

Supporting Information

A novel strategy of dramatically improving catalytic performance for light-driven thermocatalytic CO₂ reduction with CH₄ on Ru/MgO: CO₂ molecular fencing effect promoted by photoactivation

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Experimental

1. Characterization

XRD patterns of the samples of Ru/MgO and Ru/SiO₂ were obtained on a RigakuDmax X-ray diffractometer. The composition of the samples was determined on an inductively coupled plasma/optical emission spectroscopy (ICP-OES, Optima 4300DV, PerkinElmer). TEM images and High-angle annular dark-field images were obtained on a JEM-ARM200F electron microscope. XPS spectra were recorded on an X-ray photoelectron spectrometer (ESCALAB 250Xi) using Mg K α radiation. BET surface area and pore volume of the samples were measured on an ASAP2020 physisorption instrument by N₂ adsorption at -196 °C. CO₂ adsorption isotherms and CO₂ adsorption capacities of the samples were measured at 0 °C (ice water) on an ASAP2020 physisorption instrument. Thermogravimetric/mass spectrometry (TG-MS) analysis was performed on a STA449F3 thermal analyser linked with a QMS403 mass spectrometer. Fourier transform infrared (FTIR) spectra were obtained on an infrared spectrometer (Nicolet 6700). Diffuse reflectance absorption spectra were obtained on a UV3600 spectrophotometer. The Raman spectra were obtained on the LABRAN HR Evolution with excitation of light source at 532 nm.

2. Photothermocatalytic or photocatalytic tests

The photothermocatalytic or photocatalytic CO₂ reduction by CH₄ on the samples with the focused illumination from a 500 W Xe lamp was conducted on a home-made stainless steel reactor with a quartz window (*Scheme S1 for review only*).^[40, 46, 50] A gas stream of 30/30/40 vol% CH₄/CO₂/Ar, regulated by a mass flow meter (S49-31/MT), flows continuously at 90 mL min⁻¹ into the reactor containing 0.01 g of sample. The flow rate was accurately measured by soap bubble meter. To conduct the photothermocatalytic CO₂ reduction by CH₄ on samples with focused vis-IR illumination, $\lambda > 420$, 560 and 690 nm long-wave pass filter was placed in the front of the reactor quartz window. The power of the focused UV-vis-IR illumination was 5751.0 mW. The spot size of focused illumination, adjusted by a convex lens equipped on the Xe lamp, was about 10 mm. Thus, the intensity of the focused UV-vis-IR illumination was 73.2 kW m⁻² (corresponding to a solar flux concentration ratio of 73.2). The power values of the $\lambda > 420$, 560 and 690 nm focused vis-IR illumination were 4825.9, 4183.0 and 3322.7 mW, respectively. Their corresponding intensities of the focused UV-vis-IR illumination were 61.4, 53.3 and 42.3 kW m⁻², respectively. The concentration of the reactants and products was analyzed by a GC-9560 gas chromatograph (GC). The procedures of photothermocatalytic tests, the focused

illumination power measurement, the surface temperature measurement of the samples under the focused irradiation, light-to-fuel efficiency calculation, and GC analysis were detailed in the previous publications.^[40, 46, 50]

For conducting photocatalytic DRM on Ru/MgO under focused UV-vis-IR illumination, 0.01 g of the Ru/MgO sample was directly put on the stainless steel bottom of the reactor. The reactor was put in an ice-water bath to keep the photocatalytic reaction at near room temperature.

The thermodynamic maximum η_{\max} value of the reaction system is determined by the solar absorption and Carnot efficiencies according to the following equation.^[40, 46, 50]

$$\eta_{\max} = [1 - \sigma \times T_H^4 / (I_{\text{DNI}} \times C)] \times [1 - T_L / T_H]$$

Where σ is Stefan–Boltzmann constant, I_{DNI} is the direct normal solar illumination (1 kW m⁻²), C is the concentration ratio of solar flux, T_H and T_L are the high and low temperatures of the equal Carnot heat engine.

In the present case, C is equal to 73.2, upon focused UV-vis-IR illumination, the surface temperature of Ru/MgO was quickly elevated from room temperature ($T_L = 25$ °C) to an equilibrium temperature ($T_H = 490$ °C). The η_{\max} value is calculated to be 44.9%.

3. Thermocatalytic measurements

The thermocatalysis of the sample for DRM was measured under steady state in a flow fixed quartz tube reactor (with an inner diameter of 8 mm and a length of 300 mm) on a WFS-2015 online gas-phase reaction apparatus. 0.01 g of the Ru₂O₃/MgO or Ru₂O₃/SiO₂ was put in the middle of the quartz reactor supported by quartz wool. A thermocouple in close contact with the catalyst sample is placed inside the reactor to measure the reaction temperature. The reactor was placed in a tubular electrical oven to control the reaction temperature. A reducing gas of 5 vol% H₂/Ar constantly flowed at a flow rate of 30 mL min⁻¹, as controlled by a gas mass flow meter (D08-1F). The catalyst sample was heated at 10 °C min⁻¹ to 700 °C and kept for 1 h. Then the atmosphere was switched to the feed stream of 30/30/40 vol% CH₄/CO₂/Ar as balance gas, flowed at a flow rate of 90 mL min⁻¹. The reaction temperature was controlled at 490, 484 or 462 °C. Products and reactants are analyzed by gas chromatograph (GC9560).

4. Temperature programmed desorption of CO₂ (CO₂-TPD)

CO₂-TPD on the Ru/MgO or Ru/SiO₂ sample in the dark were conducted on a multifunctional adsorption apparatus (TP-5080) by using a quartz window. 0.12 g of Ru₂O₃/MgO or Ru₂O₃/SiO₂ was

heated at $10\text{ }^{\circ}\text{C min}^{-1}$ to $700\text{ }^{\circ}\text{C}$, and kept at $700\text{ }^{\circ}\text{C}$ for 30 min in a flow of 5 vol% H_2/Ar (24 mL min^{-1}) purified by a tube of deoxidant. After being cooled to room temperature, the obtained Ru/MgO or Ru/SiO₂ samples were heated to $400\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C min}^{-1}$, and kept at $400\text{ }^{\circ}\text{C}$ for 1 h in a flow of high purity helium (24 mL min^{-1} , purified by a tube of deoxidant) to remove the adsorbed H_2 . After being cooled to room temperature, the fed gas was switched to 10 vol% CO_2/He (24 mL min^{-1}) for CO_2 adsorption. After CO_2 adsorption for 0.5 h, the Ru/MgO or Ru/SiO₂ sample with pre-adsorbed CO_2 was heated at $10\text{ }^{\circ}\text{C min}^{-1}$ in a flow of high purity helium (24 mL min^{-1}) purified by a tube of deoxidant.

