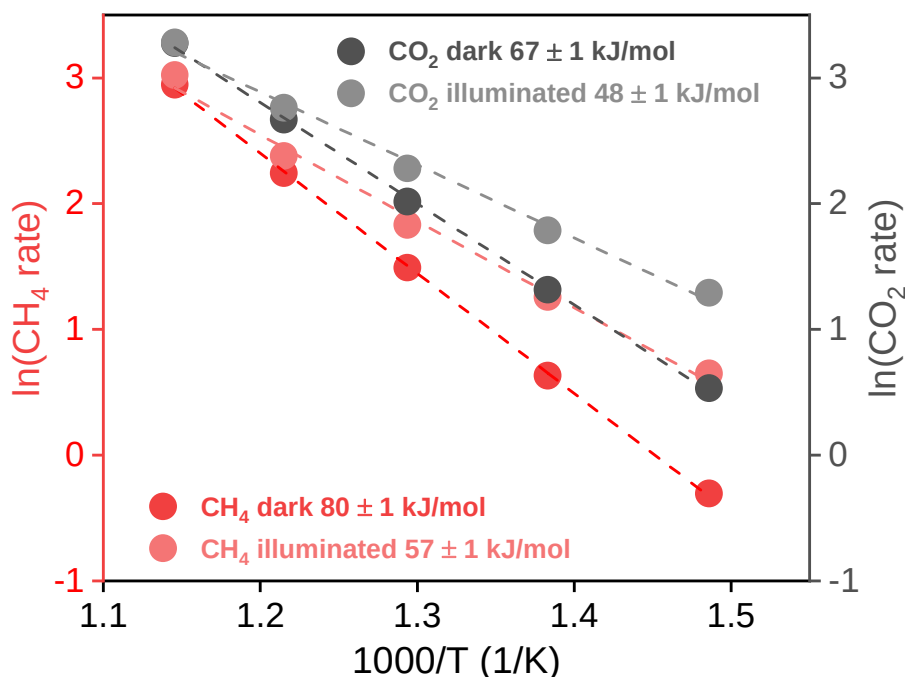
To experimentally verify that the catalyst temperature measured with the miniature thermocouple inside the catalytic layer, just below the illuminated surface is an accurate temperature estimation of the catalytic bed, a control experiment with a 2 wt.% Ni/SiO₂ (2Ni-Si) and 2Ni/CeO₂ (2Ni-Ce) catalysts was made. Visible light (610 mW/cm^2 , $400 < \lambda < 700\text{ nm}$) was used for catalyst illumination.

When comparing thermocatalytic data (black symbols) with light-assisted catalytic data (blue symbols) and the reaction selectivity is compared at equal methane conversion, the performance of 2Ni-Si catalyst overlaps perfectly in both experiments. Silica is an optically transparent insulator and nickel is not photoexcited by visible light. As a result, its photocatalytic contribution to DRM activity is negligible. When we compared the DRM activity under dark and illuminated conditions at identical measured catalyst bed temperatures (Fig. 1d, 1e and 1f), the rates were barely distinguishable and the reaction selectivity expressed as H_2/CO ratio remains the same. Based on this result, we can indirectly conclude that the actual catalyst bed temperature under dark and illuminated conditions is very similar and it is measured correctly.

The situation is very different for the 2Ni-Ce catalyst where the H_2/CO ratio and thus reaction selectivity is notably higher under light-assisted conditions at identical methane conversion, revealing an additional effect is present in addition to the light induced heating.

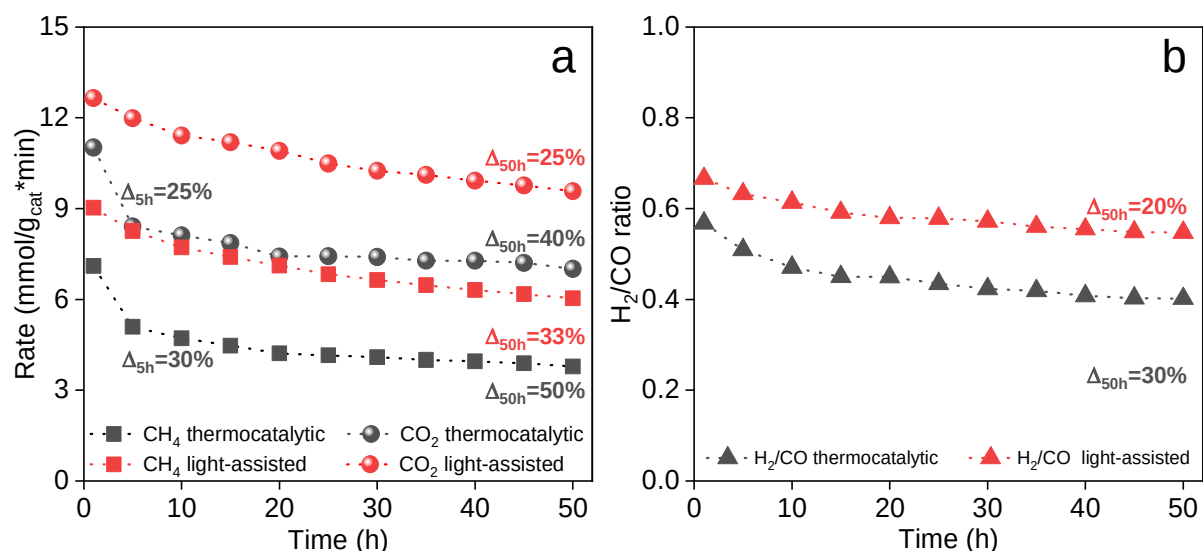
Additionally, we measured the surface temperature at different catalyst bed depths by gradually submerging the thermocouple tip from the surface (directly illuminated) to the bottom of the catalytic layer (0.5 mm below the surface), Supplementary Fig. 9e. The measured temperatures inside the catalytic layer, as a function of axial thermocouple position show minimal temperature gradients reaching up to 6 °C. As a result, catalyst bed dilution with optically transparent silica, the employed illumination power of 610 mW/cm² and reaction conditions do not produce thermal gradients that could mask the observed non-thermal phenomena. Therefore, the sample temperature scaling during light-assisted experiments in this work is a true and reliable value on which we are comparing the catalytic performance under dark and illuminated conditions.

Apparent activation energies for DRM reaction in thermocatalytic and light-assisted mode



Supplementary Figure 10. Apparent activation energies (E_a) for CH_4 and CO_2 reaction rates in thermocatalytic and light-assisted DRM reaction with the 2Ni-Ce catalyst.

