

Supplementary Information

Unraveling the hydrogen spillover in tandem propane dehydrogenation and reverse water gas shift reaction

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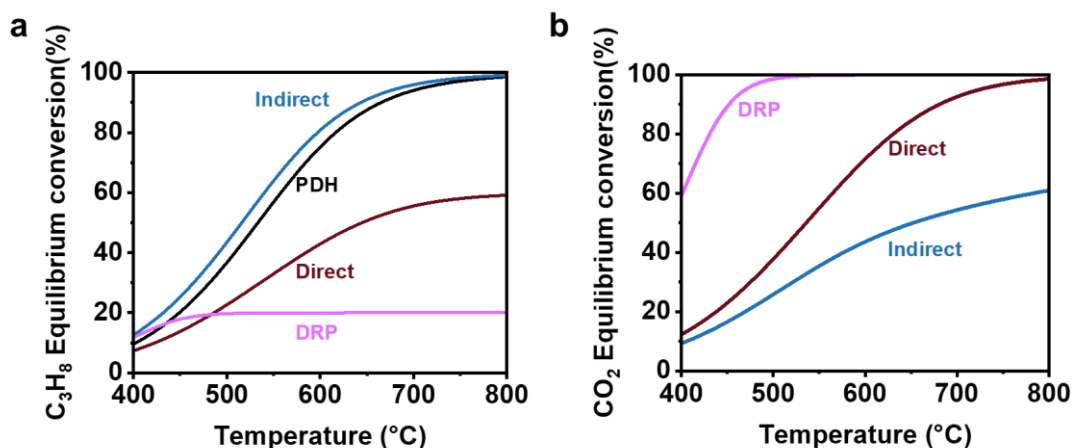
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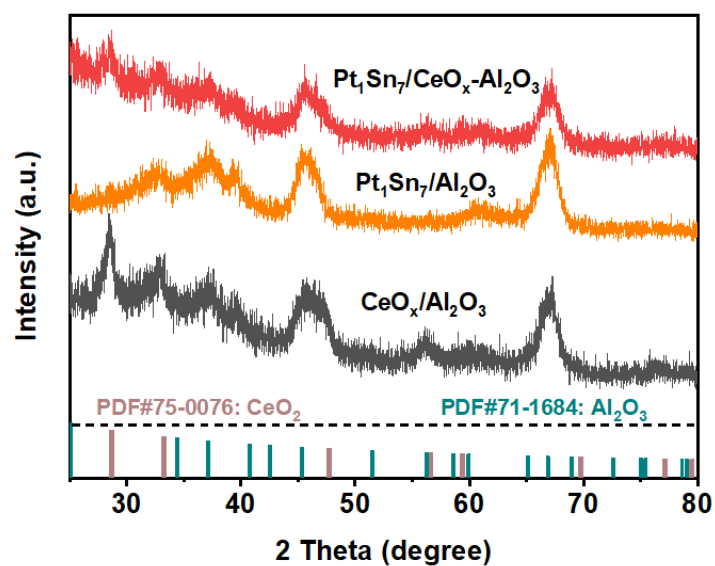
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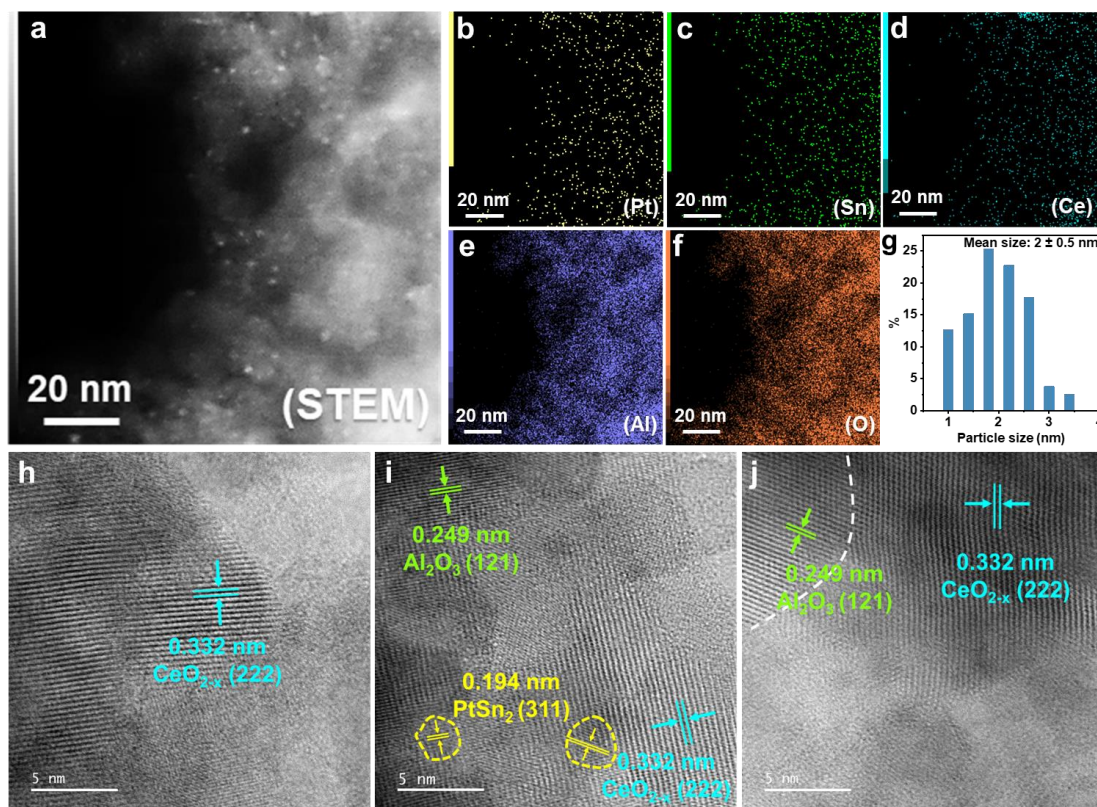
Reaction		Equation ^a	Equilibrium conversion ^b	
			C ₃ H ₈	CO ₂
DRP		$\text{C}_3\text{H}_8 + 3\text{CO}_2 = 6\text{CO} + 4\text{H}_2$	20.0 %	99.8 %
PDH		$\text{C}_3\text{H}_8 = \text{C}_3\text{H}_6 + \text{H}_2$	56.8 %	--
CO ₂ -PDH	Direct	$\text{C}_3\text{H}_8 + \text{CO}_2 = \text{C}_3\text{H}_6 + \text{CO} + \text{H}_2\text{O}$	33.0 %	55.0 %
	Indirect	$\text{C}_3\text{H}_8 = \text{C}_3\text{H}_6 + \text{H}_2$ $\text{H}_2 + \text{CO}_2 = \text{CO} + \text{H}_2\text{O}$	63.9 %	35.4 %

Supplementary Figure 1 | Calculated equilibrium conversion of C₃H₈ (a) and CO₂ (b) in PDH and CO₂-PDH as a function of temperature. Calculating conditions: atmospheric pressure, PDH: (C₃H₈ : N₂ = 5 : 30 mL·min⁻¹, C₃H₈ = C₃H₆ + H₂). CO₂-PDH (C₃H₈ : CO₂ : N₂ = 5 : 3 : 27 mL·min⁻¹, Indirect (PDH in tandem with RWGS): C₃H₈ = C₃H₆ + H₂, H₂ + CO₂ = CO + H₂O. Direct: C₃H₈ + CO₂ = C₃H₆ + CO + H₂O). DRP (C₃H₈ : CO₂ : N₂ = 5 : 3 : 27 mL·min⁻¹, C₃H₈ + 3CO₂ = 6CO + 4H₂). Calculation was done by Aspen Plus V12.

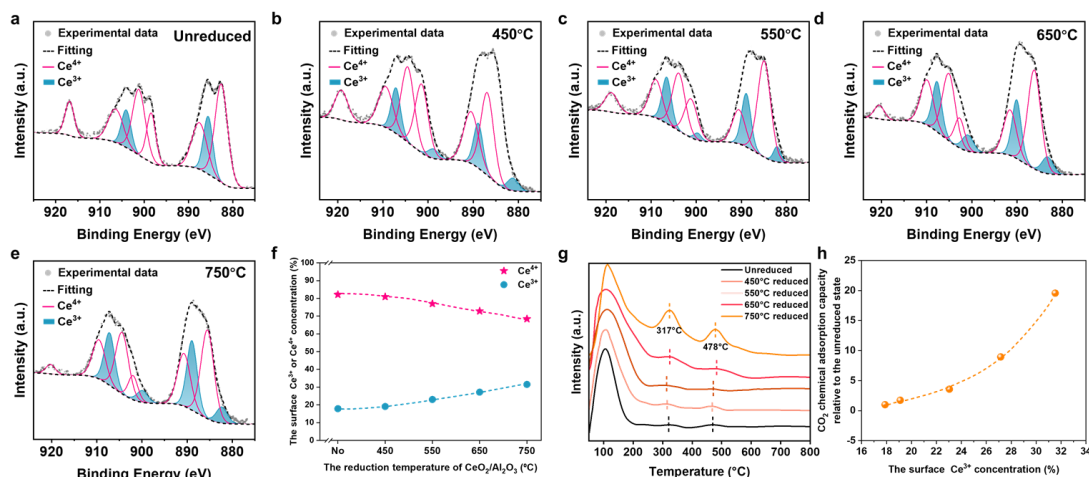


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88 Supplementary Figure 2 | XRD patterns. For $\text{CeO}_x/\text{Al}_2\text{O}_3$ supports and $\text{Pt}_1\text{Sn}_7/\text{CeO}_x\text{-}$
 89 Al_2O_3 catalysts, all XRD patterns could be indexed to a mixture phase of CeO_2 and
 90 Al_2O_3 . In addition, XRD patterns show only the diffraction peaks of CeO_2 and Al_2O_3 ,
 91 suggesting the well dispersion of Pt on the support.