5. Isotope labeling

Isotope labeling experiments on the Ru/MgO or Ru/SiO₂ with concentrated UV-vis-IR illumination were conducted in a home-made quartz funnel-like reactor (with heating device) (*Supplementary Scheme 3*) which was linked via micro pump to a tubular FTIR cell placed in the chamber of an infrared spectrometer (Nicolet 6700). 0.01 g of Ru/MgO or Ru/SiO₂ was placed in the reactor. The temperature of the sample was measured by a thermocouple which was closely contacted to the sample (*Supplementary Scheme 3*). The sample was heated to $500\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C min}^{-1}$ and kept at $500\text{ }^{\circ}\text{C}$ for pre-reduction of the sample for 30 min in a flow of 5 vol% H_2/Ar (50 mL min^{-1}) purified by a tube of deoxidant. After cooling to $400\text{ }^{\circ}\text{C}$, the flow was switched to a flow of high purity argon (50 mL min^{-1} , purified by a tube of deoxidant) for removing H_2 adsorbed on the sample for 1 h at $400\text{ }^{\circ}\text{C}$. Then, the pretreated samples were cooled to ambient temperature. After sample pretreatment, argon was turned off and charged with a mixture of 10 mL C^{18}O_2 and 290 mL argon in a recirculating closed gas circuit and adsorbed for 30 min. Then switch to a high-purity argon gas stream (50 mL min^{-1} , purified by a tube of deoxidant), heat to $650\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C min}^{-1}$ and continue heating to remove free and physically adsorbed C^{18}O_2 until C^{18}O_2 is not detected by FTIR. The high-purity argon stream is turned off and the micro-pump is turned on, and a mixture of 10 mL C^{16}O_2 , 20 mL CH_4 and 270 mL argon is charged into the circulating closed gas circuit and circulated through the system. A concentrated UV-vis-IR illumination was applied to the sample surface. FTIR spectra were recorded for the gas composition in the system.

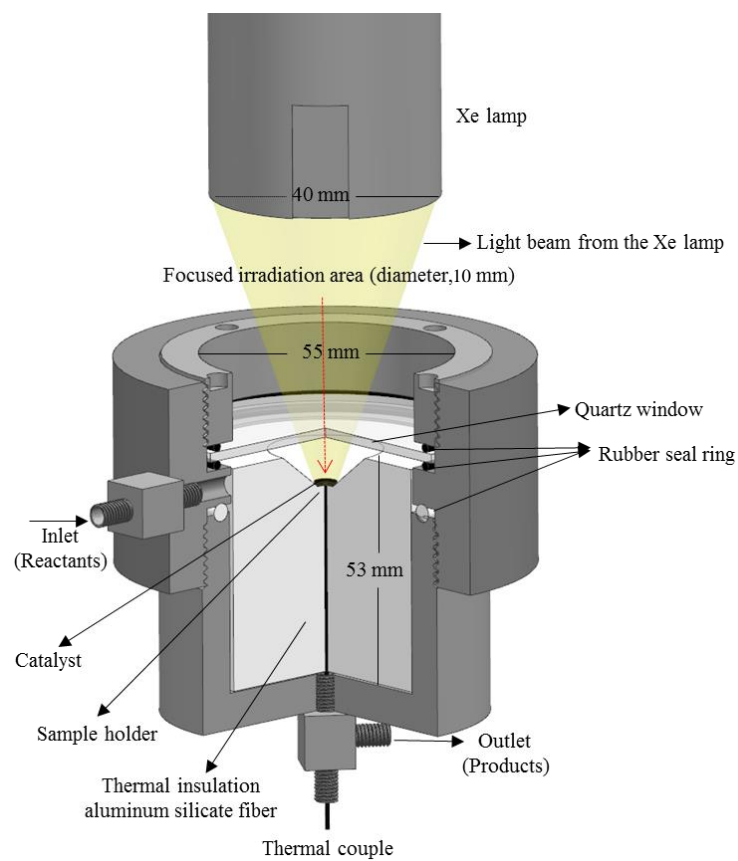
6. Controlled catalytic tests

Catalytic DRM on Ru/MgO or Ru/SiO₂ at different temperatures in the dark or under focused illumination was conducted by using a home-made quartz cylindro-conical reactor as shown in *Supplementary Scheme 3*. The temperature of Ru/MgO or Ru/SiO₂ in the reactor was controlled by a