Long term stability under thermal and light-assisted conditions



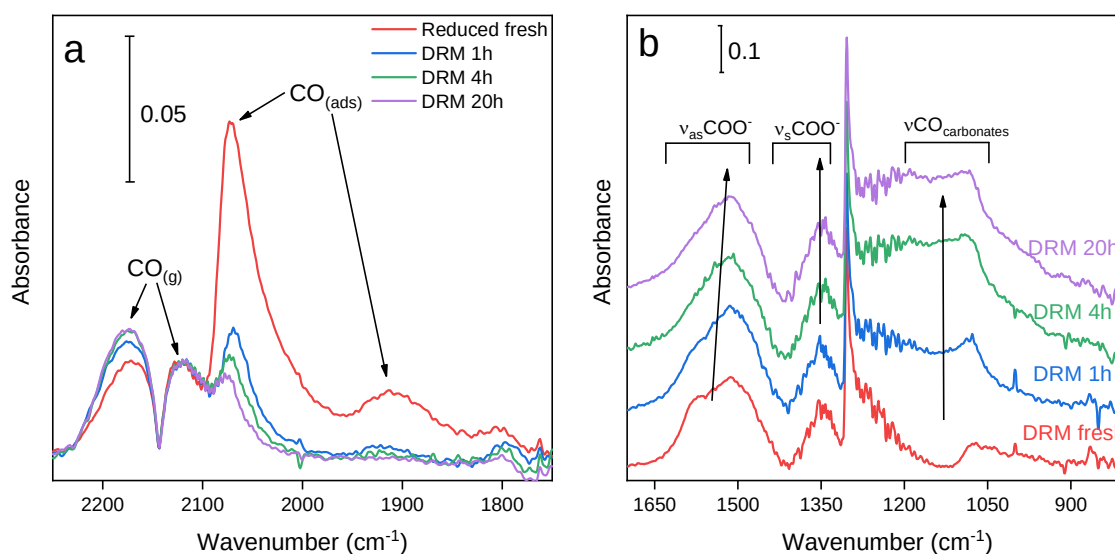
Supplementary Figure 11. Long-term catalytic performance. (a) Time-dependent CH_4 and CO_2 rates and (b) H_2 selectivity over 2Ni-Ce catalyst under thermal and photo-thermal conditions at 500 °C.

***In-situ* DRIFTS analysis of nickel surface area loss and carbonate accumulation during DRM reaction**

DRIFT spectra of carbonyl (CO chemisorption for evolution of nickel surface area) and carbonate species (for estimation of carbonate buildup) were recorded before, and after different times on stream during the light-assisted DRM reaction at 500 °C (Supplementary Fig. 12). After 2Ni-Ce catalyst reduction or DRM reaction at 500°C, the catalyst was cooled down to 200 °C in pure argon, followed by CO chemisorption in 10% CO/Ar flow. Adsorbed CO on Ni appears next to the gas phase CO in the region between 2100 and 1850 cm^{-1} .^{7,8} The highest signal of CO adsorbed on metallic nickel was determined on freshly reduced sample, directly prior to DRM reaction. The signal of adsorbed CO notably drops after exposure of catalyst to light-assisted DRM reaction at 500 °C and continuously decreases with longer time on stream. The decrease of adsorbed CO signal ($\text{CO}_{(\text{ads})}$) on the 2Ni-Ce catalyst reveals loss of active surface nickel sites either due to sintering or blocking.

During light-assisted DRM reaction, the presence of carbonates in the region between 1700 – 1000 cm^{-1} on the 2Ni-Ce catalyst increases in the initial four hours of reaction and stabilizes afterwards. The strongly adsorbed CO_2 forms stable carbonates, acting as spectators during reaction which obstruct surface lattice oxygen migration.^{1,6,9}

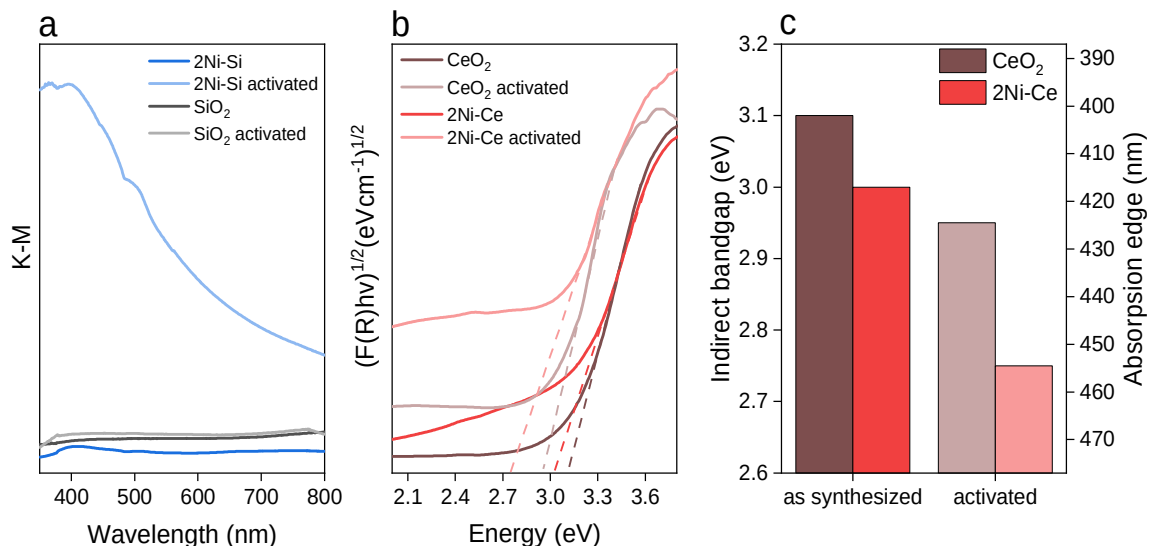
Both, continuous loss of nickel active sites and accumulation of stable carbonates, determined by *in-situ* DRIFT measurements, jointly contribute to 2Ni-Ce catalyst deactivation during light-assisted DRM reaction regardless of carbon absence due to visible light illumination (Supplementary Figs. 11-12).



Supplementary Figure 12. DRIFTS analysis at different times on stream for identification of catalyst deactivation origins. (a) DRIFT spectra of CO chemisorption at 200 °C on 2Ni-Ce sample in the presence of 10% CO/Ar and (b) DRIFT spectra of carbonates at different DRM reaction time under visible light-assisted conditions at 500 °C.