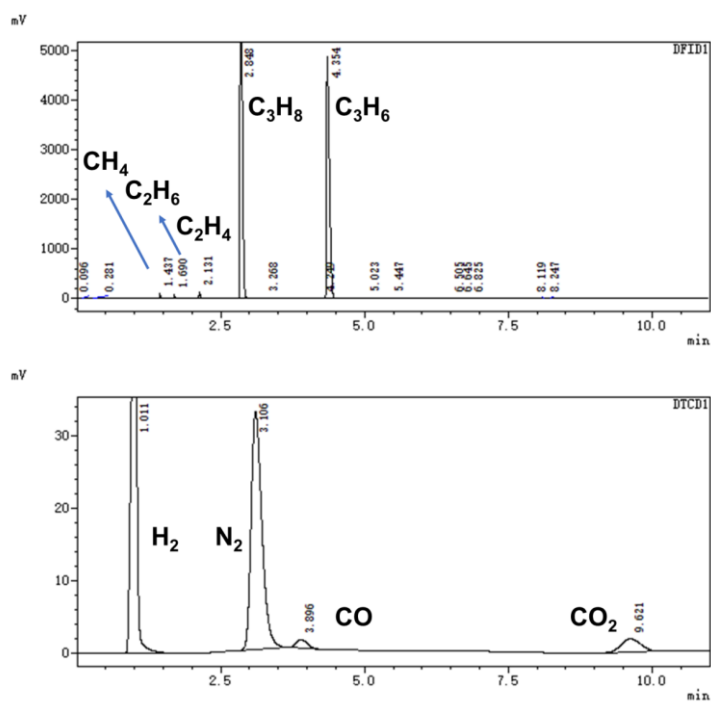


Supplementary Figure 3 | Morphology of tandem catalyst. (a) The HAADF-STEM image of $\text{Pt}_1\text{Sn}_7/\text{CeO}_x\text{-Al}_2\text{O}_3$. Elemental maps of platinum (b), tin (c), cerium (d), aluminum (e), oxygen (f), acquired by EDX. (g) Particle-size distribution. (h-j) The representative HAADF-STEM image for $\text{Pt}_1\text{Sn}_7/\text{CeO}_x\text{-Al}_2\text{O}_3$.

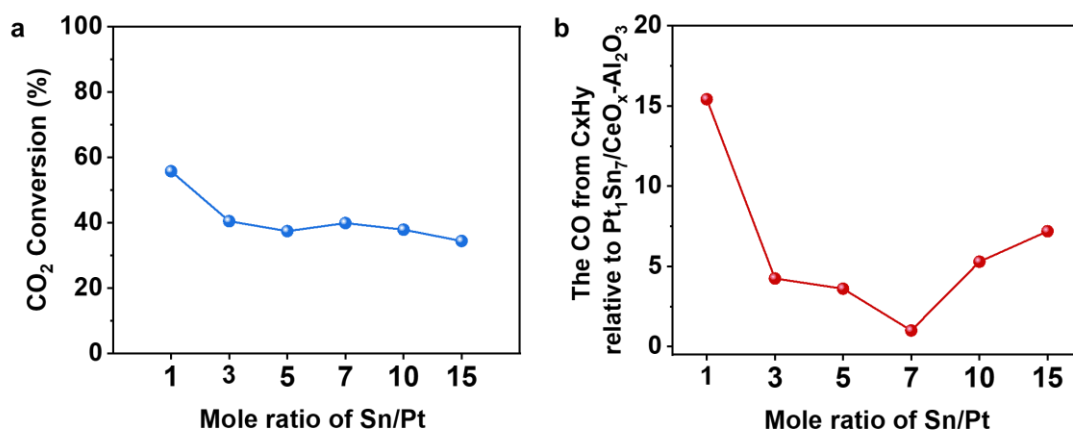


Supplementary Figure 4 | (a-e) XPS spectra for CeO₂/Al₂O₃ at different reduction temperatures, (f) The surface Ce³⁺ and Ce⁴⁺ concentration at different reduction temperatures on CeO_x/Al₂O₃ calculated from XPS spectra, (g) CO₂-TPD, and (h) The CO₂ chemical adsorption relative to unreduced state at different surface Ce³⁺ concentration (the calculated ratio of CO₂ chemical adsorption capacity (peak areas) at other reduction temperatures to the unreduced state).

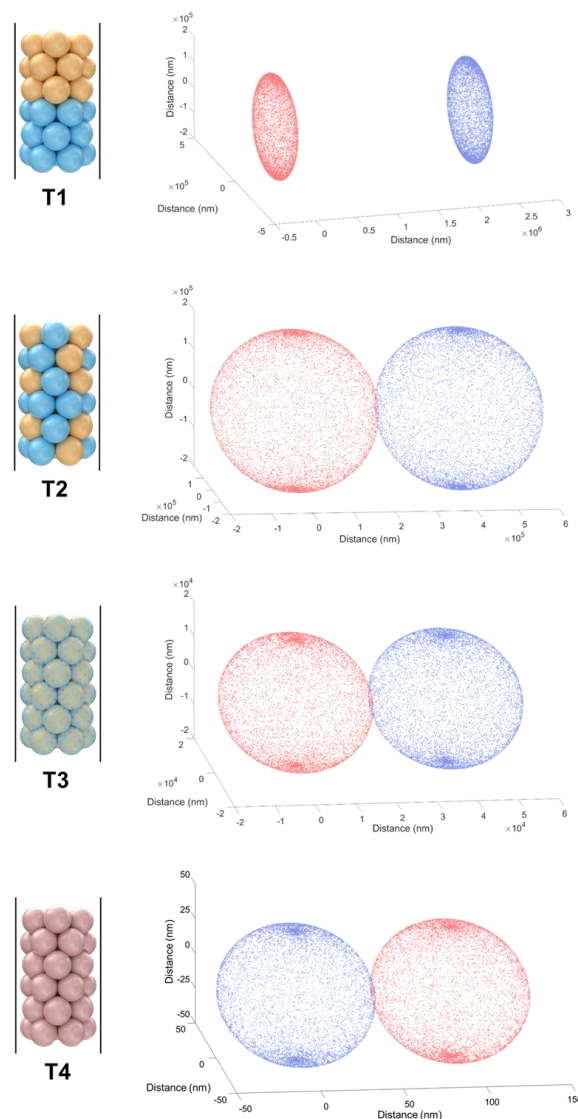
Based on the systematic XPS analysis, which demonstrate a monotonic increase in Ce³⁺ surface concentration with rising reduction temperature of the CeO₂/Al₂O₃ support under 10% H₂/Ar. This progression directly correlates with oxygen vacancy generation, as substantiated by CO₂-TPD measurements showing an increasing in CO₂ chemical adsorption capacity (~317°C and ~478°C, the physical adsorption at ~100°C). The chemical adsorption capacity of CO₂ increases significantly with increasing Ce³⁺ concentration confirms that oxygen vacancies serve as dominant CO₂ activation sites, validating our strategy to engineer CO₂ activation sites via oxygen vacancies.



Supplementary Figure 5 | Results of product peaks from Shimadzu GC 2014C (From computer screenshot). FID and TCD chart of the outlet gas from CO₂-PDH on Pt₁Sn₇/CeO_x-Al₂O₃ at 500 °C. No products other than CO, CO₂, N₂, H₂ and hydrocarbons were detected in the outlet gas.



Supplementary Figure 6 | (a) CO₂ conversion and (b) The relative CO from hydrocarbons to Pt₁Sn₇/CeO_x-Al₂O₃ of the CO₂-PDH reaction at different Sn/Pt molar ratios on Pt₁Sn_x/CeO_x-Al₂O₃. Catalytic testing conditions: 550 °C, atmospheric pressure, 150 mg of catalyst, C₃H₈ : CO₂ : N₂ = 5 : 3 : 27 mL·min⁻¹. There was no significant alteration in CO₂ conversion as the molar ratio of Sn to Pt gradually increased. However, it demonstrates that the contribution of dry reforming showed a reverse volcano peak relationship when Sn to Pt was gradually increased. as compared to Pt₁Sn₇/CeO_x-Al₂O₃, the reverse volcano peak relationship shows the lowest CO production from hydrocarbons, indicating the Pt₁Sn₇/CeO_x-Al₂O₃ catalysts have the strongest ability to inhibit the dry reforming.



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131 Supplementary Figure 7. The estimated distance ($d_{\text{PtSn-CeO}_x}$) between PtSn and CeO_x
 132 with different integrated modes using the Monte Carlo method on the MATLAB
 133 software.

134 For these modes, inter-particle distances were computationally analyzed using
 135 MATLAB.

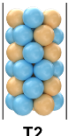
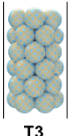
136 Monte Carlo method: Generated random point samples within/spherical surfaces of
 137 radius R.