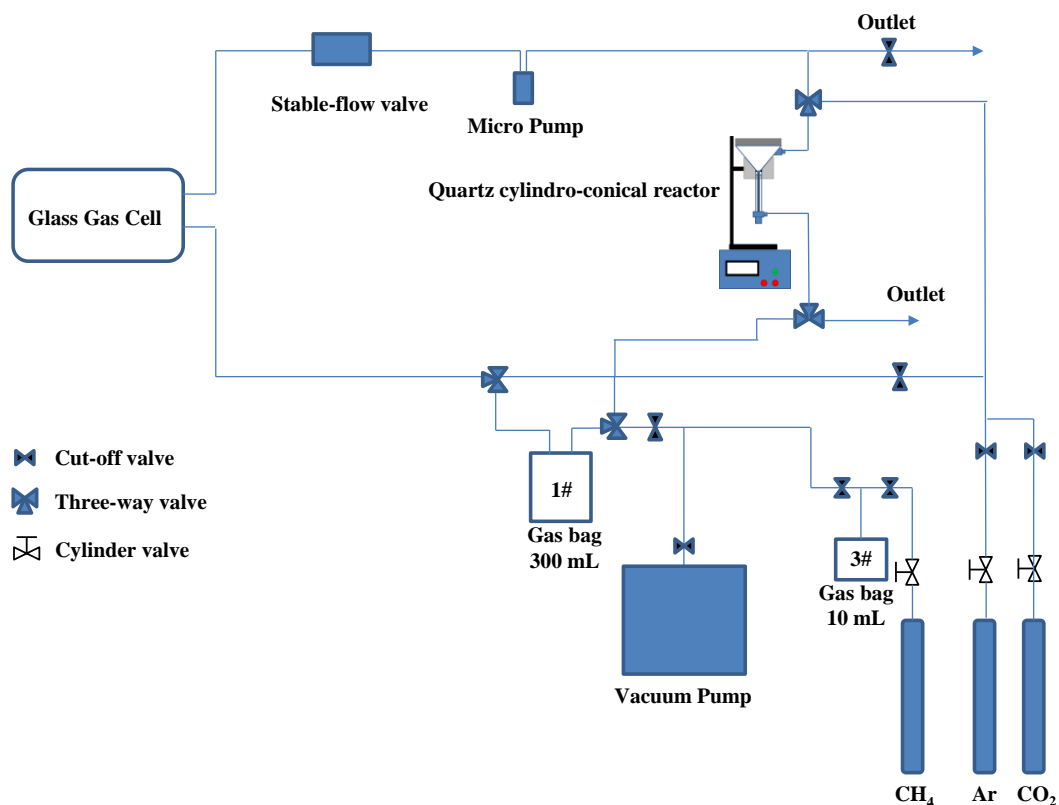
heating package. 0.007 g of Ru/MgO or Ru/SiO₂ was pre-reduced with 5 vol% H₂/Ar (30 mL min⁻¹) at 500 °C for 0.5 h. After the pre-reduction, the stream of 5 vol% H₂/Ar was switched to a stream of 10/10/80 vol% CH₄/CO₂/Ar at 50 mL min⁻¹ for catalytic DRM at the different temperatures in the dark or under focused illumination of UV-vis-IR, $\lambda > 420$ 560 and 690 nm vis-IR. The products and reactants were analyzed by gas chromatograph (GC9560).

7. CH₄ temperature programmed oxidation by pre-adsorbed CO₂ (CH₄-TPO-CO₂)

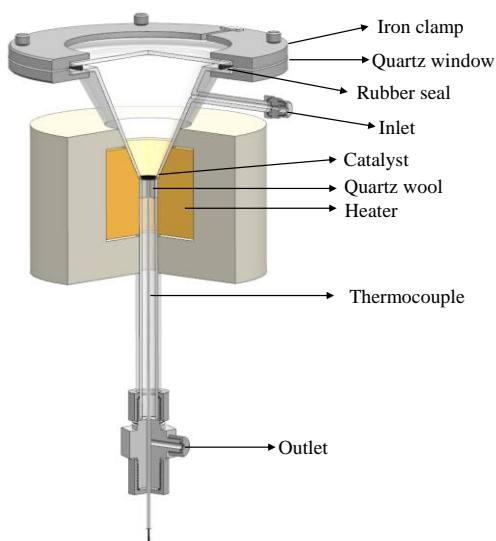
CH₄-TPO-CO₂ on the samples of Ru/MgO or Ru/SiO₂ was performed in the dark or under focused UV-vis-IR illumination using a home-made quartz cylindro-conical reactor with heating device in a circulating air circuit (*Supplementary Scheme S2 and S3 for review only*).^[46] 0.008 g of Ru/MgO or Ru/SiO₂ was heated to 500 °C at 10 °C min⁻¹ and kept at 500 °C for 30 min in reducing atmosphere of 5 vol% H₂/Ar (50 mL min⁻¹) purified by a tube of deoxidant. After being cooled to 400 °C, the 5 vol% H₂/Ar flow was switched to a flow of high purity argon (50 mL min⁻¹, purified by a tube of deoxidant) for removing H₂ adsorbed on the sample for 1 h at 400 °C. After cooled to room temperature, the flow of pure argon was switched to a flow of pure CO₂ (50 mL min⁻¹) for 30 min to adsorb CO₂. Then, the CO₂ stream was switched to a flow of high purity argon (50 mL min⁻¹, purified by a tube of deoxidant) to remove free and physically adsorbed CO₂. Finally, the samples (the samples are after pre-sorption of CO₂) were reacted in the dark or under UV-vis-IR illumination in a circulating gas stream of CH₄ mixture (20 mL CH₄ mixed with 280 mL of argon, purified by a tube of deoxidant) at a heating rate of 10 °C min⁻¹. FTIR spectra of the gas composition in the system were recorded.



Scheme S1. Schematic illustration of a home-made reactor for conducting photothermocatalytic CO₂ reduction by methane on the samples under focused illumination from a 500 W Xe lamp without using additional electric heater (*only for review*).^[40, 46, 50]



Scheme S2. Flow chart of CH₄ temperature programmed oxidation by pre-adsorbed CO₂ (*only for review*).^[46]



Scheme S3. Schematic diagram of a home-made quartz cylindro-conical reactor for catalytic DRM testing of samples at different temperatures in the dark or under focused UV-vis-IR illumination, isotope labelling experiments and CH₄ temperature programmed oxidation by pre-adsorbed CO₂ (*only for review*).^[46]