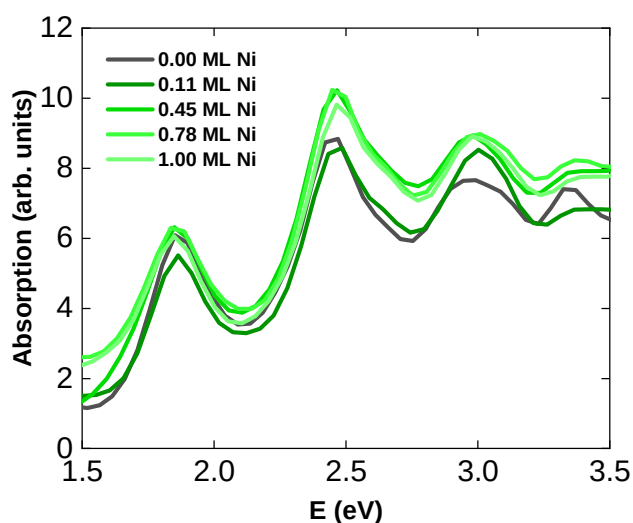
In-situ UV-Vis DRS measurements

Activation of the 2Ni-Ce catalyst was performed in a 5 % H₂/N₂ flow at 500 °C, followed by isothermal dwell for 30 minutes. Sample was analyzed at 400 °C to mimic the catalyst's working state during the reaction. For comparison purposes and to analyze the effect of activation, as synthesized (fully oxidized) samples were also analyzed.



Supplementary Figure 13. Indirect bandgap estimation. (a) UV-Vis spectra of 2Ni-Si catalyst and bare SiO₂ before and after activation. (b) Tauc plot analysis of optical bandgap energies for 2Ni-Ce and CeO₂ samples. (c) Bandgap values for the bare CeO₂ and 2Ni-Ce catalyst before and after activation.

Bandgap reduction after activation, compared to the as-synthesized samples, originates from partial filling of the 4f orbital upon Ce⁴⁺ to Ce³⁺ reduction, thus generating new energy states within the bandgap which enables light absorption in the visible part of the light spectrum (Fig. 3, UV-Vis absorbance).¹⁰ Experimentally, we also observe that nickel is essential for successful photoexcitation in the visible range and for the observed unit cell expansion. In Supplementary Fig. 14, we model the absorption profile of a CeO₂(111) slab with increasing Ni surface concentration, ranging from 0 to 1 full monolayer. The absorption of light increases as the amount of Ni increases.



Supplementary Figure 14. Absorption profiles for CeO₂(111) with varying Ni surface coverage, calculated by DFT.

Temperature Programmed Isotopic Exchange (TPIE)

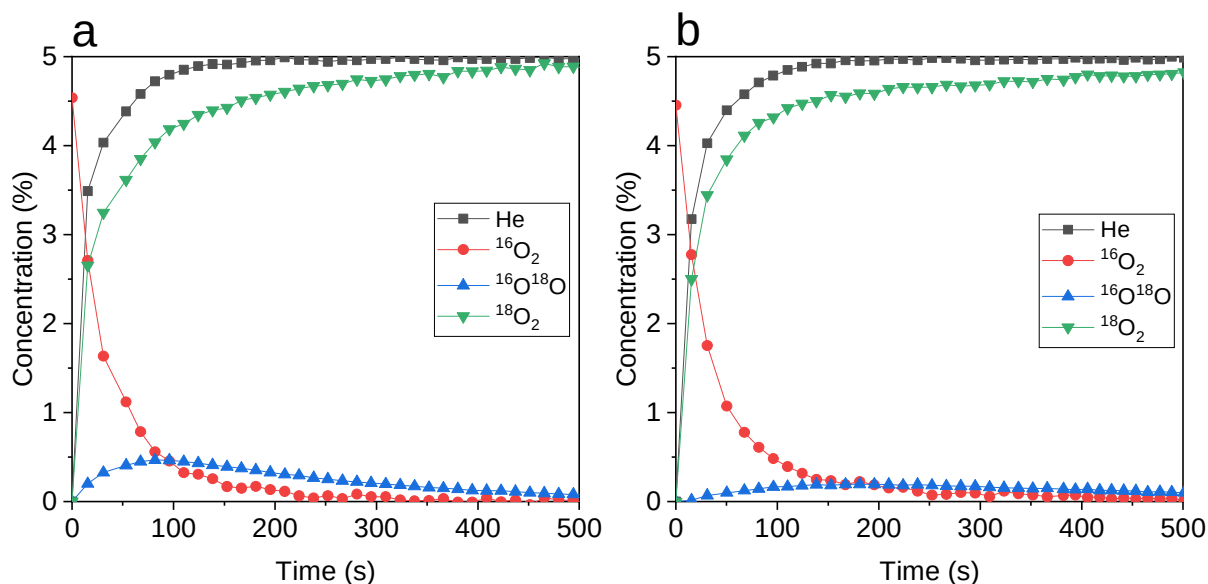
Supplementary Table 3. Total $^{18}\text{O}_2$ exchange during TPIE experiment over CeO_2 and 2Ni-Ce samples.

Sample	Thermo $^{18}\text{O}_2$ consumption (mmol/g _{cat})	Light-assisted $^{18}\text{O}_2$ consumption (mmol/g _{cat})	Thermo Total fraction of $^{18}\text{O}_2$ exchange (%)	Light-assisted Total fraction of $^{18}\text{O}_2$ exchange (%)
CeO_2	4.85	4.82	83	83
2Ni-R	4.83	5.18	83*	89*