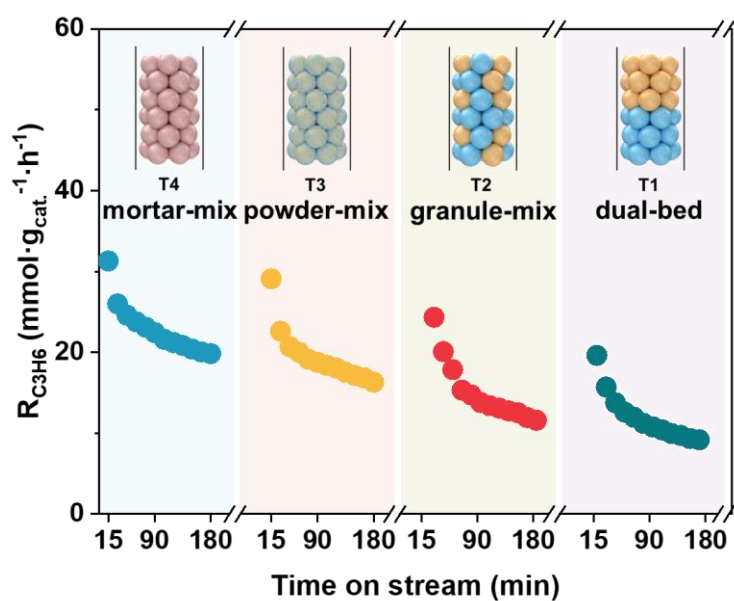
138 Distance calculation: Euclidean distances between corresponding points computed.

139 Statistical analysis: Distance distribution profiling.

140 Visualization: MATLAB plotting functions mapped distances as functions of R_1 and R_2 .

Supplementary Table 1. The values of distance ($d_{\text{PtSn-CeO}_x}$) between PtSn and CeO_x with different integration modes. Calculated based on the Monte Carlo method on the MATLAB software.

Sample	Models	Actual distance	Theoretical distance
dual-bed (T1)	 T1	3 mm	3.4 mm
granule-mix (T2)	 T2	0.4-0.8 mm	0.472 mm
powder-mix (T3)	 T3	0.05-0.075 mm	0.059 mm
mortar-mix (T4)	 T4	100-200 nm	118 nm



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146 Supplementary Figure 8 | The TOS profiles for dual-bed (T1), granule-mix (T2),
 147 powder-mix (T3) and mortar-mix (T4). Catalytic testing conditions: integral reactor,
 148 atmospheric pressure, 150 mg catalyst, WHSV of propane = 4.6 h⁻¹, C₃H₈ : CO₂ : N₂ =
 149 5 : 3 : 27 mL·min⁻¹.

Supplementary Table 2. The calculated effluent compositions under DRP, PDH-RWGS and the experimental data of this work.

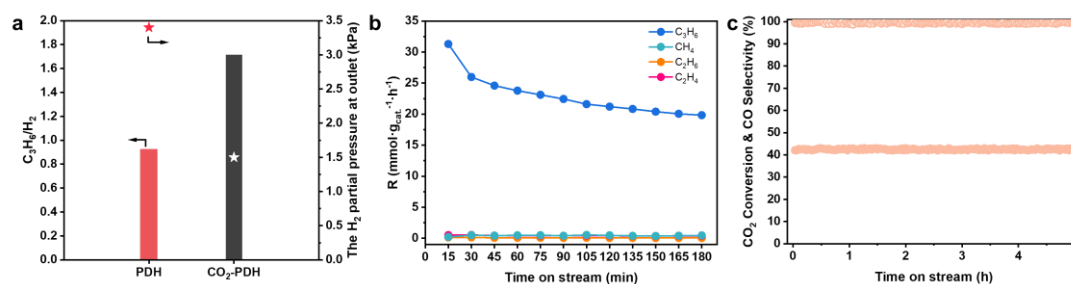
Scenario	CO/CO ₂		CO/C ₃ H ₈		C ₃ H ₆ /H ₂	
	500 °C	550 °C	500 °C	550 °C	500 °C	550 °C
Full Dry Reforming	0.93	1.57	0.56	0.95	0.50	0.50
Hybrid Pathway	1.19	0.93	0.33	0.57	1.54	1.51
Experimental ^a	0.20	0.87	0.12	0.46	1.70	1.34

^athe CO/CO₂, CO/C₃H₈ and C₃H₆/H₂ ratios at 15 minutes at 500/550 °C. Catalytic testing conditions: atmospheric pressure, WHSV of propane = 4.6 h⁻¹, C₃H₈ : CO₂ : N₂ = 5 : 3 : 27 mL·min⁻¹.

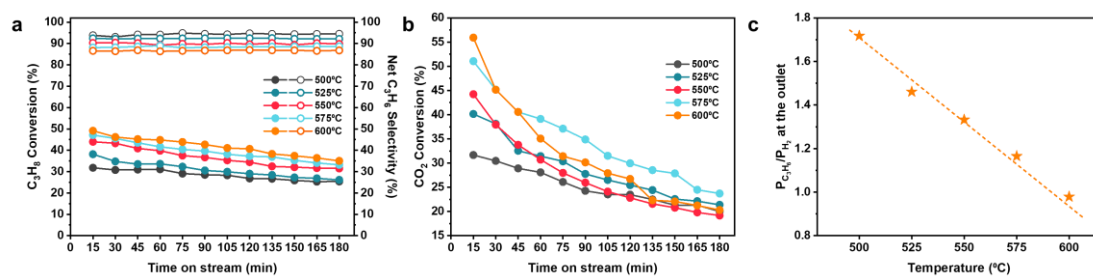
Assuming two scenarios:

1. Full dry reforming dominance: All CO₂ conversion attributed to dry reforming.
2. Hybrid pathway: at 550 °C, 35.4% CO₂ conversion via RWGS + 8.6% via dry reforming; at 500 °C, 25.8% CO₂ conversion via RWGS + 6% via dry reforming.

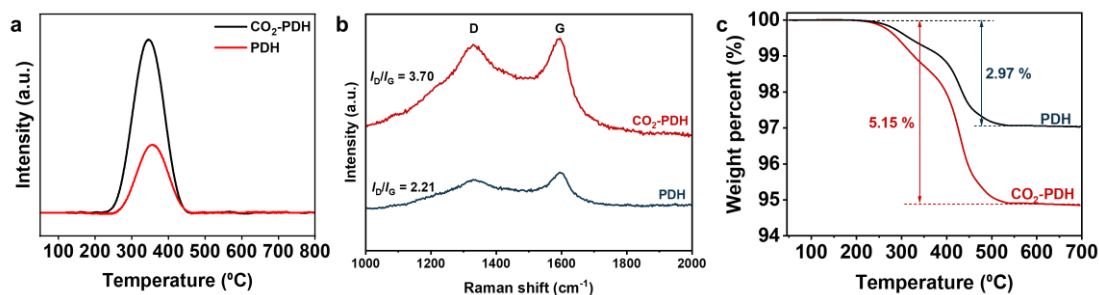
Under these two hypothetical scenarios, at 500°C and 550°C, the CO/CO₂ and CO/C₃H₈ ratios, and the C₃H₆/H₂ ratios as well as the experimental values to elucidate the minimal contribution of dry reforming. The experimental results reveal close alignment when RWGS dominates with minor dry reforming contributions at all temperature. Therefore, in this work, the RWGS dominates instead of dry reforming.



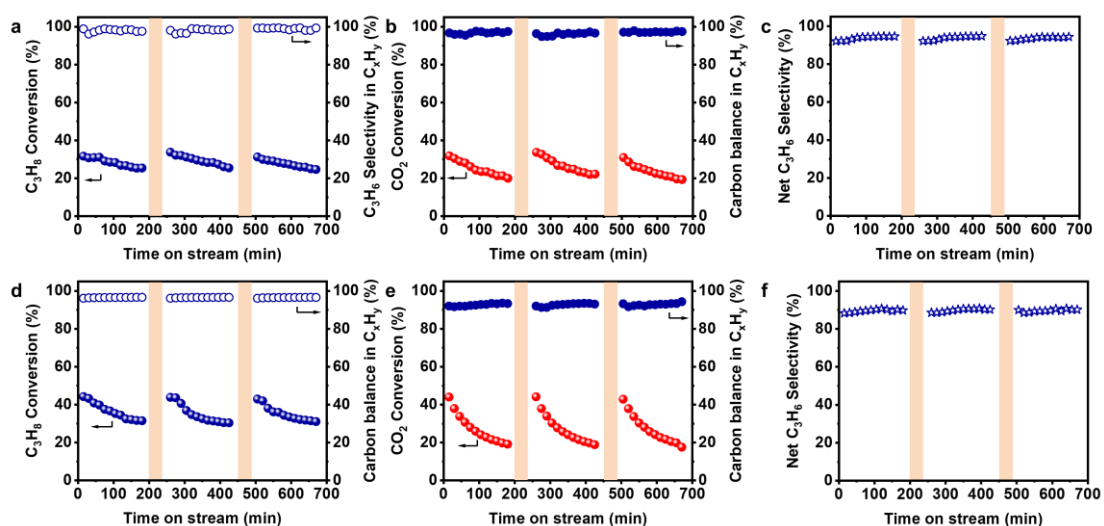
Supplementary Figure 9 | (a) The C_3H_6 to H_2 ratio and Hydrogen partial pressure at the reactor outlet (15 min). (b) The STY-TOS profiles tandem catalyst (T4). Catalytic testing conditions: $Pt_1Sn_7/CeO_x-Al_2O_3$, 500°C, atmospheric pressure, 150 mg of catalyst, CO_2 -PDH, $C_3H_8 : CO_2 : N_2 = 5 : 3 : 27 \text{ mL} \cdot \text{min}^{-1}$; PDH, $C_3H_8 : N_2 = 5 : 30 \text{ mL} \cdot \text{min}^{-1}$. (c) RWGS on tandem catalyst (T4) at 500 °C. Catalytic testing conditions: $Pt_1Sn_7/CeO_x-Al_2O_3$, 500°C, atmospheric pressure, 100 mg of catalyst, $H_2 : CO_2 : N_2 = 45 : 15 : 5 \text{ mL} \cdot \text{min}^{-1}$. Under the PDH and CO_2 -PDH reaction conditions, it is noteworthy that a lower H_2 partial pressure and higher C_3H_6 to H_2 ratio at the outlet in CO_2 -PDH (1.7) versus PDH (0.9, lower than 1 might due to the extent of coking). Furthermore, we observed no significant methane formation under the reaction conditions, and the RWGS reaction exhibited nearly 100% selectivity toward CO. Therefore, the C_3H_6 to H_2 ratio greater than 1 indicates in situ H_2 consumption via RWGS. This suggests that more hydrogen is consumed in situ by the RWGS reaction during the CO_2 -PDH reaction.