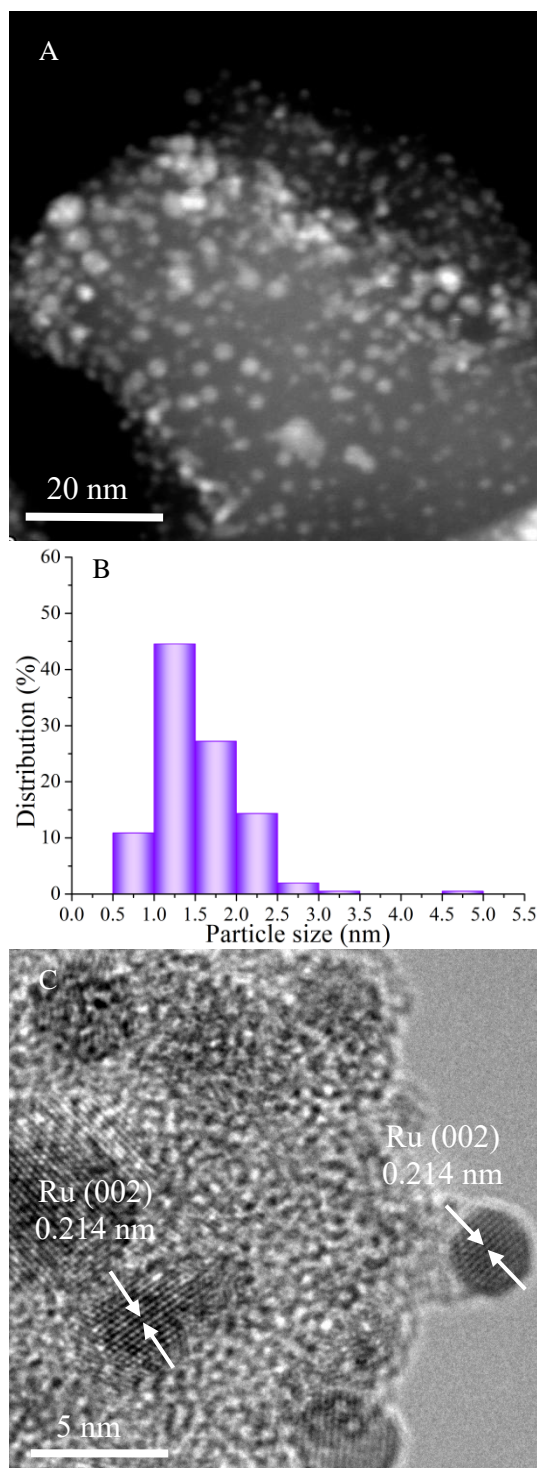


Figure S1. HAADF image (A), and size distribution of Ru NPs in Figure S1A (B), and HRTEM image (C) of Ru/SiO₂.

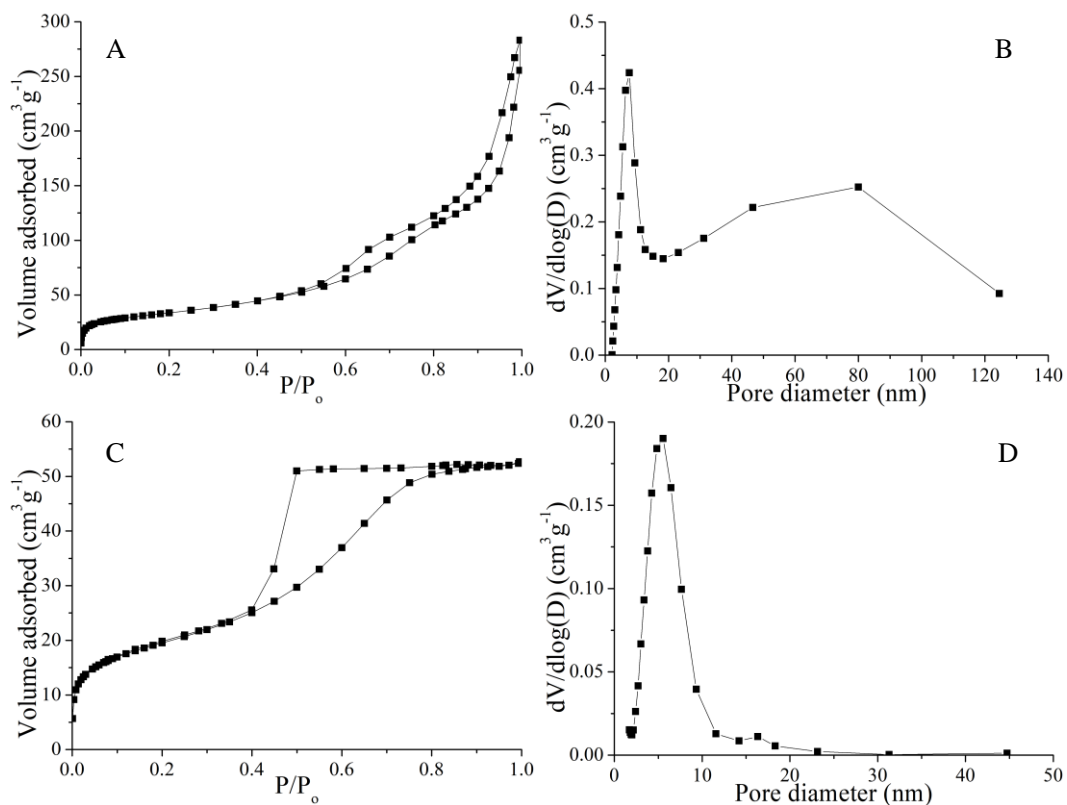


Figure S2. N₂ adsorption-desorption isotherm and BJH adsorption pore size distribution of Ru/MgO (A and B) and Ru/SiO₂ (C and D).