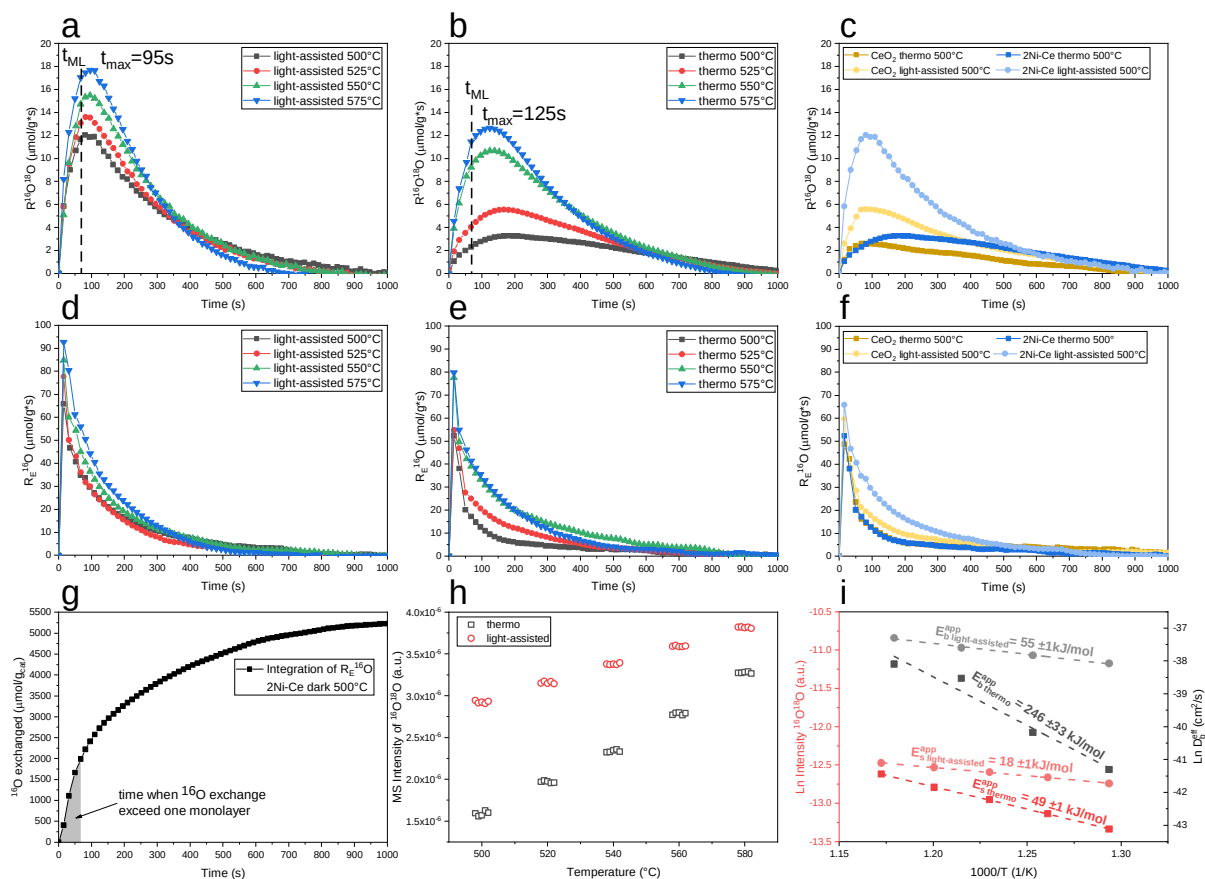
* No exchange between $^{18}\text{O}_2$ and Ni^{16}O occurs because no scrambled $^{16}\text{O}^{18}\text{O}$ was identified during temperature programmed experiment with 2Ni-Si sample (Fig. 2C in the manuscript).

Transient Isothermal Isotopic Exchange (TIIE)

The effect of visible light on the dynamics and energetics of oxygen exchange in the 2Ni-Ce catalyst was analyzed using TIIE between 500 and 575 °C (Supplementary Figs. 15-17).



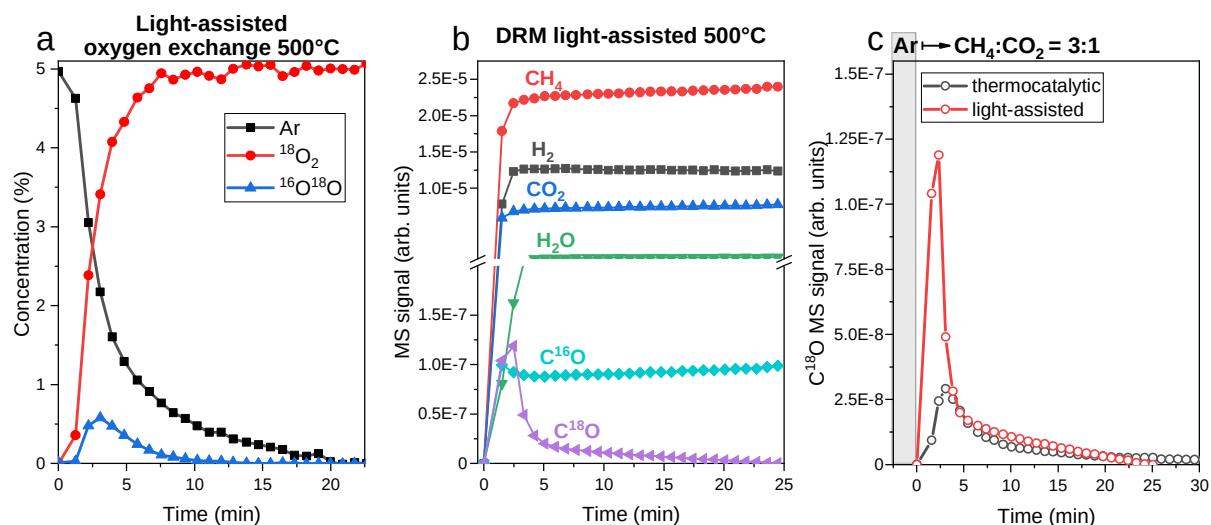
Supplementary Figure 15. Transient isothermal $^{18}\text{O}_2$ isotopic exchange experiments. Transient concentration response curves of He, $^{16}\text{O}_2$, $^{18}\text{O}_2$ and $^{16}\text{O}^{18}\text{O}$ gases during $^{18}\text{O}_2$ – TIIE experiments over 2Ni-Ce sample under light-assisted (a) and thermal (b) conditions at 525 °C.