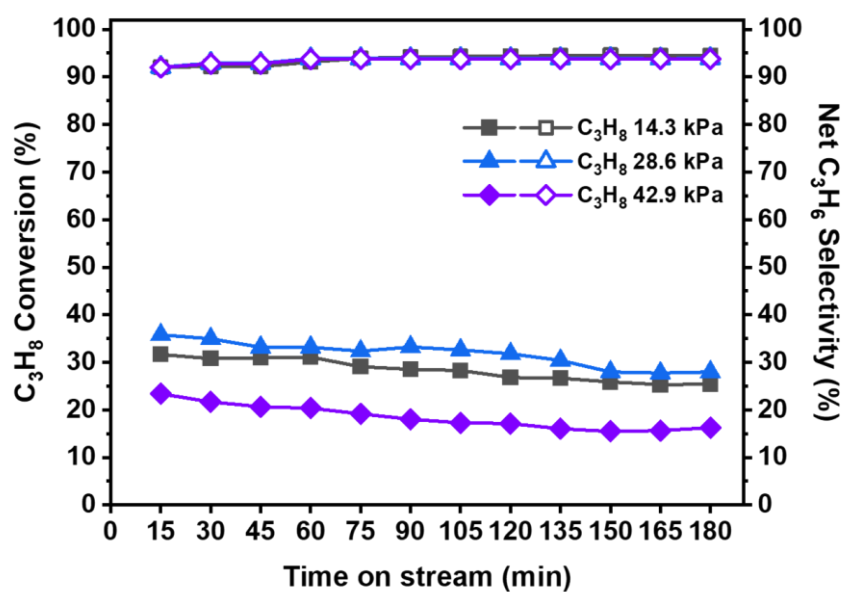
Supplementary Figure 10. (a) Different reaction temperature on Pt₁Sn₇/CeO_x-Al₂O₃. Catalytic testing conditions: 500/525/550/575/600 °C, atmospheric pressure, 150 mg catalyst, WHSV of propane = 4.6 h⁻¹, C₃H₈ : CO₂ : N₂ = 5 : 3 : 27 mL·min⁻¹.



Supplementary Figure 11 | O₂-TPO (a), Raman spectroscopy (b) and TGA (c) after 3 hours of PDH or CO₂-PDH on Pt₁Sn₇/CeO_x-Al₂O₃. O₂-TPO results demonstrate significantly higher coke deposition in CO₂-PDH compared to PDH after 3 hours of reaction. Raman spectroscopy further corroborates this observation, revealing a notably higher D/G band ratio for CO₂-PDH, indicative of accelerated carbon accumulation during the reaction process. TGA quantitatively confirms these findings, showing that coke formation in CO₂-PDH reaches approximately 1.7 times that of PDH after 3 hours of reaction.

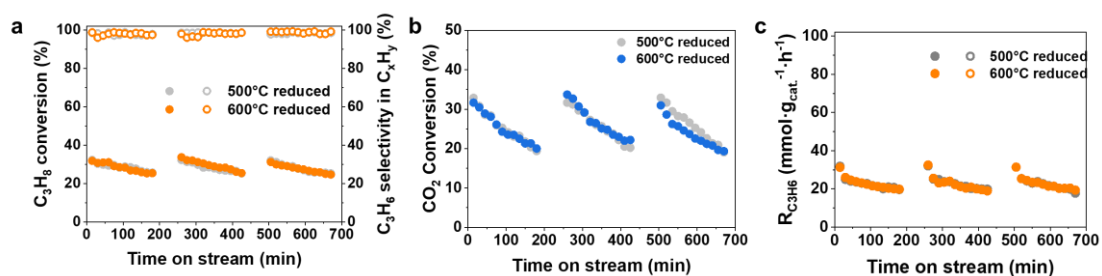


Supplementary Figure 12 | Long-term stability test with catalyst regeneration: Pt₁Sn₇/CeO_x-Al₂O₃, C₃H₈ : CO₂ : N₂ = 5 : 3 : 27 mL·min⁻¹. Time course of (a) C₃H₈ conversion, C₃H₆ selectivity in C_xH_y, CO₂ conversion, (b) carbon balance derived C₃H₈ and (c) net C₃H₆ selectivity at 500 °C, (d) C₃H₈ conversion and C₃H₆ selectivity in C_xH_y, (e) CO₂ conversion and carbon balance derived C₃H₈ and (f) net C₃H₆ selectivity at 550 °C.

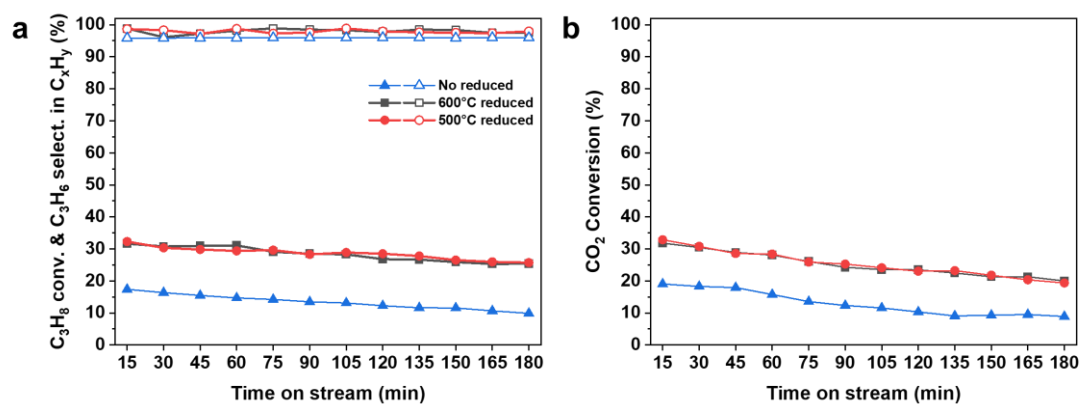


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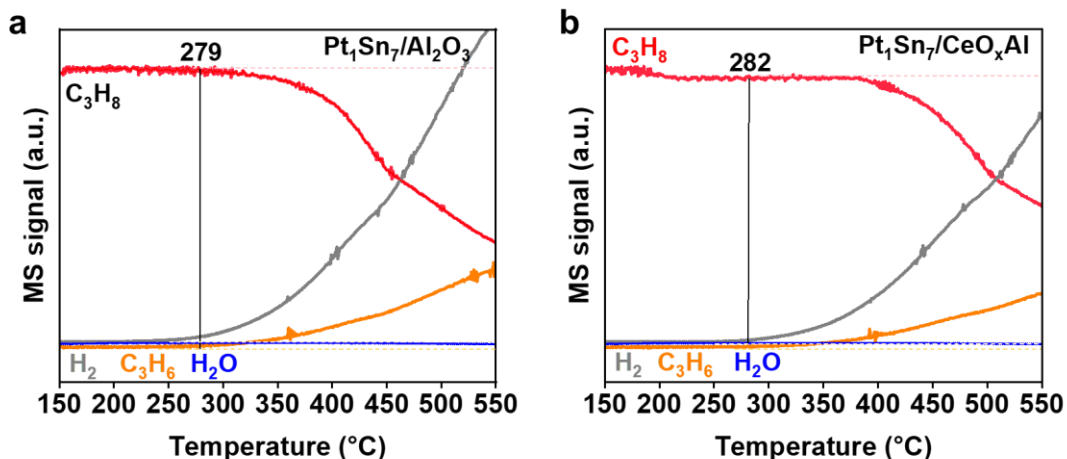
199 Supplementary Figure 13 | The performance at different C_3H_8 partial pressure on
 200 $Pt_{1.5}Sn_{0.5}/CeO_x-Al_2O_3$. Catalytic testing conditions: 500°C, atmospheric pressure, 150 mg
 201 catalyst. 14.3 kPa, $C_3H_8 : CO_2 : N_2 = 5 : 3 : 27 \text{ mL} \cdot \text{min}^{-1}$; 28.6 kPa, $C_3H_8 : CO_2 : N_2$
 202 $= 10 : 6 : 19 \text{ mL} \cdot \text{min}^{-1}$; 42.9 kPa, $C_3H_8 : CO_2 : N_2 = 15 : 9 : 11 \text{ mL} \cdot \text{min}^{-1}$.