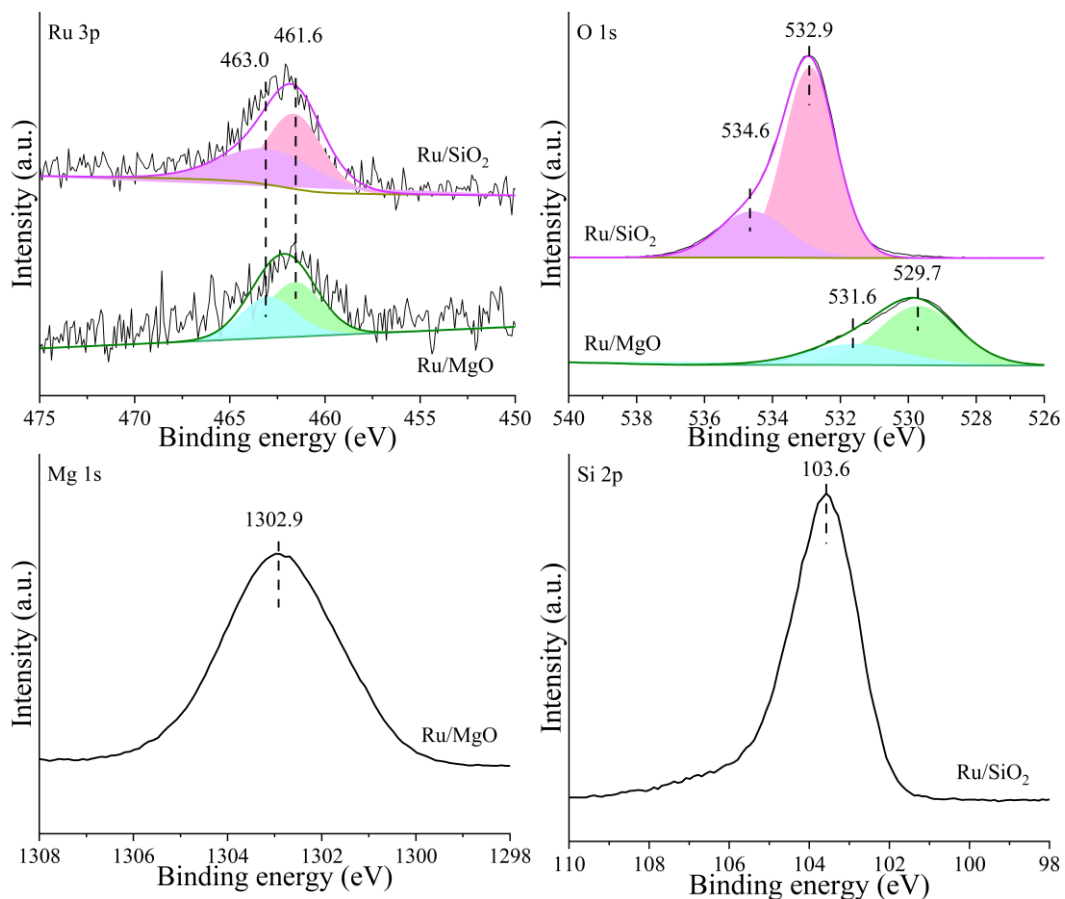


Figure S3. XPS spectra of Ru $3p_{3/2}$, O $1s$, Mg $1s$ and Si $2p_{3/2}$ for Ru/MgO and Ru/SiO₂. Mg $1s$ peak in Ru/MgO is located around 1302.9 eV, which is assigned to that of Mg²⁺ in MgO^[49] Si $2p_{3/2}$ peak in Ru/SiO₂ is located around 103.6 eV, which is assigned to that of Si⁴⁺ in SiO₂.^[49]

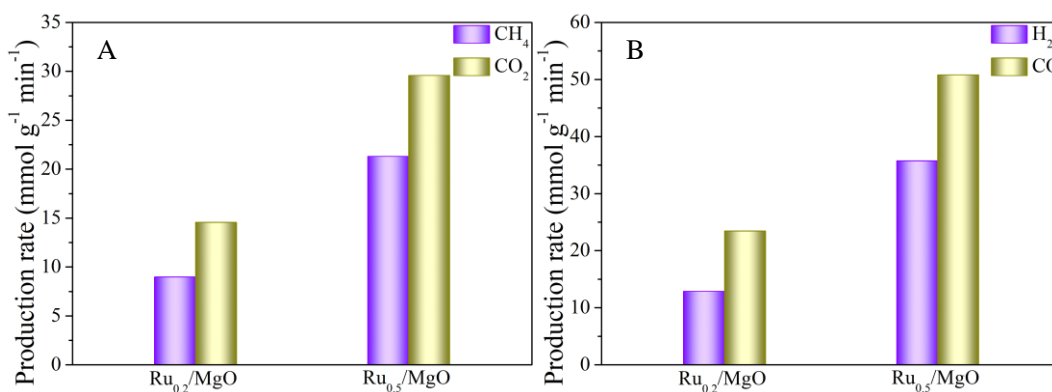


Figure S4. The r_{CH_4} and r_{CO_2} (A), r_{H_2} and r_{CO} (B) for light-driven thermocatalytic DRM on Ru_{0.5}/MgO (0.5 wt% Ru/MgO) and Ru_{0.2}/MgO (0.2 wt% Ru/MgO) under concentrated UV-vis-IR illumination.

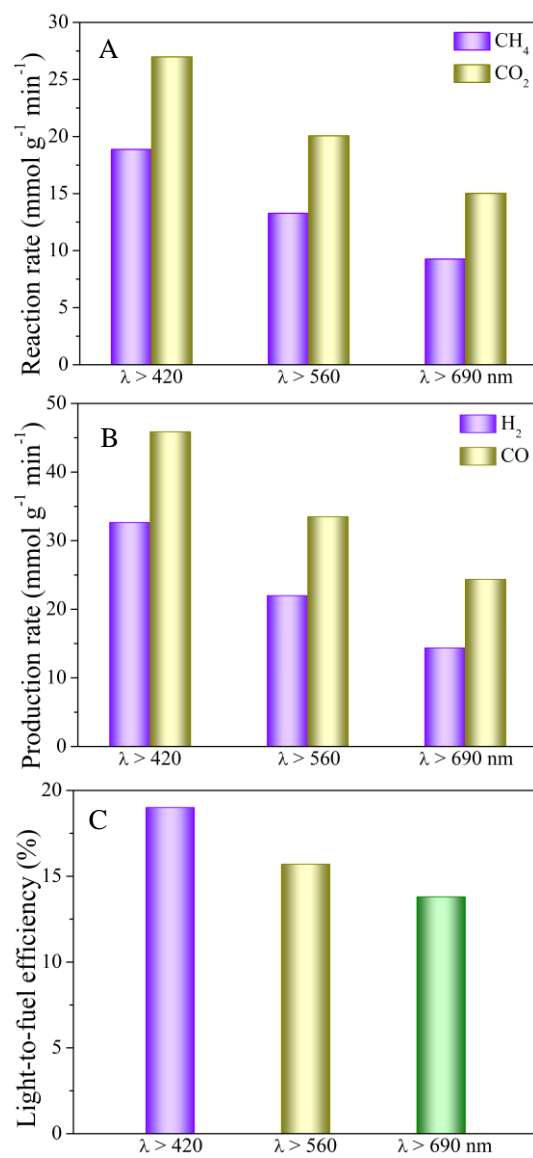


Figure S5. Reaction rates (A), production rates (B), and light-to-fuel efficiency (C) of Ru/MgO for photothermocatalytic DRM with concentrated vis-IR irradiation.