Supplementary Figure 16. Transient $^{18}\text{O}_2$ isotopic exchange experiments at different temperatures and estimation activation energies for surface and bulk oxygen diffusion. Rate of $^{16}\text{O}^{18}\text{O}$ production ($\mu\text{mol/g}\cdot\text{s}$) during TIIE experiment over 2Ni-Ce sample with (a) and without (b) illumination at temperatures between 500 and 575 $^{\circ}\text{C}$. Comparison of $^{16}\text{O}^{18}\text{O}$ production rate under thermal and light-assisted conditions between 2Ni-Ce and bare CeO_2 samples (c). Transient overall rate (R_E) of ^{16}O atoms exchange ($\mu\text{mol/g}\cdot\text{s}$) over 2Ni-Ce sample in temperature range between 500 $^{\circ}\text{C}$ and 575 $^{\circ}\text{C}$ under light-assisted (d) and thermal conditions (e). Comparison of $R_E^{16\text{O}}$ rate exchange rate between 2Ni-Ce and bare CeO_2 samples (f). Integration of $R_E^{16\text{O}}$ production rate as a function of time for 2Ni-Ce sample at 500 $^{\circ}\text{C}$ under thermal conditions (g). TIIE experiment using continuous flows of 5 % O_2/Ar and isotopically labeled 5% $^{18}\text{O}_2/\text{Ar}$ on 2Ni-Ce sample at different temperatures, under thermal and light-assisted conditions (h). Apparent activation energies for surface and bulk oxygen mobility for 2Ni-Ce sample under thermal and light-assisted conditions (i).

To elucidate the active role of structural oxygen in suppressing carbon formation and accumulation, the 2Ni-Ce catalyst containing isotopically labeled lattice oxygen (Ce^{18}O_2) was subjected to the DRM reaction at 500 $^{\circ}\text{C}$ under both thermal and light-assisted conditions. Lattice oxygen in ceria before the transient dark and illuminated DRM experiments was exchanged in an identical manner with isotopically labeled $^{18}\text{O}_2$ in the 2Ni-Ce sample by performing a TIIE oxygen exchange experiment at 500 $^{\circ}\text{C}$ under visible light illumination. The dark and illuminated DRM reaction was performed with non labelled reactants, so the origin of oxygen in the produced CO could be distinguished by monitoring the $m/z = 29$ and $m/z = 30$ signals using mass spectrometry. The $m/z = 30$ signal corresponds to C^{18}O formed through the participation of labeled lattice oxygen from ceria, whereas the $m/z = 29$ signal represents CO containing oxygen originating from the continuously supplied CO_2 . The most intense C^{16}O signal at $m/z = 28$ was omitted because of strong contribution from C^{16}O_2 fragmentation and thus

not reliable quantification. Notably, under light-assisted DRM conditions, the formation of $C^{18}O$ was both faster and more pronounced than under purely thermal conditions, demonstrating enhanced participation of lattice oxygen in carbon containing product (CO).



Supplementary Figure 17. Experimental verification of lattice oxygen participation in DRM reaction. (a) Isothermal exchange of lattice ^{16}O in 2Ni-Ce catalyst with $^{18}O_2$ oxygen under light-assisted conditions at 500 °C prior to catalytic reaction. (b) Transient formation of isotopically labeled $C^{18}O$ during light-assisted DRM reaction using 2Ni-Ce containing isotopically labelled lattice ^{18}O . (c) Comparison of transient $C^{18}O$ evolution (m/z= 30) during DRM reaction at 500 °C under dark and light-assisted conditions at 500 °C.

Rate of oxygen exchange

The transient rate of $^{16}\text{O}^{18}\text{O}$ evolution during isothermal step change 5% $^{16}\text{O}_2/\text{Ar} \rightarrow 5\% ^{18}\text{O}_2/\text{He}$ of isotopically labeled oxygen exchange conducted in a continuous flow reactor was estimated by following relationship:

$$R_{^{16}\text{O}^{18}\text{O}} (\mu\text{mol}^{16}\text{O}^{18}\text{O} * \text{g}^{-1} * \text{s}^{-1}) = \frac{F_T}{W} * y_{^{16}\text{O}^{18}\text{O}} (t) \quad (10)$$

$y_{^{16}\text{O}^{18}\text{O}} (t)$ is the mole fraction of $^{16}\text{O}^{18}\text{O}$ at a given time t of the transient experiment, F_T is the total molar flow rate ($\mu\text{mol} * \text{s}^{-1}$) at the outlet of the reactor and W is the mass of the sample used.

Similar to $R_{^{16}\text{O}^{18}\text{O}}$ rate the transient rate of $^{16}\text{O}_2$ gas formation was estimated base on following relationship:

$$R_{^{16}\text{O}_2} (\mu\text{mol}^{16}\text{O}_2 * \text{g}^{-1} * \text{s}^{-1}) = \frac{F_T}{W} * y_{^{16}\text{O}_2} (t) \quad (11)$$

The estimation of overall rate of ^{16}O atoms exchange from the solid material (R_E) base on following relationship:

$$R_E (\mu\text{mol}^{16}\text{O} * \text{g}^{-1} * \text{s}^{-1}) = 2R_{^{16}\text{O}_2} + R_{^{16}\text{O}^{18}\text{O}} \quad (12)$$

The highest rate of $^{16}\text{O}^{18}\text{O}$ evolution under light-assisted conditions ($12 \mu\text{mol}/\text{g}_{\text{cat}} * \text{s}$) was four-fold higher compared to thermal conditions at a constant catalyst temperature of 500°C ($3 \mu\text{mol}/\text{g}_{\text{cat}} * \text{s}$). Also, the occurrence of maximum $^{16}\text{O}^{18}\text{O}$ rates shifted to shorter time $t_{\text{max}} \approx 95 \text{ s}$ under light-assisted compared to thermal conditions $t_{\text{max}} \approx 125 \text{ s}$, respectively. Higher $^{16}\text{O}^{18}\text{O}$ rates and shorter time clearly signify that illumination accelerates surface oxygen exchange and bulk oxygen diffusion compared to purely thermal conditions.¹¹

Same observation was noticed on bare CeO_2 when comparing thermal and light-assisted conditions. Regardless of the temperature, in both cases when 2Ni-Ce or bare CeO_2 are illuminated with visible light, the initial rates of $^{16}\text{O}^{18}\text{O}$ production and ^{16}O atoms exchange increase (Supplementary Fig. 16A-F). This implies on higher intrinsic rate of surface $^{16}\text{O}/^{18}\text{O}$ exchange as well as subsurface ^{16}O diffusion towards the surface as the effect of visible light. However, in bare CeO_2 visible light is less effective towards accelerating lattice oxygen mobility (Supplementary Fig. 16C and 16F), signifying the effect of Ni on oxygen bonding strength and an important visible light absorbing component in the catalyst.

