Supplementary Materials

Preparation and Characterization of Highly Dispersed Ru/CeZrO$_2$ Catalyst for CO$_2$ Methanation with Improved Activity

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This document contains the effect of Ce/Zr ratio on the activity (Figure S1), volumetric CO chemisorption of (a) Ru/CeZrO_2-C and (b) Ru/CeZrO_2-P (Figure S2), EDX mappings of (1) Ce and (2) Zr on (a) Ru/CeZrO_2-P, (b) Ru/CeZrO_2-C, (c) Ru/CeZrO_2-P-spent, and (d) Ru/CeZrO_2-C-spent (Figure S3), EPR spectra of Ru/CeZrO_2-P and Ru/CeZrO_2-C (Figure S4), the XPS spectra of Ru 3p over Ru/CeZrO_2-P catalyst after the 100-h stability test (Figure S5), Quasi *in-situ* XPS spectra of O 1s on (a) Ru/CeZrO_2-P (b) Ru/CeZrO_2-C (Figure S6), comparison with the reported Ru catalysts for CO_2 methanation (Table S1), Quasi *in-situ* XPS results of the concentration of Ce^{3+} (%) (Table S2), assignments of the bands of *in-situ* DRIFT experiments on the catalysts (Table S3).

Supplementary Figures

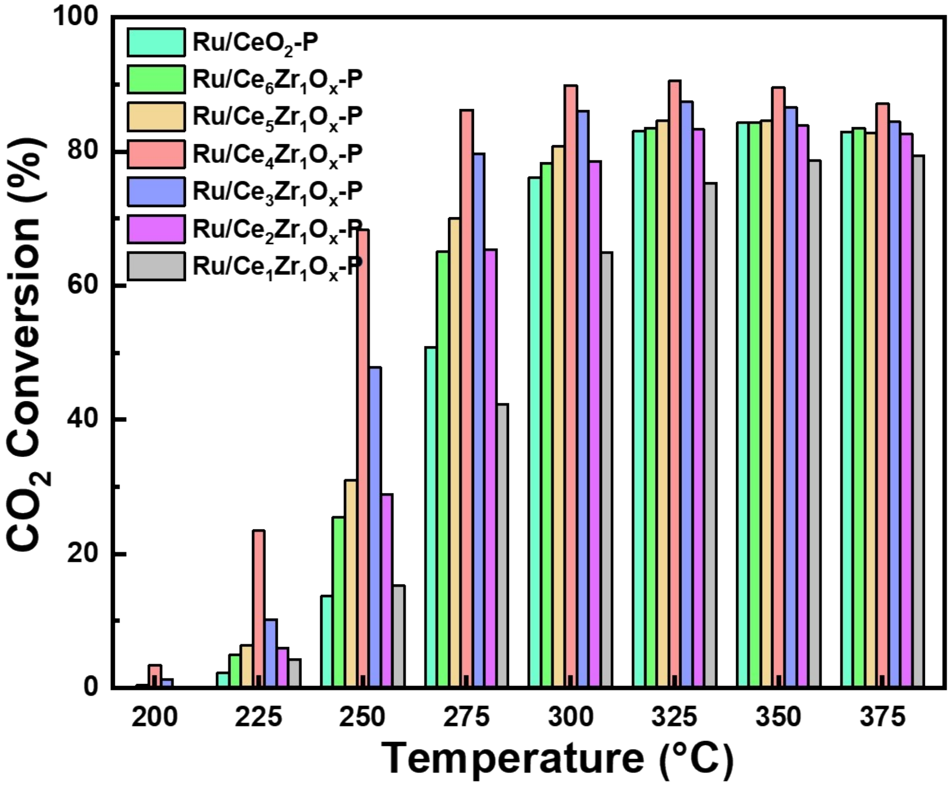

Figure S1. The effect of Ce/Zr molar ratio on CO_2 methanation activity.