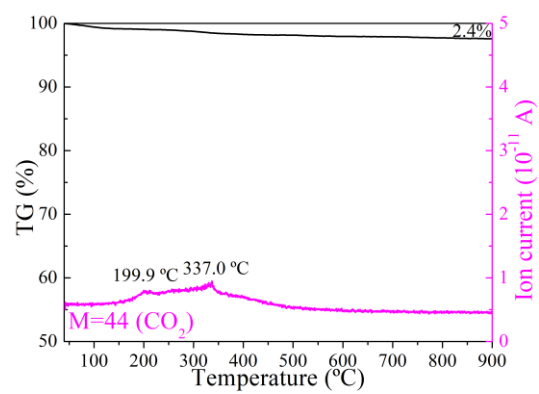


Figure S6. TG-MS profiles of the used Ru/SiO₂ catalyst after 10 hours of light-driven thermocatalytic evaluation.

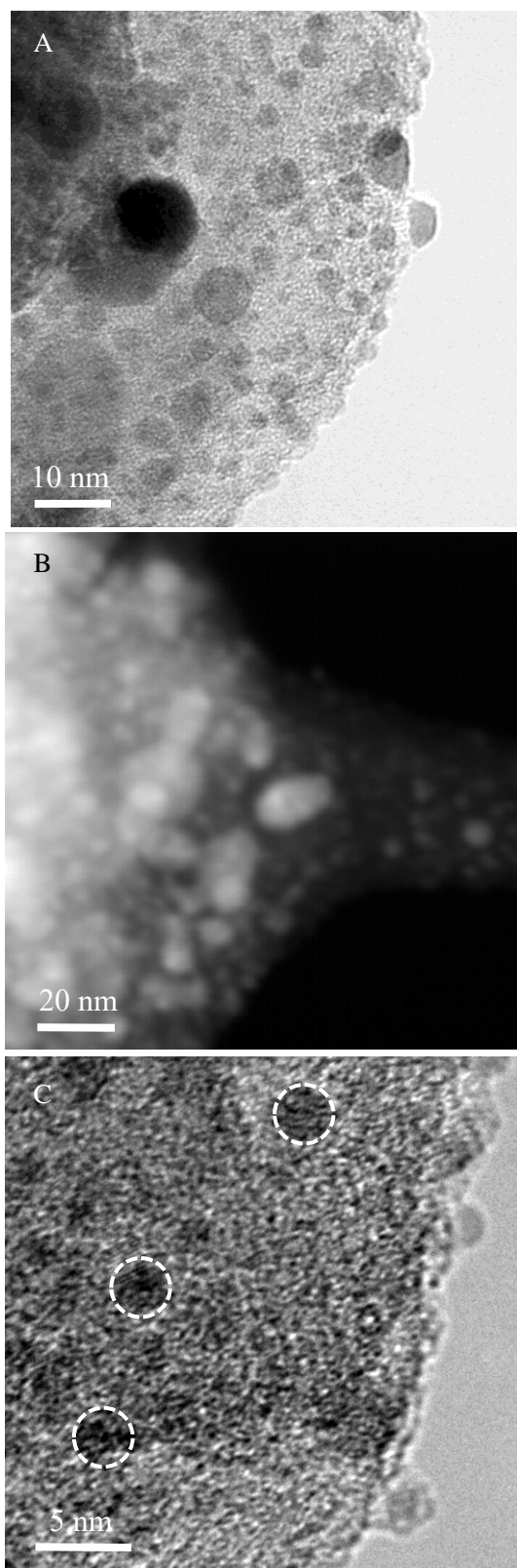


Figure S7. TEM (A), HAADF (B) and HRTEM (C) images of the used Ru/SiO₂ catalyst after 10 hours of light-driven thermocatalytic evaluation.

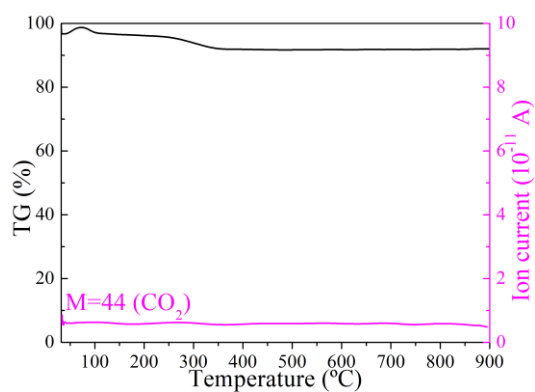


Figure S8. TG-MS profiles of the used Ru/MgO catalyst after 50 hours of light-driven thermocatalytic evaluation. The weight loss in the range of 290~350 °C is attributed to the decomposition of Mg(OH)₂ formed on the surface of MgO by the surface hydration of MgO due to the exposure of the Ru/MgO catalyst to air with humidity.