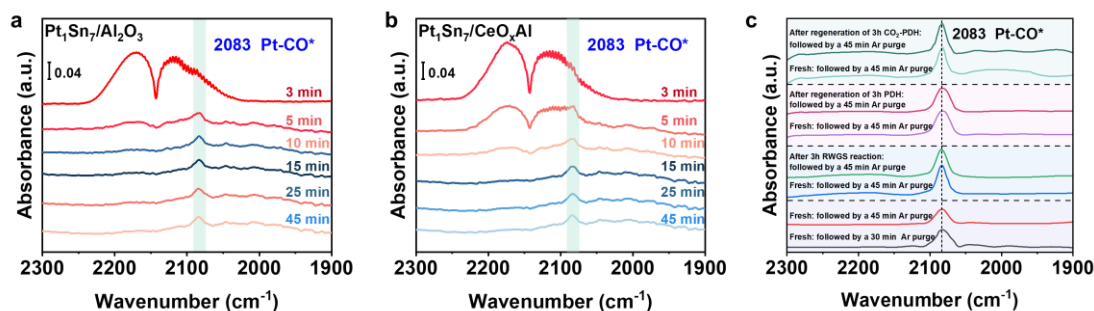
Supplementary Figure 14 | Long-term stability test with catalyst regeneration: $\text{Pt}_{10}\text{Sn}_7/\text{CeO}_x\text{-Al}_2\text{O}_3$, $\text{C}_3\text{H}_8 : \text{CO}_2 : \text{N}_2 = 5 : 3 : 27 \text{ mL} \cdot \text{min}^{-1}$. Time course of C_3H_8 and CO_2 conversion, C_3H_6 selectivity and C_3H_6 formation rate. Catalytic testing conditions: 500 °C, integral reactors, atmospheric pressure, 150 mg catalyst, WHSV of propane = 4.6 h^{-1} , $\text{C}_3\text{H}_8 : \text{CO}_2 : \text{N}_2 = 5 : 3 : 27 \text{ mL} \cdot \text{min}^{-1}$, regeneration: 45 min regeneration at 500 °C in flowing 20 % O_2/N_2 ($35 \text{ mL} \cdot \text{min}^{-1}$), and 1 h reduction at 500/600 °C in flowing 40 % H_2/N_2 ($35 \text{ mL} \cdot \text{min}^{-1}$).



Supplementary Figure 15 | The performance of CO_2 -PDH at different reduction temperature on $Pt_{10}Sn_7/CeO_x-Al_2O_3$. Catalytic testing conditions: 500°C, atmospheric pressure, 150 mg catalyst, WHSV of propane = $4.6\ h^{-1}$, $C_3H_8 : CO_2 : N_2 = 5 : 3 : 27\ mL \cdot min^{-1}$.



Supplementary Figure 16 | C-H bond activation. (a) Mass spectral (MS) signals of C_3H_8 , C_3H_6 and H_2 (m/z equals 41, 29 and 2, respectively) in TPSR experiments with fresh (a) Pt_1Sn_7/Al_2O_3 or (b) $Pt_1Sn_7/CeO_x-Al_2O_3$ catalysts. Catalytic condition: All carried out on a fixed-bed reactor equipped with a Mass Spectrometry OmniStar from Pfeiffer Vacuum. 100 mg of sample was treated in a flow rate of $35\text{ mL}\cdot\text{min}^{-1}$ of 40 vol% H_2/Ar at $600\text{ }^\circ\text{C}$ for 1 h and cooled down to $50\text{ }^\circ\text{C}$ in Ar ($35\text{ mL}\cdot\text{min}^{-1}$). After switching to C_3H_8/Ar ($5\text{ mL}\cdot\text{min}^{-1}$ C_3H_8 , $30\text{ mL}\cdot\text{min}^{-1}$ Ar) for 30 min, the sample was heated at a rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ up to $600\text{ }^\circ\text{C}$. Which shows that on the Pt_1Sn_7/Al_2O_3 and $Pt_1Sn_7/CeO_x-Al_2O_3$ catalysts revealed initial activation temperatures of $279\text{ }^\circ\text{C}$ and $282\text{ }^\circ\text{C}$. This demonstrated that adding CeO_2 did not alter the activation ability of C-H bonds.

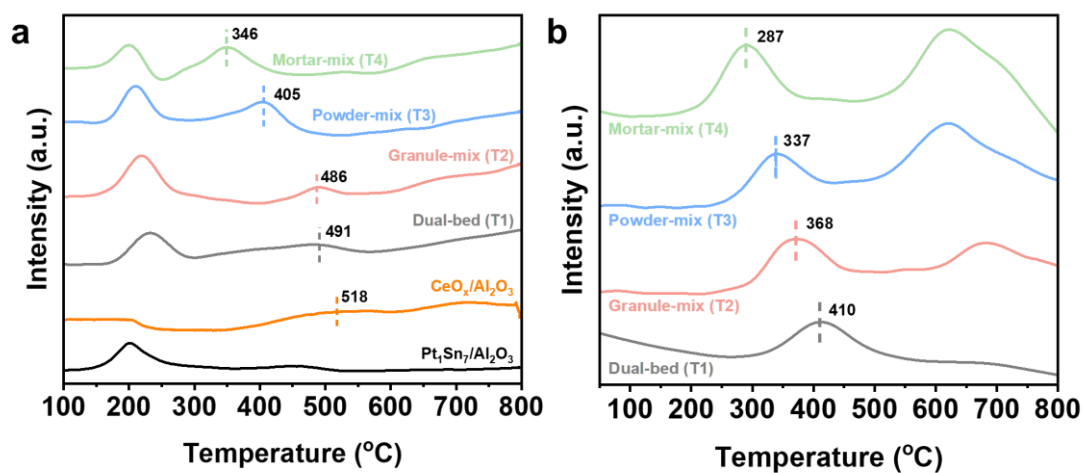


Supplementary Figure 17 | In situ CO-DRIFTS for the catalysts with (a) Fresh $\text{Pt}_1\text{Sn}_7/\text{Al}_2\text{O}_3$, (b) Fresh $\text{Pt}_1\text{Sn}_7/\text{CeO}_x\text{-Al}_2\text{O}_3$, (c) $\text{Pt}_1\text{Sn}_7/\text{CeO}_x\text{-Al}_2\text{O}_3$: fresh, after 3h RWGS reaction, after regeneration of 3h PDH and after regeneration of 3h CO_2 -PDH. The band at 2083 cm^{-1} is ascribed to CO linearly adsorbed on Pt. Based on the consistent Pt-CO* band position at 2083 cm^{-1} across all tested conditions, we conclude that no Pt-Ce alloy formation. Test condition of (a) and (b): the fresh catalysts in (a) and (b) were heated from ambient temperature to 600°C at a rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ and retained at 600°C in a flow rate of $35\text{ mL}\cdot\text{min}^{-1}$ of 40 vol% H_2/Ar .

Test condition of (c): For catalysts after 3h RWGS reaction, catalytic testing conditions: 500°C , atmospheric pressure, $\text{CO}_2 : \text{H}_2 : \text{N}_2 = 6 : 2 : 27\text{ mL}\cdot\text{min}^{-1}$. For after regeneration of 3h PDH and after regeneration of 3h CO_2 -PDH, catalytic testing conditions: 500°C , atmospheric pressure, $\text{C}_3\text{H}_8 : \text{N}_2 = 5 : 30\text{ mL}\cdot\text{min}^{-1}$, $\text{C}_3\text{H}_8 : \text{CO}_2 : \text{N}_2 = 5 : 3 : 27\text{ mL}\cdot\text{min}^{-1}$, regeneration: 45 min regeneration at 500°C in flowing 20% O_2/N_2 ($35\text{ mL}\cdot\text{min}^{-1}$), and 1 h reduction at 600°C in flowing 40% H_2/N_2 ($35\text{ mL}\cdot\text{min}^{-1}$). For catalysts that need to undergo RWGS, PDH, and CO_2 -PDH reactions, after characterizing the CO-DRIFTS of the fresh catalyst, they are directly heated to the reaction temperature for testing.