The dispersion of Ru was calculated based on the volume of chemisorbed CO by using the following equation:

$$D\% = \frac{V_{\text{ad}} \times M_{\text{metal}} \times \text{SF}}{\text{p} \times V_{\text{m}} \times \text{d}_{\text{r}}}$$

where D denotes the dispersion of Ru particles; V_{ad} (ml g^{-1}) is volume of chemisorbed CO at STP; M_{metal} is the molecular weight of Ru (101.07 g mol^{-1}); *SF* is the stoichiometric factor (Ru:CO molar ratio in the chemisorption experiment) which is taken as 1; p is the weight fraction of Ru in the catalysts as determined by ICP-OES; V_m is molar volume of CO (22.4 L mol^{-1}) at standard temperature and pressure (STP); d_r is the reduction degree of Ru, determined by quasi *in-situ* XPS analysis.

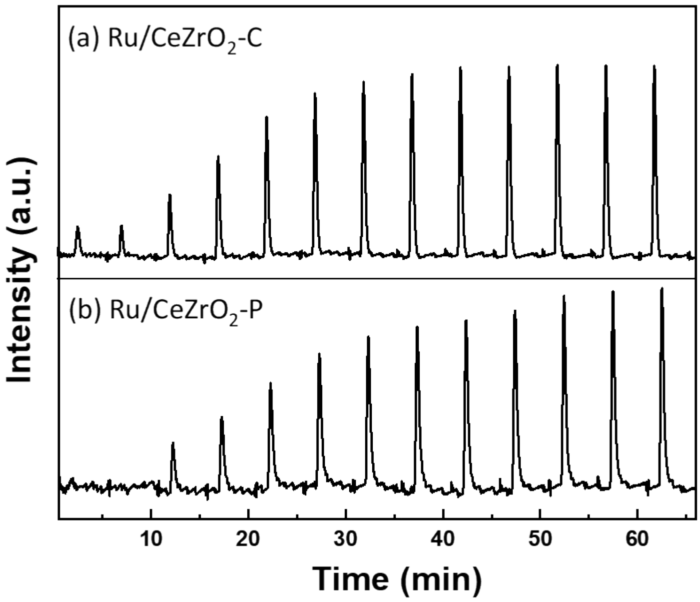

Figure S2. Volumetric CO chemisorption of (a) Ru/$CeZrO_2$-C and (b) Ru/$CeZrO_2$-P. (The number of pulses needed for Ru/$CeZrO_2$-P and Ru/$CeZrO_2$-C are approximately 13. The peak intensity rises steadily in the first pulses of the CO adsorption period until saturation, when it stabilizes at a constant level. When the peak intensity stays constant for three times, the pulse experiment shuts down automatically.)