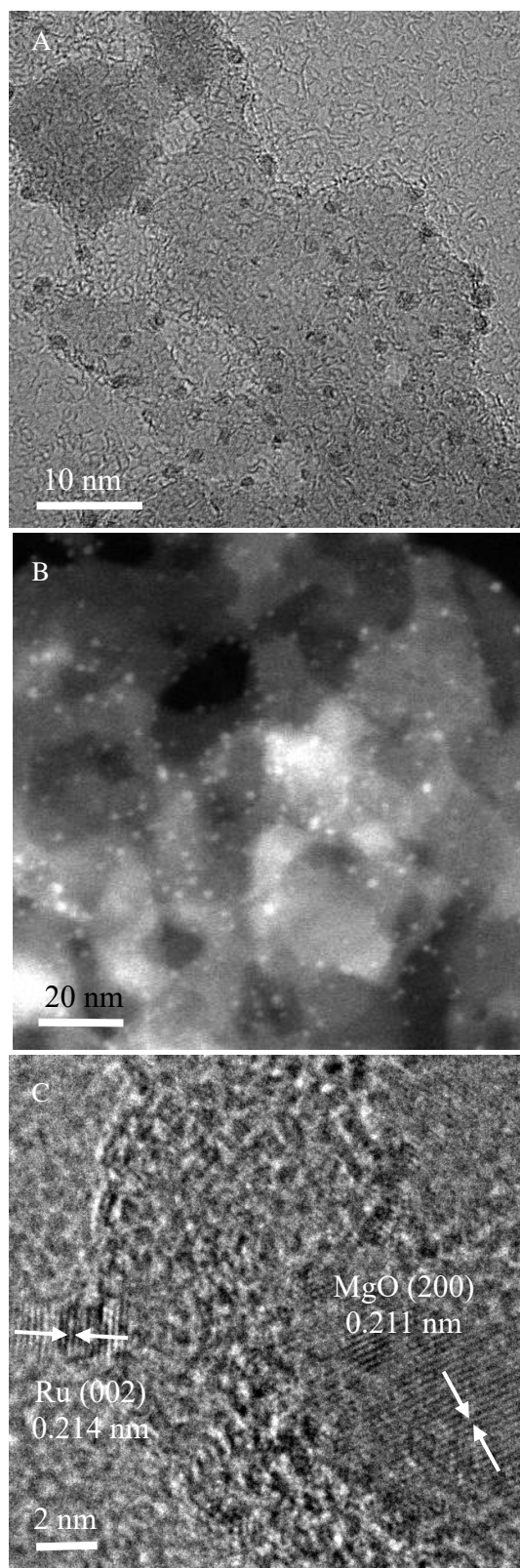


Figure S9. TEM (A), HAADF (B) and HRTEM (C) images of the used Ru/MgO catalyst after 50 hours of light-driven thermocatalytic evaluation.

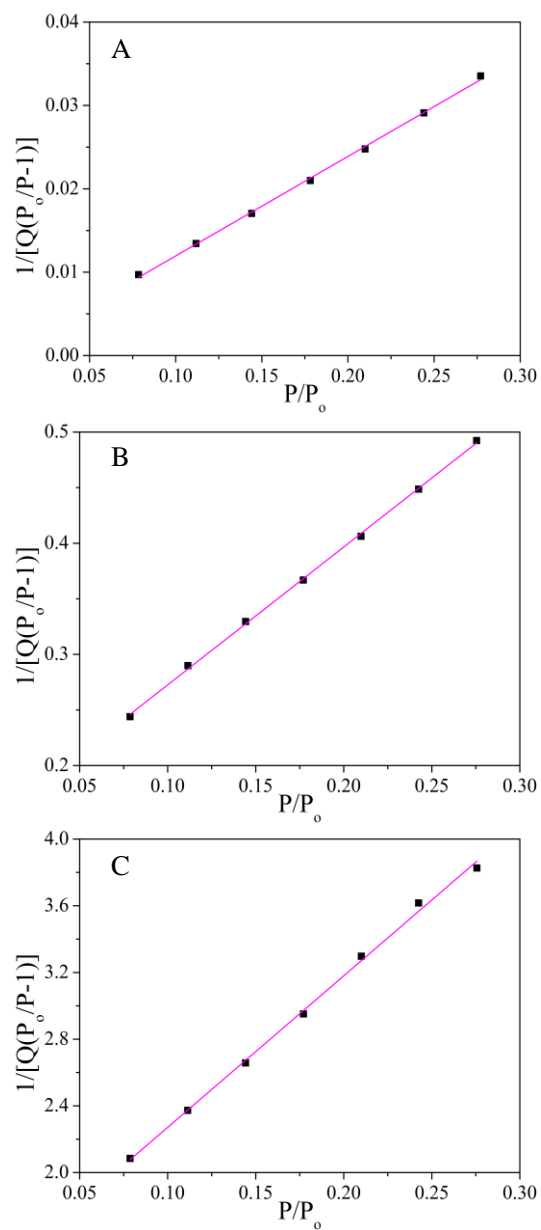


Figure S10. The profiles of P/P_0 vs $1/[Q(P_0/P-1)]$ for Ru/MgO (A), Ru/SiO₂ (B) and SiO₂ (C) based on their CO₂ adsorption isotherms at 0 °C (Figure 4).

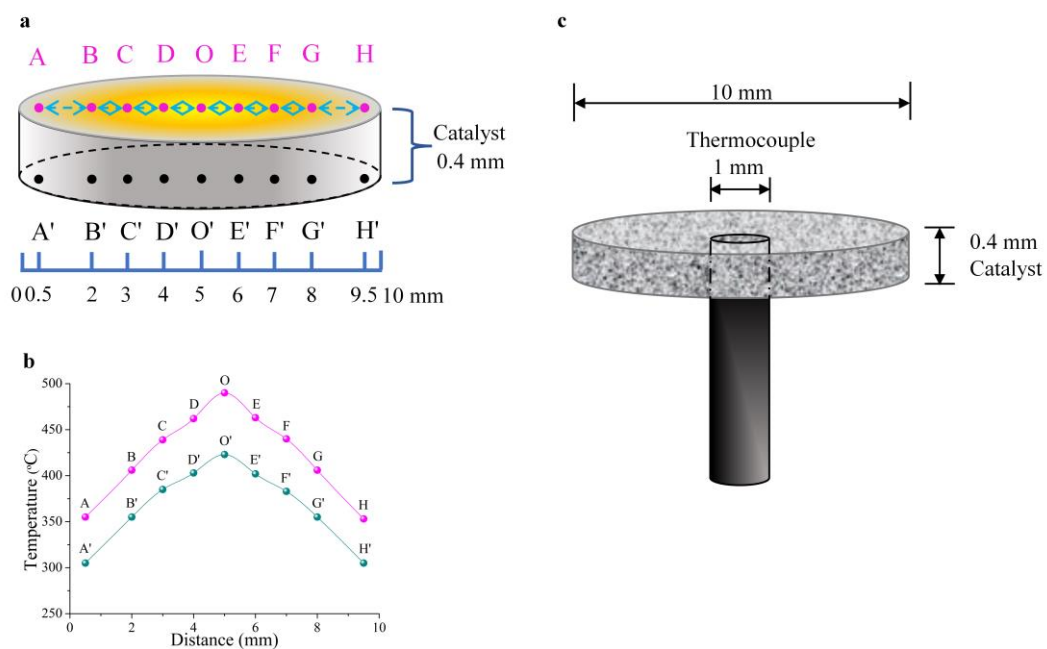


Figure S11. Schematic diagram of the temperature of each position of the sample during Ru/MgO photothermocatalytic DRM under concentrated UV-vis-IR illumination (a and b). Schematic diagram of sample thickness and thermocouple position (c).