Equivalent number of monolayers of exchangeable oxygen N_E

After integration of the $R_{^{16}\text{O}^{18}\text{O}} (t)$ and $R_{^{16}\text{O}_2} (t)$ curve with time, the concentration of exchangeable ^{16}O atoms ($\mu\text{mol} * \text{g}_{\text{cat}}^{-1}$) in the solid material at any time during the oxygen exchange process can be estimated. Based on the amount of exchangeable ^{16}O atoms from solid ($Q^{16}\text{O}$), the equivalent number of monolayers in CeO_2 was estimated by following equation:

$$N = \frac{Q^{16}\text{O} * N_A}{\text{SSA} * \alpha} \quad (13)$$

Where N_A is Avogadro's number ($\text{atom} * \text{mol}^{-1}$), SSA is the specific surface area of the CeO_2 ($\text{m}^2 * \text{g}_{\text{cat}}^{-1}$) and α is the number density of surface oxygen atoms ($\text{atom} * \text{nm}^{-2}$) of the solid. The average number density of surface oxygen atoms in CeO_2 , considering an equal distribution of (100), (110) and (111) faces is estimated between 13.1 and 14.4.¹² During TPIE and TIIE experiment, the amount of structural

^{16}O atoms exchanged can be calculated as a function of time. Moreover, by knowing the temperature ramp during TPIE the exact temperature at which first monolayer ($N = 1$) of structural oxygen atoms (surface oxygen) is exchanged can be determined. Similar analogy goes with TIE experiment where exact time of first structural oxygen monolayer exchange can be estimated at specific temperature (Supplementary Fig. 16G).

Apparent activation energies for surface and bulk oxygen exchange

For estimating the apparent activation energy of surface oxygen exchange (E_s^{app}) we performed TIE experiment using simultaneously same continuous flows of 5% $^{16}\text{O}_2/\text{Ar}$ and isotopically labeled 5 % $^{18}\text{O}_2/\text{Ar}$ at different temperatures (Supplementary Fig. 16H). Through $^{16}\text{O}^{18}\text{O}$ gas production intensities using Arrhenius relationship as a function of temperature ($\ln^{16}\text{O}^{18}\text{O}$ Intensity versus $1/T$),¹³ E_s^{app} under thermal and light-assisted conditions for 2Ni-Ce were estimated (Supplementary Fig. 16I).

According to Peil *et al.* the effective diffusion coefficient (D_b^{eff}) for oxygen diffusion within the subsurface and bulk of the solid can be determined using the pseudo-steady state of $^{16}\text{O}^{18}\text{O}$ production rate at time equal to $t_{s.s.}$ ¹⁴ following the relationship:

$$D_b^{\text{eff}} = \pi t_{s.s.} \left(\frac{N_\alpha}{C_{\alpha 0}} \right)^2 \quad (14)$$

Where $C_{\alpha 0}$ is the initial concentration of structural atomic oxygen in the bulk of the solid material and N_α is the flux ($\text{mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$) of atomic oxygen from bulk to the surface given by:

$$N_\alpha = \frac{F_T}{W_{\text{SSA}}} * Y_{^{16}\text{O}^{18}\text{O}}(t_{s.s.}) \quad (15)$$

Due to the experimental uncertainty in $t_{s.s.}$, accurately determining D_b^{eff} was not possible. However, the apparent activation energies for bulk lattice oxygen diffusion (E_b^{app}) were estimated based on time (t_{ML}) when exchanged structural oxygen first exceeded amount of one monolayer. The mentioned t_{ML} was determined by integration of $R_E^{16}\text{O}$ production rate as a function of time (Supplementary Fig. 16G). Via $^{18}\text{O}^{16}\text{O}$ production rate at t_{ML} using Arrhenius relationship as a function of temperature ($\ln D_b^{\text{eff}}$ versus $1/T$),¹⁵ the E_b^{app} for 2Ni-Ce under thermal and light-assisted conditions were estimated (Supplementary Fig. 16I).

By considering the $^{16}\text{O}^{18}\text{O}$ rates directly after first oxygen monolayer exchange at TIE experiment $t_{\text{ML}} \approx 68$ s (Supplementary Fig. 16A-B and 16G), the apparent activation energy of bulk oxygen diffusivity (E_b^{app}) were estimated.¹³ The apparent activation energies of surface oxygen exchange (E_s^{app}) were estimated from measured $^{16}\text{O}^{18}\text{O}$ rates at different temperatures in continuously oxygen exchange mode $^{16}\text{O}_2 + ^{18}\text{O}_2 \rightarrow 2^{16}\text{O}^{18}\text{O}$ (Supplementary Fig. 16H).

Supplementary Table 4. Refined average unit-cell volumes and standard deviation (SD) values obtained for 2Ni-Ce and CeO₂ materials at different temperatures in dark and under illumination. The values are graphically presented in Fig. 3A in the manuscript.

	2Ni-Ce		CeO ₂	
	Unit cell volume, Å ³	SD, Å ³	Unit cell volume, Å ³	SD, Å ³
dark RT	158.51	0.016	158.51	0.02
light	158.68	0.018	158.53	0.02
dark RT	158.49	0.017	158.5	0.02
25°C	158.47	0.017	158.49	0.015
100°C	158.53	0.019	158.5	0.018
150°C	158.54	0.021	158.52	0.02
200°C	158.58	0.023	158.57	0.021
250°C	158.66	0.025	158.63	0.021
300°C	158.80	0.025	158.77	0.032