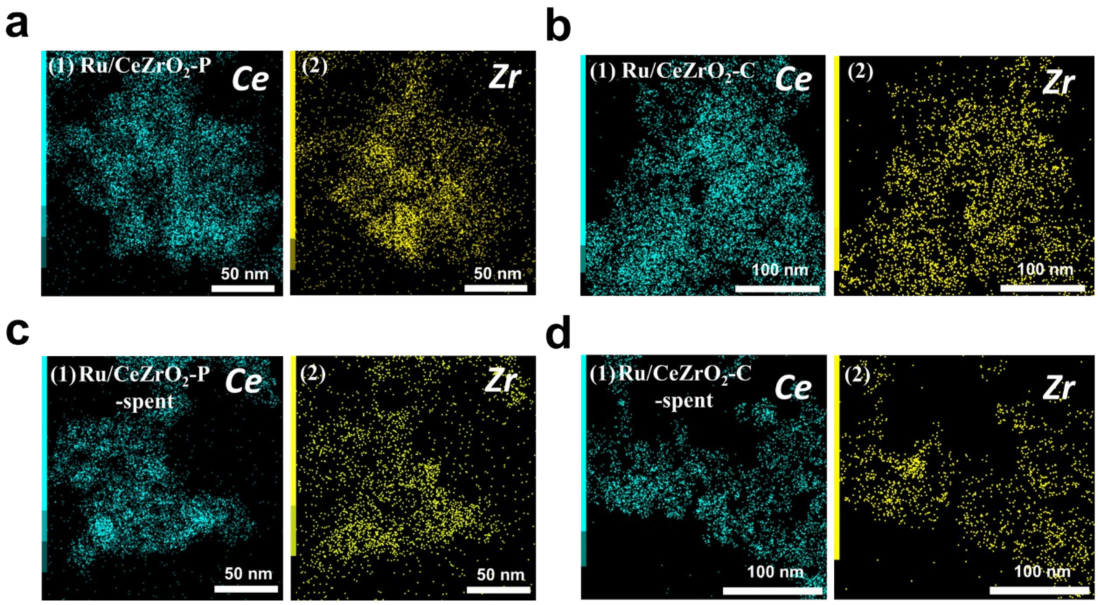

Figure S3. EDX mappings of (1) Ce and (2) Zr on (a) Ru/CeZrO_2-P, (b) Ru/CeZrO_2-C, (c) Ru/CeZrO_2-P-spent, and (d) Ru/CeZrO_2-C-spent.

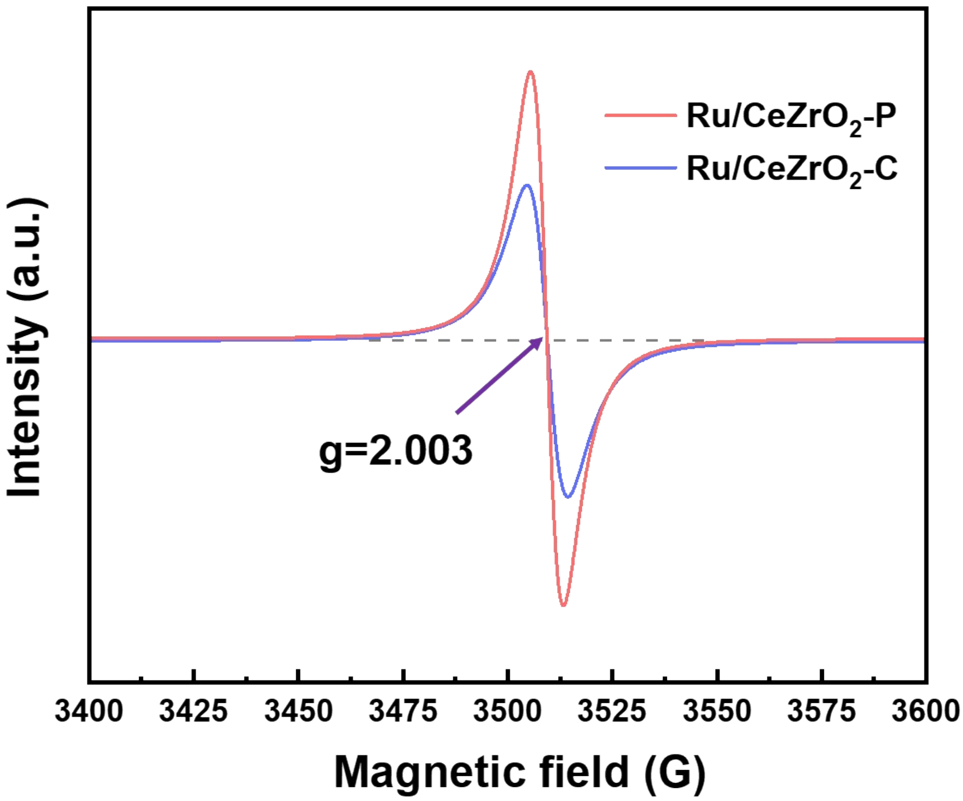

Figure S4. EPR spectra of Ru/$CeZrO_2$-P and Ru/$CeZrO_2$-C.