All of catalysts were cooled down to 30°C and the backgrounds (8 cm^{-1} resolution, 64 scans) were collected after Ar purging in a flow rate of $35\text{ mL}\cdot\text{min}^{-1}$ for at least 1 h. With the addition of a flow of $3\text{ mL}\cdot\text{min}^{-1}$ of CO, the adsorption of CO molecules on the surface of the catalysts continued for 45 min. After that, the DRIFTS spectra were recorded till no visible change in the absorption band intensities under Ar purging. Which shows that both the $\text{Pt}_1\text{Sn}_7/\text{Al}_2\text{O}_3$ and $\text{Pt}_1\text{Sn}_7/\text{CeO}_x\text{-Al}_2\text{O}_3$ catalysts displayed the same infrared characteristic peak at 2083 cm^{-1} , suggesting identical Pt coordination

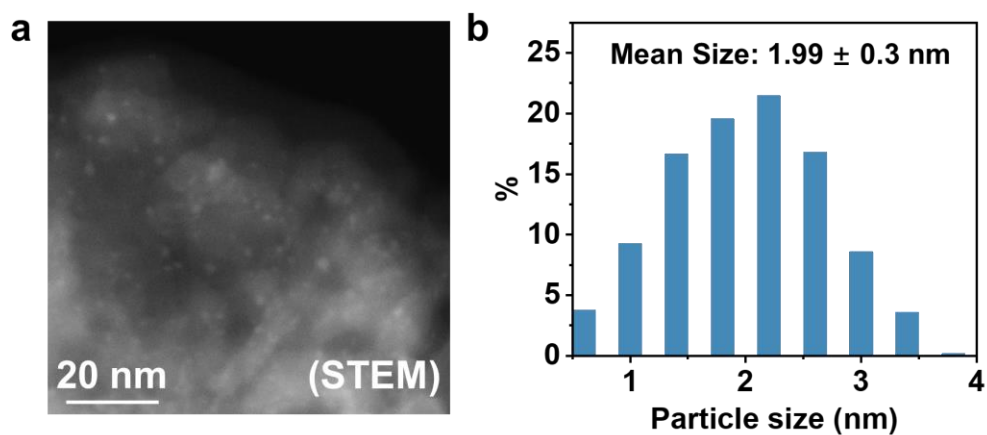
253 environments in both. From figure (c), the results confirm consistent Pt-CO* band
254 positions across all states, indicating preservation of the catalyst's geometric and
255 electronic structure throughout reaction cycles.
256



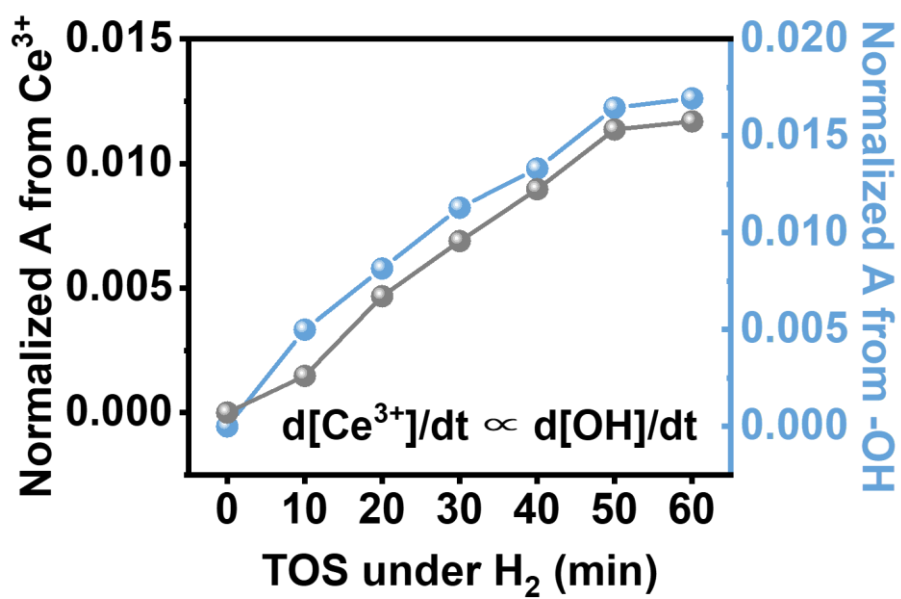
Supplementary Figure 18 | (a) H₂-TPR and (b) H₂-TPD for the catalysts with Pt₁Sn₇/Al₂O₃ and CeO_x/Al₂O₃ in different modes.

Supplementary Table 3. Quantitative H₂ consumption profiles in H₂-TPR with varied configurations.

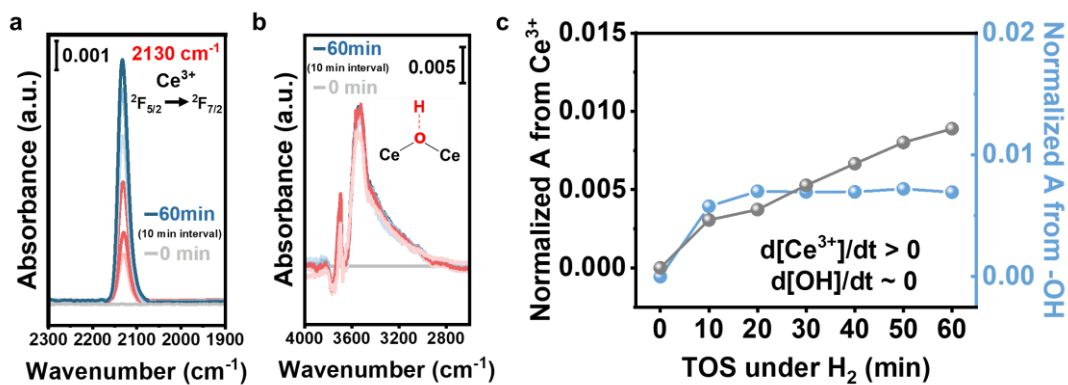
Mode	Peak Center (°C)	H ₂ (cm ³ /g _{cat.} STP)	Peak Center (°C)	H ₂ (cm ³ /g _{cat.} STP)
T1 (dual-bed)	232	1.39	491	0.27
T2 (granule-mix)	219	1.36	486	0.44
T3 (powder-mix)	210	1.41	405	1.28
T4 (mortar-mix)	199	1.34	346	1.62



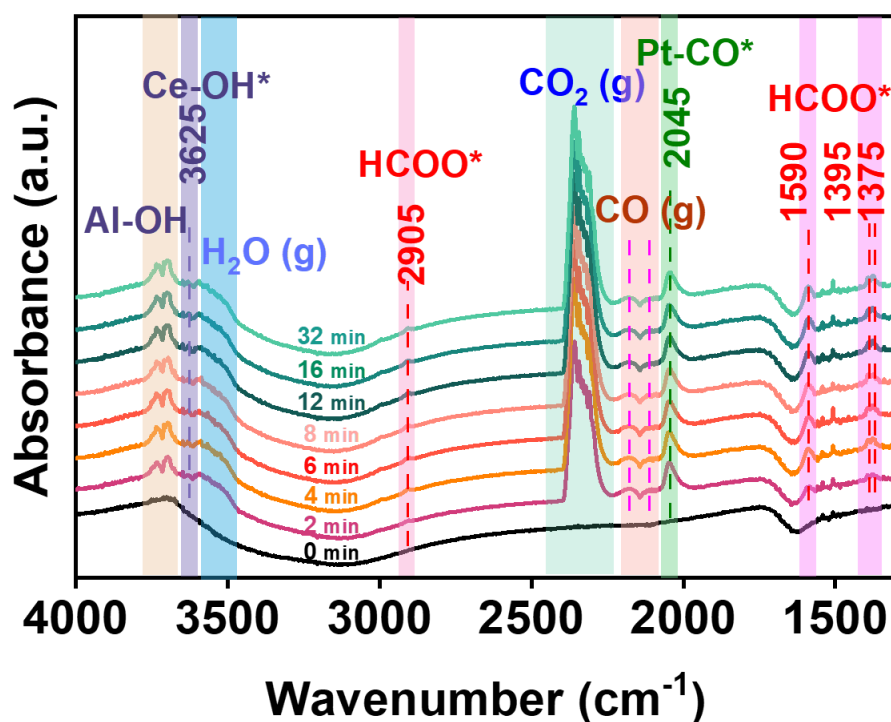
Supplementary Figure 19 | Morphology of $\text{Pt}_1\text{Sn}_7/\text{Al}_2\text{O}_3$ catalyst. (a) The HAADF-STEM image of $\text{Pt}_1\text{Sn}_7/\text{Al}_2\text{O}_3$. (b) Particle-size distribution. Which exhibits the same particle size distribution as the $\text{Pt}_1\text{Sn}_7/\text{CeO}_x\text{-Al}_2\text{O}_3$ catalyst shown in Supplementary Figure 3.



270
 271 Supplementary Figure 20 | Correlation between the maximum absorbance of the
 272 normalized from -OH and Ce³⁺ in the DRIFTS spectra of Pt₁Sn₇/CeO_x-Al₂O₃ from Fig.
 273 4c and d.



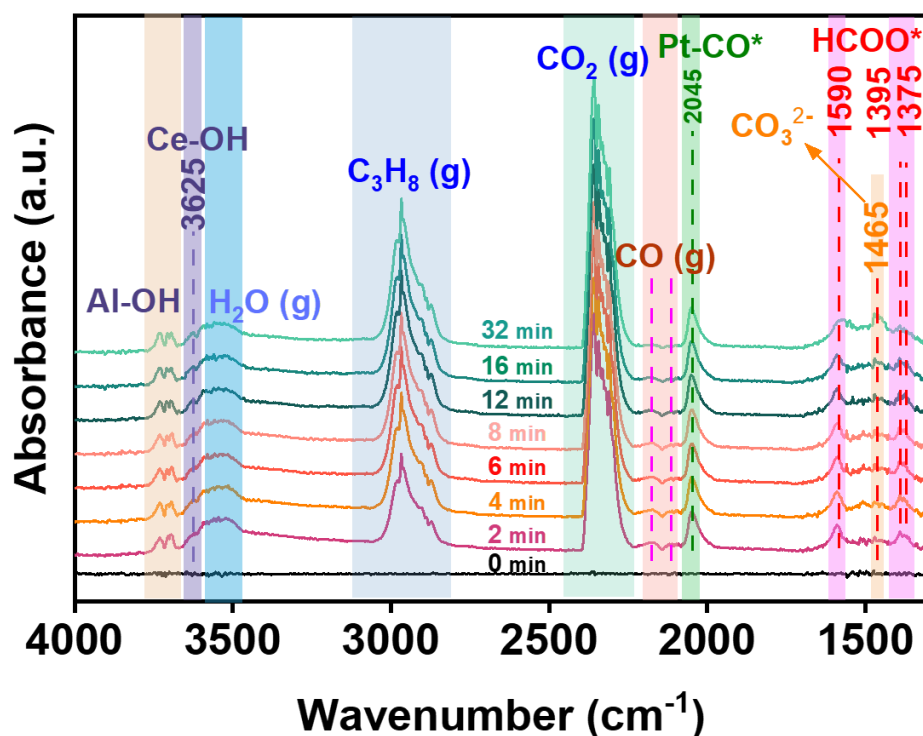
Supplementary Figure 21 | DRIFTS spectra for the (a) hydroxyl, (b) Ce³⁺ region and (c) correlation between the maximum absorbance of the normalised from -OH and Ce³⁺ in the DRIFTS spectra of CeO_x/Al₂O₃ collected under H₂ at 500 °C.