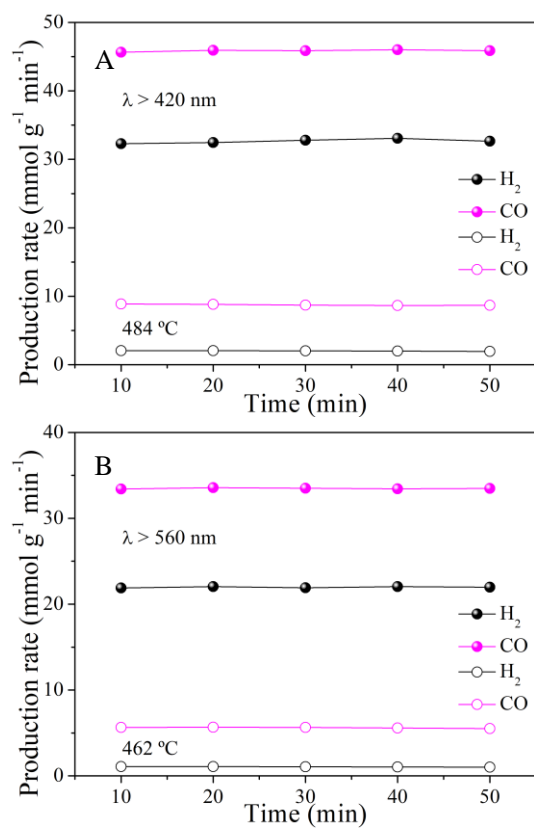


Figure S12. Time course of production rates for photothermocatalytic DRM with concentrated vis-IR illumination and thermocatalytic DRM on Ru/MgO at the temperature the same as the maximum T_{eq} of corresponding photothermocatalytic DRM: $\lambda > 420$ nm and 484 °C (A), $\lambda > 560$ nm and 462 °C (B).

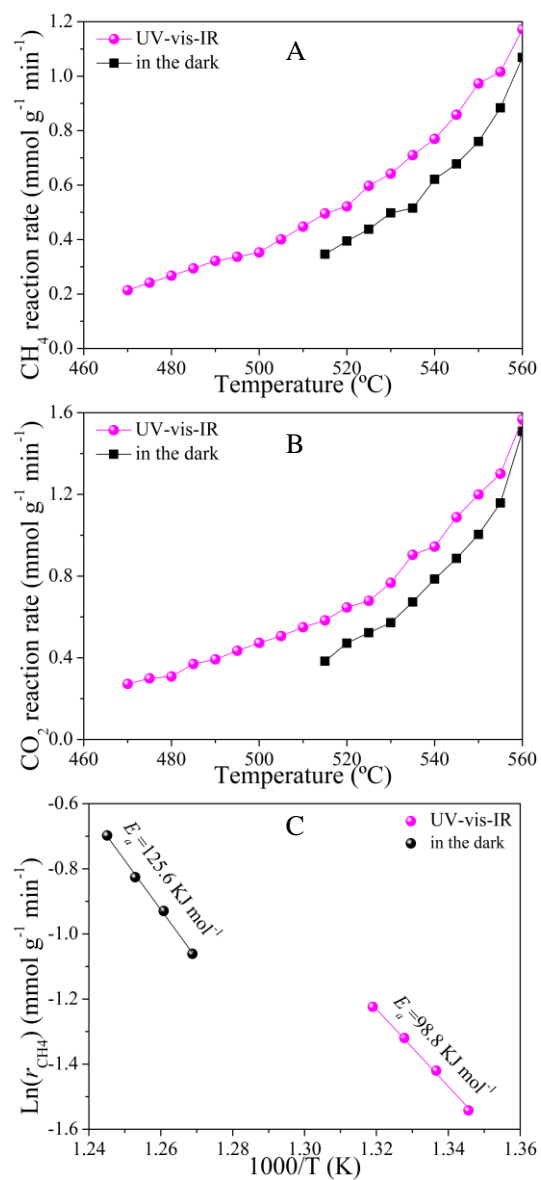


Figure S13. The values of r_{CH_4} (A) and r_{CO_2} (B) vs T , and $\ln(r_{\text{CH}_4})$ vs $1/T$ (C) for DRM on Ru/SiO₂ with concentrated UV-vis-IR illumination and in the dark.

Table S1: Comparison of light-driven catalytic DRM activity of various catalysts.

Catalyst	Feed composition	Light intensity (kW m ⁻²)	H ₂ production rate (mmol g ⁻¹ min ⁻¹)*	Light-to-fuel efficiency (%)	Reference
Ru/MgO	30/30/40 vol% CH ₄ /CO ₂ /Ar	73.2	43.51	19.4	This work
Pt/black TiO ₂	50/50 vol% CH ₄ /CO ₂	1 (heating to 650 °C)	2.15		18
		1 (heating to 550 °C)	1.18		
Cu-CNN/Pd-BDCNN	10/10/80 vol% CH ₄ /CO ₂ /Ar	3	0.01		23
Pt/TaN	50/50 vol% CH ₄ /CO ₂	4.2 (heating to 500 °C)	~1.1		24
Pt-Si-CeO ₂	10/10/80 vol% CH ₄ /CO ₂ /Ar	30 (heating to 600 °C)	1.5		26
Pt/mesoporous-TiO ₂	10/14/24 vol% CH ₄ /CO ₂ /N ₂	32.2 (heating to 500 °C)	2.98		27
Rh/SrTiO ₃	1/1/98 vol% CH ₄ /CO ₂ /Ar	0.56	~0.9	5.9	28
Rh/Ce _x WO ₃	20/20/60 vol% CH ₄ /CO ₂ /Ar	18	~0.04	~2.7	43
Pt/Al ₂ O ₃ -CeO ₂	10/10/80 vol% CH ₄ /CO ₂ /Ar	30 (heating to 700 °C)	10.95		44
Pt/La ₂ O ₃	8/8/84 vol% CH ₄ /CO ₂ /Ar	194.2	21.41	8	45
Cu _{19.8} Ru _{0.2} (single-Ru atomic catalyst)	50/50 vol% CH ₄ /CO ₂	192 ~80	33	~15 ~9	47

MgO/Pt/Zn-CeO ₂	10/10/80 vol%	30	5.93		53
	CH ₄ /CO ₂ /Ar	(heating to 600 °C)			
	10.2/10.2/79.6				
Pt/CeO ₂ -MNR	vol%	371.1	5.70	10.3	54
	CH ₄ /CO ₂ /Ar				

*: The rate of H₂ production per unit mass of catalyst.