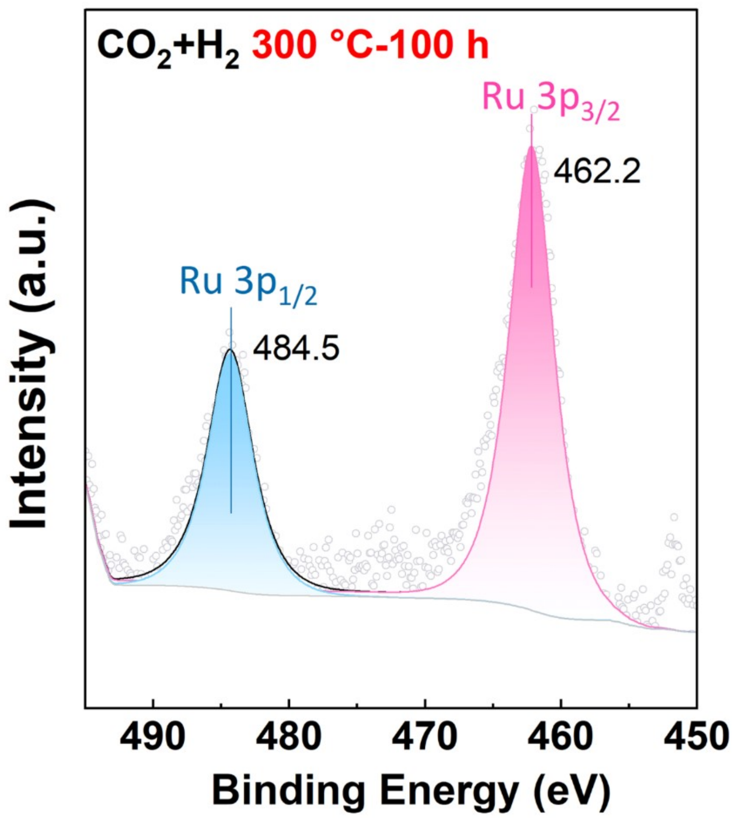

Figure S5. The XPS spectra of Ru 3p over Ru/CeZrO_2-P catalyst after 100-hr stability test.