279

280 Supplementary Figure 22 | In situ DRIFTS during RWGS for Pt₁Sn₇/CeO_x-Al₂O₃. Test
 281 condition: the fresh catalyst (50 mg powdered sample) was filled into the reactor and
 282 flushed with Ar (50 mL·min⁻¹) at 300 °C for 1 h to remove the adsorbates. Then, the
 283 catalysts were heated from 300 °C to 600 °C at a rate of 10 °C·min⁻¹ and retained at
 284 600 °C in a flow rate of 35 mL·min⁻¹ of 40 vol% H₂/Ar. After this, the catalysts were
 285 cooled down to 500 °C and the backgrounds (8 cm⁻¹ resolution, 64 scans) were collected
 286 after Ar purging in a flow rate of 35 mL·min⁻¹ for at least 1 h. the background spectra
 287 (a resolution of 8 cm⁻¹, 64 scans) were collected. Afterwards, a H₂/CO₂/Ar mixture with
 288 a flow rate of 35 mL·min⁻¹ (5 mL·min⁻¹ H₂, 5 mL·min⁻¹ CO₂, 25 mL·min⁻¹ Ar) was
 289 introduced into the reactor for 58 min. DRIFTS spectra were collected every 1 min.

290



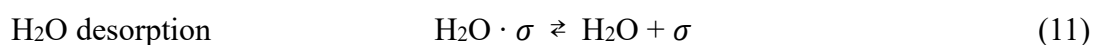
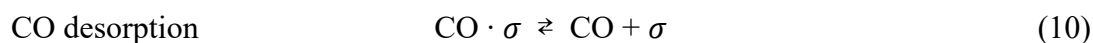
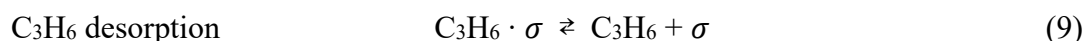
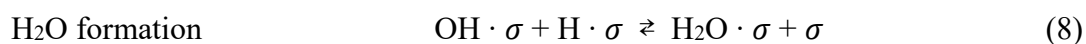
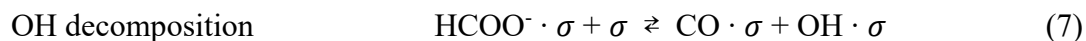
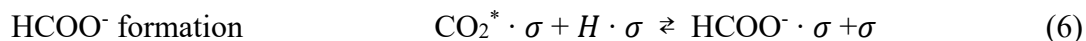
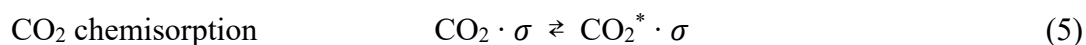
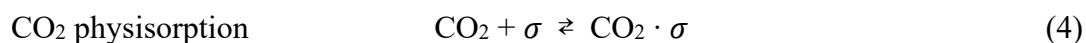
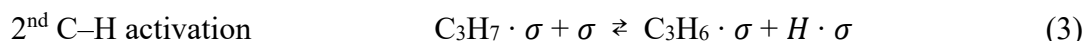
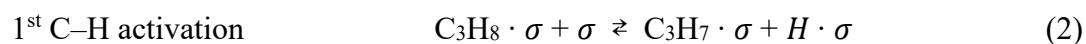
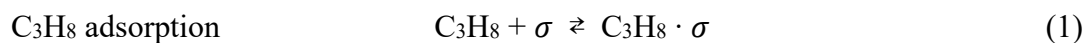
Supplementary Figure 23 | In situ DRIFTS during CO₂-PDH for Pt₁Sn₇/CeO_x-Al₂O₃.
 Test condition: the fresh catalyst (50 mg powdered sample) was filled into the reactor and flushed with Ar (50 mL·min⁻¹) at 300 °C for 1 h to remove the adsorbates. Then, the catalysts were heated from 300 °C to 600 °C at a rate of 10 °C·min⁻¹ and retained at 600 °C in a flow rate of 35 mL·min⁻¹ of 40 vol% H₂/Ar. After this, the catalysts were cooled down to 500 °C and the backgrounds (8 cm⁻¹ resolution, 64 scans) were collected after Ar purging in a flow rate of 35 mL·min⁻¹ for at least 1 h. the background spectra (a resolution of 8 cm⁻¹, 64 scans) were collected. Afterwards, a C₃H₈/CO₂/Ar mixture with a flow rate of 35 mL·min⁻¹ (5 mL·min⁻¹ C₃H₈, 3 mL·min⁻¹ CO₂, 27 mL·min⁻¹ Ar) was introduced into the reactor for 32 min directly after pre-reduced. DRIFTS spectra were collected every 1 min.

Kinetic analysis of CO₂-PDH

(A) Kinetic modeling of CO₂-PDH on Pt₁Sn₇/CeO_x-Al₂O₃

Based on the PDH+RWGS pathways on the Pt₁Sn₇/CeO_x-Al₂O₃, and in order to further understand the effect of CO₂ on the rate of propylene production in this reaction systems, we have carried out the derivation of the reaction kinetics and the fitting of the corresponding kinetic equations, and matched the fitting results with the experiments to accurately obtain the rate-determining step of the CO₂-PDH reaction on the Pt₁Sn₇/CeO_x-Al₂O₃ catalyst.

The kinetics for this reaction has been previously studied, combined with the PDH+RWGS pathways, we conducted conventional quasi-stationary approximation approaches for kinetic analysis to understand the RDS on Pt₁Sn₇/CeO_x-Al₂O₃ catalyst, and considered the following Langmuir-Hinshelwood type mechanism:



Such a primitive step in the elementary step can be divided into four parts: the first part: for the propane dehydrogenation reaction, the Propane is firstly physically adsorbed at the Pt site, followed by the first and second dehydrogenation steps to produce adsorbed propylene and H. In the second part, for the activation of CO₂, the first step occurs by physical adsorption of CO₂ in the reactive oxygen vacancies, and it is worth noting that CO₂ is a thermodynamically stable molecule with the standard formation enthalpy of -393.5 kJ·mol⁻¹, therefore, the chemisorption step is necessary. What then occurs is the chemical activation of CO₂; part 3: the generation of HCOO⁻ from hydrogen produced by propane dehydrogenation and the chemical activated CO₂, and the HCOO⁻ further decomposition, the OH* and CO* were generated, OH* and H* further generate H₂O, the product of the RWGS reaction; and part 4: the desorption of the products C₃H₆, CO, and H₂O.

327 Based on the raw of mass action, the reaction rate of each elementary step as
 328 follows,

$$r_i = \vec{r}_i - \overleftarrow{r}_i = \vec{k}_i \prod_j \vec{P}_j \prod_j \vec{\theta}_j - \overleftarrow{k}_i \prod_j \overleftarrow{P}_j \prod_j \overleftarrow{\theta}_j \quad (12)$$

329 In equation (12), $\vec{k}_i$ is the rate constants for forward and $\overleftarrow{k}_i$ is the reverse
 330 reactions in step i. $\vec{P}_j(\vec{\theta}_j)$ and $\overleftarrow{P}_j(\overleftarrow{\theta}_j)$ are the pressure (coverage) of the reactant and
 331 product species in step i, respectively. Pressure and coverage were used for gas-phase
 332 molecules and surface adsorbates, respectively. The specific representation of each
 333 reaction rate is shown below:

$$r_1 = \vec{k}_1 P_{C_3H_8} (1 - \theta) - \overleftarrow{k}_1 \theta_{C_3H_8} \quad (13) \quad r_2 = \vec{k}_2 \theta_{C_3H_8} (1 - \theta) - \overleftarrow{k}_2 \theta_{C_3H_7} \theta_H \quad (14)$$

$$r_3 = \vec{k}_3 \theta_{C_3H_7} (1 - \theta) - \overleftarrow{k}_3 \theta_{C_3H_6} \theta_H \quad (15) \quad r_4 = \vec{k}_4 P_{CO_2} (1 - \theta) - \overleftarrow{k}_4 \theta_{CO_2} \quad (16)$$

$$r_5 = \vec{k}_5 \theta_{CO_2} - \overleftarrow{k}_5 \theta_{CO_2}^* \theta_H \quad (17) \quad r_6 = \vec{k}_6 \theta_{CO_2}^* \theta_H - \overleftarrow{k}_6 \theta_{HCOO^-} (1 - \theta) \quad (18)$$

$$r_7 = \vec{k}_7 \theta_{HCOO^-} (1 - \theta) - \overleftarrow{k}_7 \theta_{OH} \theta_{CO} \quad (19) \quad r_8 = \vec{k}_8 \theta_{OH} \theta_H - \overleftarrow{k}_8 \theta_{H_2O} (1 - \theta) \quad (20)$$

$$r_9 = \vec{k}_9 \theta_{C_3H_6} - \overleftarrow{k}_9 P_{C_3H_6} (1 - \theta) \quad (21) \quad r_{10} = \vec{k}_{10} \theta_{CO} - \overleftarrow{k}_{10} P_{CO} (1 - \theta) \quad (22)$$

$$r_{11} = \vec{k}_{11} \theta_{H_2O} - \overleftarrow{k}_{11} P_{H_2O} (1 - \theta) \quad (23)$$

334 In equation (13) to (23), all of the P_i , θ_i , $(1 - \theta)$ are dimensionless values. P_i ,
 335 θ_i , $(1 - \theta)$ are the relative pressure of i to the standard pressure, coverage of i , and
 336 the fraction of vacant adsorption site.