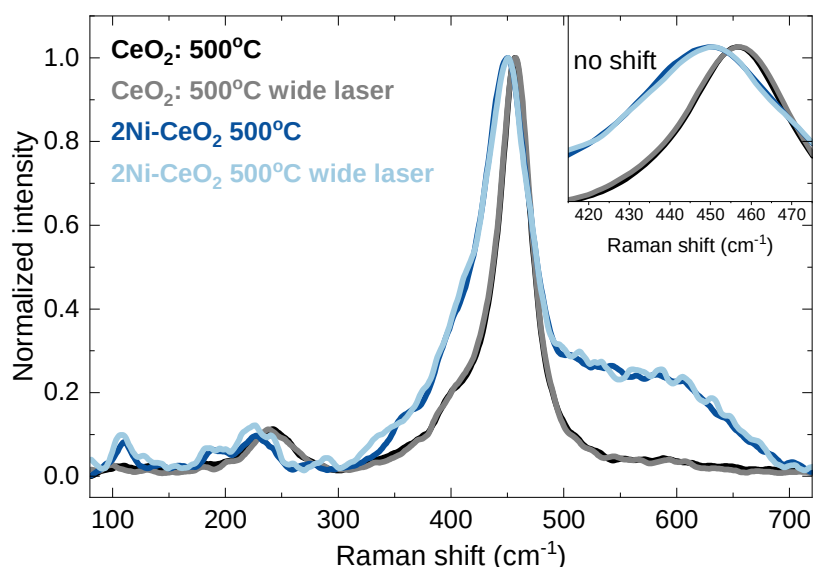
***In-situ* Raman spectroscopy**

The Raman interpretation relies on correlated spectral changes rather than single-band assignments. The F_{2g} mode of fluorite CeO₂ is sensitive to heating, strain, phonon confinement, particle size effects, local disorder, and oxygen-vacancy/Ce³⁺ formation. Similarly, the 540-560 cm⁻¹ D1 region and the approximately 590-600 cm⁻¹ LO/disorder-related region partially overlap and are not uniquely diagnostic when analyzed independently. Therefore, the spectra were evaluated by comparing bare CeO₂ and 2Ni-Ce under identical dark-heating and illumination protocols. This interpretation follows established Raman descriptions of ceria-based catalysts, where F_{2g} softening and broadening and defect-related bands reflect overlapping structural, size, strain, reduction, and oxygen-defect contributions rather than a single unique origin.

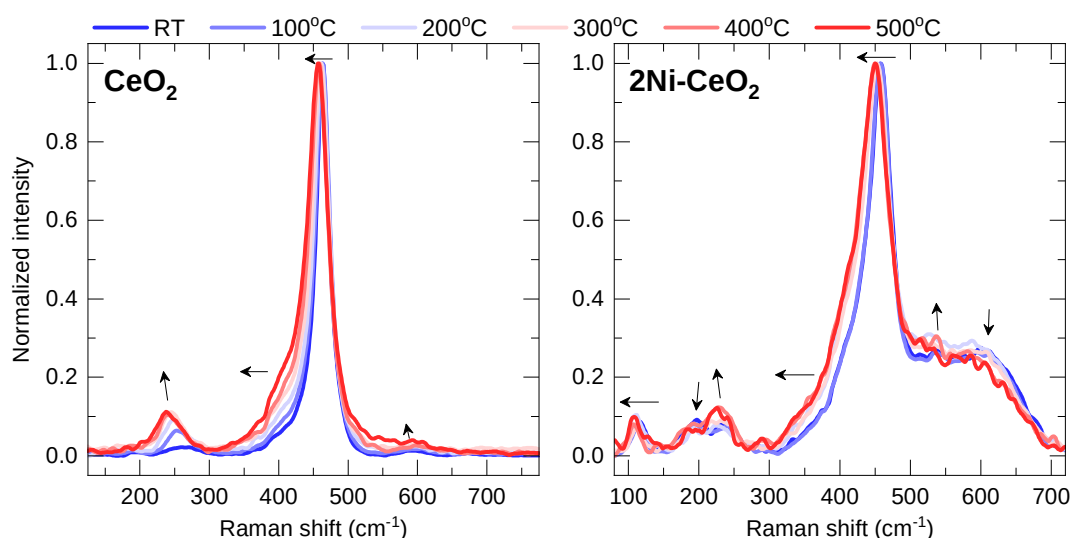
The observed F_{2g} shifts (temperature runs and illuminated at RT) exceed the spectral resolution of the Raman setup used in this work (approximately 1.9-2.5 cm⁻¹ for the 488nm laser). The relevant F_{2g} shifts are about 7 cm⁻¹ for bare CeO₂ during dark heating, ~ 12 cm⁻¹ for 2Ni-Ce during dark heating, and about ~ 5 cm⁻¹ for 2Ni-Ce under broadband illumination at room temperature. These peak-position changes are therefore considered experimentally significant.

The main Raman observations are summarized in Supplementary Table 5. The 500 °C dark/light comparison is shown in Supplementary Fig. 18, while the temperature-dependent Raman response under broadband illumination is shown in Supplementary Fig. 19. Together, these data support a continuous transition from a room-temperature light-triggered response in 2Ni-Ce to a high-temperature thermally evolved state, where additional illumination no longer produces a comparable extra F_{2g} shift or defect-band growth.

Overall, the Raman data are consistent with light-assisted lattice relaxation and defect/vacancy-related spectral evolution in Ni-decorated ceria. However, Raman spectroscopy alone does not uniquely identify a specific defect type. The assignment is based on correlated Raman trends and their agreement with reversible XRD lattice expansion, ¹⁸O₂ isotopic exchange, and TD-DFT calculations.



Supplementary Figure 18. Raman analysis of light and thermal effects on structure and defects in ceria. Raman spectra of CeO₂ and 2Ni-Ce recorded at 500 °C in dark and under broadband illumination. Spectra were collected with external broadband illumination, $\lambda = 400\text{--}600\text{ nm}$, $I = 410\text{ mW/cm}^2$. The inset highlights the F_{2g} region. Additional illumination at 500 °C does not induce a comparable extra F_{2g} shift or defect-band growth in 2Ni-Ce, indicating that the material is already close to a thermally established structural state.



Supplementary Figure 19. Raman analysis of thermal effects on structure and defects in ceria under illumination. Temperature-dependent Raman spectra of CeO₂ and 2Ni-Ce recorded under broadband illumination. Spectra were collected under broadband illumination, $\lambda = 400\text{--}600\text{ nm}$, $I = 410\text{ mW/cm}^2$, during heating from room temperature to 500 °C. Bare CeO₂ demonstrates mainly thermal F_{2g} softening, whereas 2Ni-Ce shows stronger F_{2g} softening/broadening with redistribution in the D1/LO and low-frequency regions relevant to surface oxygen defects. The data complement the dark-heating series in Fig. 3B, C of the main manuscript and support a continuous evolution of the defect/vacancy-related spectral profile from the room-temperature light-triggered response toward the high-temperature thermally evolved state.