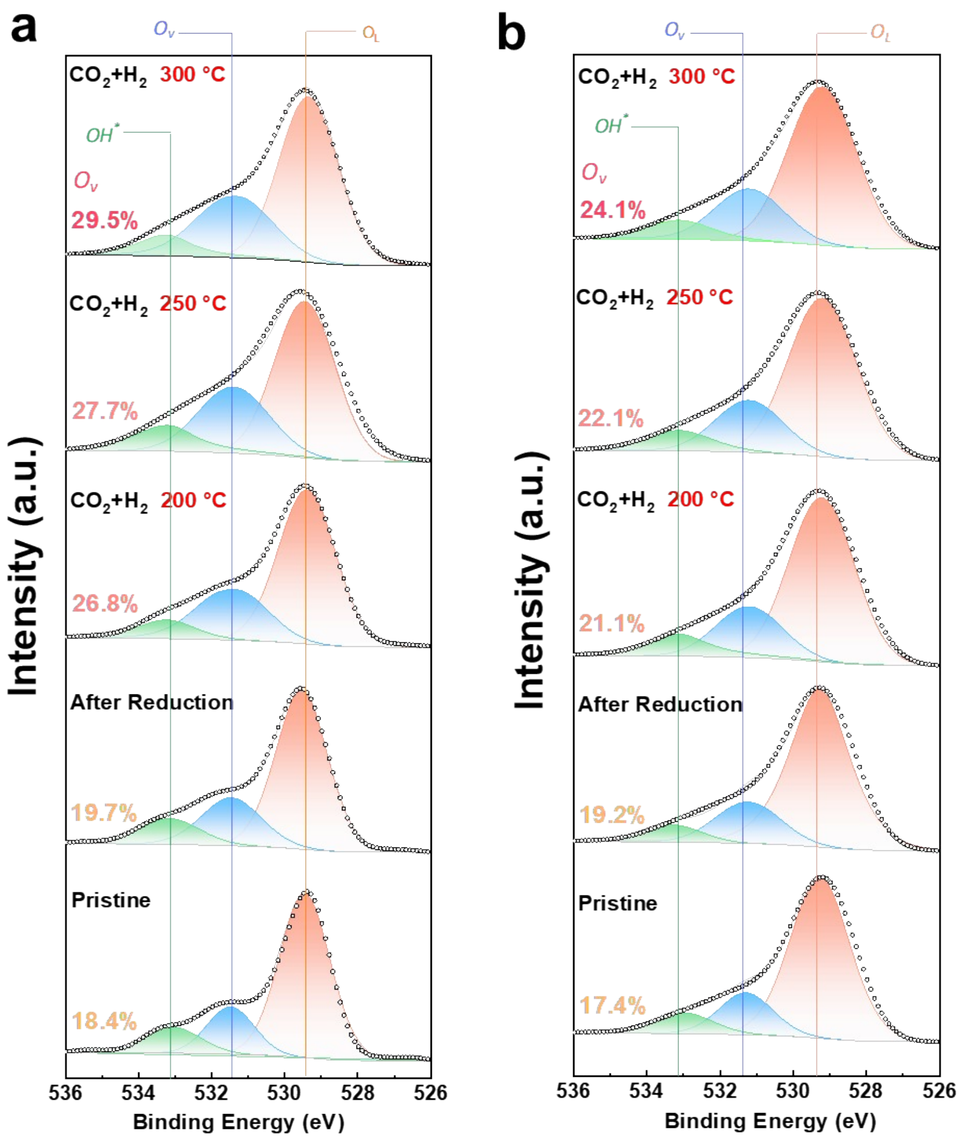

Figure S6. Quasi *in-situ* XPS spectra of O 1s on (a) Ru/$CeZrO_2$-P (b) Ru/$CeZrO_2$-C.

Supplementary Tables

Table S1. Comparison with the reported Ru catalysts for CO_2 methanation.

Catalyst	Temperature (°C)	Pressure (atm)	GHSV ($cm^3\ h^{-1}\ g_{cat}^{-1}$)	CO_2 Conversion (%)	CH_4 formation rate ($\mu mol_{CH4}\ g_{cat}^{-1}\ s^{-1}$)	Ref.
RT001	300	1	5600	73.0	5.1	S1
Ru/TiO_2(8-5)	300	1	24,000	41.5	12.3	S2
Ru/R-TiO_2-air-H_2	300	1	12,000	89.2	19.9	S3
Ru/TiO_2-600	300	1	72,000	21.5	28.8	S4
Ti350Ru450	200	1	6000	12.6	2.1	S5
Ru(1%)-TiO_2	300	1	400,000	7.6	73.9	S6
1.9wt% Ru-Mo-O_x	300	1	10,000	26.0	1.0	S7
Ru/CeO_2/r	300	1	72,000	73.0	65.2	S8
Ru/CeO_2	300	1	360	95.0	1.0	S9
Ru/α-Al_2O_3	300	1	360	51.0	0.5	S9
3Ru/CeO_2	300	1	60,000	85.0	65.5	S10
Ru/CeO_2-P	300	1	60,000	85.0	100.2	S11
2Ru/CeZr(AcAc)	300	1	60,000	18.0	13.4	S12
Ru/$CeZrO_2$-P	300	1	60,000	89.9	107.0	This work

Table S2 Quasi *in-situ* XPS results of the concentration of Ce^{3+} (%).

	$Ru/CeZrO_2$-P	$Ru/CeZrO_2$-C
Pristine	15.5	12.4
After Reduction	40.1	16.9
200 °C	47.5	36.4
250 °C	54.2	42.9
300 °C	58.6	44.1

Table S3. Assignments of the bands of *in-situ* DRIFT experiments on the catalysts.

Wavenumber (cm^{-1})	Assignments	Reference
2060 cm^{-1}	linear-CO^*	S3, S13
1610 cm^{-1}	m-$HCOO^*$	S14-S18
1595 cm^{-1}, 1540 cm^{-1}, 1390 cm^{-1}, 1360 cm^{-1}	b-$HCOO^*$	
1500 cm^{-1}, 1440 cm^{-1}	CO_3^*	S11, S19
3015 cm^{-1}, 1302 cm^{-1}	CH_4 (g)	S7, S20

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