Supplementary Table 5. Raman observations supporting a low-temperature light-driven structural response in 2Ni-Ce; assignments based on established ceria Raman literature.^{16–19}

Raman observation	Related physics
Bare CeO ₂ : F_{2g} softens from ~463 to 456 cm ⁻¹ during dark heating to 500 °C; the 500-620 cm ⁻¹ region remains weak, (Fig. 3B) .	Baseline thermal response of pristine CeO ₂ : mainly anharmonic F_{2g} softening with limited defect/disorder evolution.
2Ni-Ce: F_{2g} softens more strongly, from ~462 to 450 cm ⁻¹ , with D1/LO and 150-250 cm ⁻¹ alterations, (Fig. 3C, D) .	Ni decoration increases lattice susceptibility to strain, relaxation, and defect/disorder evolution.
Broadband illumination at room temperature: bare CeO ₂ is nearly unchanged; 2Ni-Ce shifts from ~462 to 457 cm ⁻¹ and broadens, (Fig. 3E) .	Low-temperature light response is specific to Ni-decorated CeO ₂ and is not reproduced by bare CeO ₂ .
Illuminated 2Ni-Ce: D1-side intensity at ~540-560 cm ⁻¹ increases, the LO/disorder contribution at ~590-600 cm ⁻¹ flattens, and the 150–250 cm ⁻¹ region redistributes, (Fig. 3E, G) .	Correlated defect/vacancy- and disorder-related evolution; not assigned from a single Raman band.
At 500 °C, additional broadband illumination causes no comparable extra F_{2g} shift or defect-band growth in 2Ni-Ce (Supplementary Fig. 18) .	The high-temperature state is already close to a thermally established structure.
Under broadband illumination during heating, CeO ₂ and 2Ni-Ce evolve continuously with temperature (Supplementary Fig. 19) .	The defect/vacancy-related spectral profile gradually approaches the thermally evolved high-temperature state.
Shorter-wavelength illumination gives stronger F_{2g} softening/broadening and stronger ca. 540–560 cm ⁻¹ response, (Fig. 3F, G) .	Wavelength-dependent Ni-ceria photoresponse; also consistent with stronger absorption/photothermal contribution at shorter wavelengths.

Supplementary References

1. Lorber, K. *et al.* CO₂ Activation over Nanoshaped CeO₂ Decorated with Nickel for Low-Temperature Methane Dry Reforming. *ACS Appl. Mater. Interfaces* **14**, 31862–31878 (2022).
2. Zhang, F. *et al.* Effects of Zr Doping into Ceria for the Dry Reforming of Methane over Ni/CeZrO₂ Catalysts: In Situ Studies with XRD, XAFS, and AP-XPS. *ACS Catal.* **10**, 3274–3284 (2020).
3. Djinić, P., Osojnik Črnivec, I. G., Erjavec, B., Pintar, A. Influence of active metal loading and oxygen mobility on coke-free dry reforming of Ni–Co bimetallic catalysts. *Appl. Catal. B Environ.* **125**, 259–270 (2012).
4. Afzal, S. *et al.* Controlling the rate of change of Ni dispersion in commercial catalyst by ALD overcoat during dry reforming of methane. *Int. J. Hydrogen Energy* **45**, 12835–12848 (2020).
5. Bartholomew, C. H. & Farrauto, R. J. *Fundamentals of Industrial Catalytic Processes*. (Wiley, 2005). doi:10.1002/9780471730071.
6. Lorber, K. *et al.* Non-oxidative calcination enhances the methane dry reforming performance of Ni/CeO_{2-x} catalysts under thermal and photo-thermal conditions. *J. Mater. Chem. A* **12**, 19910–19923 (2024).
7. Németh, M., Somodi, F. & Horváth, A. Interaction between CO and a Coke-Resistant NiIn/SiO₂ Methane Dry Reforming Catalyst: A DRIFTS and CO Pulse Study. *J. Phys. Chem. C* **123**, 27509–27518 (2019).
8. Paredes-Nunez, A., Jbir, I., Bianchi, D. & Meunier, F. C. Spectrum baseline artefacts and correction of gas-phase species signal during diffuse reflectance FT-IR analyses of catalysts at variable temperatures. *Appl. Catal. A Gen.* **495**, 17–22 (2015).
9. Vayssilov, G. N., Mihaylov, M., Petkov, P. St., Hadjiivanov, K.I., Neyman, K. M. Reassignment of the Vibrational Spectra of Carbonates, Formates, and Related Surface Species on Ceria: A Combined Density Functional and Infrared Spectroscopy Investigation. *J. Phys. Chem. C* **115**, 23435–23454 (2011).
10. Lorber, K. *et al.* On the mechanism of visible-light accelerated methane dry reforming reaction over Ni/CeO_{2-x} catalysts. *Appl. Catal. B Environ.* **301**, 120745 (2022).
11. Vasiliades, M.A., Harris, D., Stephenson, H., Boghosian, S., Efstathiou, A.M. A Novel Analysis of Transient Isothermal ¹⁸O Isotopic Exchange on Commercial CexZr_{1-x}O₂-Based OSC Materials. *Top. Catal.* **62**, 219–226 (2019).
12. Madier, Y., Descorme, C., Le Govic, A.M., Duprez, D. Oxygen Mobility in CeO₂ and CexZr_(1-x)O₂ Compounds: Study by CO Transient Oxidation and ¹⁸O/¹⁶O Isotopic Exchange. *J. Phys. Chem. B* **103**, 10999–11006 (1999).
13. Christou, S.Y., Bradshaw, H., Butler, C., Darab, J., Efstathiou, A.M. Effect of Thermal Aging on the Transient Kinetics of Oxygen Storage and Release of Commercial CexZr_{1-x}O_{2-x} based Solids. *Top. Catal.* **52**, 2013–2018 (2009).
14. Peil, K. Surface phenomena during the oxidative coupling of methane over Li/MgO. *J. Catal.* **131**, 143–155 (1991).
15. Vasiliades, M.A. *et al.* Deciphering the role of nano-CeO₂ morphology on the dry reforming of methane over Ni/CeO₂ using transient and isotopic techniques. *Appl. Catal. B Environ. Energy* **350**, 123906 (2024).
16. Loridant, S. Raman spectroscopy as a powerful tool to characterize ceria-based catalysts. *Catal. Today* **373**, 98–111 (2021).
17. Xu, Y. *et al.* Resolving a Decade-Long Question of Oxygen Defects in Raman Spectra of Ceria-Based Catalysts at Atomic Level. *J. Phys. Chem. C* **123**, 18889–18894 (2019).
18. Taniguchi, T. *et al.* Identifying Defects in Ceria-Based Nanocrystals by UV Resonance Raman Spectroscopy. *J. Phys. Chem. C* **113**, 19789–19793 (2009).
19. Schmitt, R. *et al.* A review of defect structure and chemistry in ceria and its solid solutions. *Chem. Soc. Rev.* **49**, 554–592 (2020).