337 (B) Kinetic Analysis based on quasi-stationary approximation

338 According to the quasi-stationary approximation, when a certain step is considered
 339 as the rate-determining step, other steps can be regarded to be in equilibrium. Therefore,
 340 the equilibrium constants are provided as follows:

$$K_1 = \frac{\theta_{C_3H_8}}{P_{C_3H_8}(1-\theta)} \quad (24) \quad K_2 = \frac{\theta_{C_3H_7}\theta_H}{\theta_{C_3H_8}(1-\theta)} \quad (25) \quad K_3 = \frac{\theta_{C_3H_6}\theta_H}{\theta_{C_3H_7}(1-\theta)} \quad (26)$$

$$K_4 = \frac{\theta_{CO_2}}{P_{CO_2}(1-\theta)} \quad (27) \quad K_5 = \frac{\theta_{CO_2}^*}{\theta_{CO_2}} \quad (28) \quad K_6 = \frac{\theta_{HCOO^-}(1-\theta)}{\theta_{CO_2}^*\theta_H} \quad (29)$$

$$K_7 = \frac{\theta_{OH}\theta_{CO}}{\theta_{HCOO^-}(1-\theta)} \quad (30) \quad K_8 = \frac{\theta_{H_2O}(1-\theta)}{\theta_{OH}\theta_H} \quad (31) \quad K_9 = \frac{P_{C_3H_6}(1-\theta)}{\theta_{C_3H_6}} \quad (32)$$

$$K_{10} = \frac{P_{CO}(1-\theta)}{\theta_{CO}} \quad (33) \quad K_{11} = \frac{P_{H_2O}(1-\theta)}{\theta_{H_2O}} \quad (34)$$

341 Note that K_i cannot be defined when the step i is considered as the RDS (ten
342 equilibrium constants can be used). Besides, the conservation of the number of
343 adsorption site is considered as follows:

$$\sum \theta_i + (1-\theta) = 1 \quad (35)$$

$$\theta_{C_3H_8} + \theta_{C_3H_7} + \theta_H + \theta_{C_3H_6} + \theta_{CO_2} + \theta_{CO_2}^* + \theta_H + \theta_{HCOO^-} + \theta_{OH} + \theta_{CO} + \theta_{H_2O} + (1-\theta) = 1 \quad (36)$$

344 Each θ_i except $(1-\theta)$ is expressed as a function of K_i , P_j , and $(1-\theta)$, then
345 the site conservation equation is solved for $(1-\theta)$. Thus, each coverage and reaction
346 rate can be expressed as a function of K_i , and P_j :

$$\theta_m = f_m(K_i, P_j) \quad (37)$$

$$r_m = \overrightarrow{r_m} - \overleftarrow{r_m} = \overrightarrow{k_m} \prod_m \overrightarrow{P_m} \prod_j f_m(K_i, P_j) - \overleftarrow{k_m} \prod_m \overleftarrow{P_j} \prod_m g_m(K_i, P_j) \quad (38)$$

347 Then, K_i and P_j except $P_{C_3H_8}$ which makes r_m a function of $P_{C_3H_8}$ or P_{CO_2}
348 are regarded as constants in a series of catalytic experiments, which makes r_m a
349 function of $P_{C_3H_8}$ or P_{CO_2} . This function can be approximated to a simplified form at
350 a certain limit of coefficients included in the equation as follows:

$$r_m = k \cdot P_{C_3H_8}^\alpha \cdot P_{CO_2}^\beta \quad (39)$$

351 where, k is an apparent rate constant. α , and β represent kinetic parameters that
352 can be obtained by regressing the measured rate data to these rate equations.

353 In this work, based on the experimentally obtained the reaction orders for
354 $P_{C_3H_8}$, $\alpha = 1$, P_{CO_2} , $\beta = 0.5$, and for step (1): C_3H_8 physisorption, step (4-5): CO_2

physisorption, CO₂ chemisorption, step (7-11): OH formation, H₂O formation, C₃H₆ desorption, CO desorption, H₂O desorption, Since the mathematically derived reaction orders when they are used as RDS are far from the experimental results, they will not be shown and discussed here. So, no further derivation of the above steps will be made in this part.

In the following section, full derivation of the rate equation is shown for steps (3) for better understanding.

The contribution of each reverse reaction was ignored because the experimental reactions were done in differential conditions (Heat and mass transport limitations at the catalyst pellet and the bed scale have been eliminated in order to measure rates of intrinsic chemical origins. In this reaction conditions, the C₃H₈ conversion at very low level: < 10%, where $P_{C_3H_8}, P_{CO_2} \gg P_{C_3H_6}, P_{CO}, P_{H_2O}$).

Assuming step (3) as the RDS:

When step (3) (2nd C-H activation) as the RDS, the overall reaction rate can be expressed using equation

$$r_3 = \overrightarrow{k_3}\theta_{C_3H_7}(1 - \theta) - \overleftarrow{k_3}\theta_{C_3H_6}\theta_H \quad (15)$$

In this condition, the K_i (except K_3) can be defined using quasi-stationary approximation, so that θ_i can be obtained by K_i :

$$\theta_{CO_2} = K_4 P_{CO_2} (1 - \theta) \quad (40)$$

$$\theta_{C_3H_6} = K_9^{-1} P_{C_3H_6} (1 - \theta) \quad (41)$$

$$\theta_{CO} = K_{10}^{-1} P_{CO} (1 - \theta) \quad (42)$$

$$\theta_{H_2O} = K_{11}^{-1} P_{H_2O} (1 - \theta) \quad (43)$$

$$\theta_{CO_2}^* = K_4 K_5 P_{CO_2} (1 - \theta) \quad (44)$$

$$\theta_{HCOO^-} = (K_4 K_5 K_6)^{0.5} (K_7 K_8 K_{10} K_{11})^{-0.5} P_{CO}^{0.5} P_{H_2O}^{0.5} P_{CO_2}^{0.5} (1 - \theta) \quad (45)$$

$$\theta_H = (K_4 K_5 K_6 K_7 K_8 K_{10} K_{11})^{-0.5} P_{CO}^{0.5} P_{H_2O}^{0.5} P_{CO_2}^{-0.5} (1 - \theta) \quad (46)$$

$$\theta_{OH} = (K_4 K_5 K_6 K_7 K_8^{-1} K_{10} K_{11}^{-1})^{0.5} P_{CO}^{-0.5} P_{H_2O}^{0.5} P_{CO_2}^{0.5} (1 - \theta) \quad (47)$$

$$\theta_{C_3H_7} = (K_1^2 K_2^2 K_4 K_5 K_6 K_7 K_8 K_{10} K_{11})^{0.5} P_{CO}^{-0.5} P_{H_2O}^{-0.5} P_{C_3H_8} P_{CO_2}^{0.5} (1 - \theta) \quad (48)$$

$$\theta_{C_3H_8} = K_1 P_{C_3H_8} (1 - \theta) \quad (49)$$

372 We were able to notice that each equation (40-49) have $(1 - \theta)$ in its final result,
 373 and in this kinetic reaction conditions, where $P_{C_3H_8}, P_{CO_2} \gg P_{C_3H_6}, P_{CO}, P_{H_2O}$.
 374 Meanwhile, the equation (13) can be regarded as a function of $P_{C_3H_8}$ and/or P_{CO_2} . So,
 375 based on equation (40-49), each red-colored part is decomposed into $P_{CO_2}, P_{C_3H_8}$ and
 376 a constant F_i as follows:

$$\theta_{CO_2} = F_{CO_2} P_{CO_2} (1 - \theta), (F_{CO_2} = K_4) \quad (50)$$

$$\theta_{C_3H_6} = F_{C_3H_6} (1 - \theta), (F_{C_3H_6} = K_9^{-1} P_{C_3H_6}) \quad (51)$$

$$\theta_{CO} = F_{CO} (1 - \theta), (F_{CO} = K_{10}^{-1} P_{CO}) \quad (52)$$

$$\theta_{H_2O} = F_{H_2O} (1 - \theta), (F_{H_2O} = K_{11}^{-1} P_{H_2O}) \quad (53)$$

$$\theta_{CO_2}^* = F_{CO_2}^* P_{CO_2} (1 - \theta), (F_{CO_2}^* = K_4 K_5) \quad (54)$$

$$\theta_{HCOO^-} = F_{HCOO^-} P_{CO_2}^{0.5} (1 - \theta), \quad (55)$$

$$F_{HCOO^-} = (K_4 K_5 K_6)^{0.5} (K_7 K_8 K_{10} K_{11})^{-0.5} P_{CO}^{0.5} P_{H_2O}^{0.5}$$

$$\theta_H = F_H P_{CO_2}^{-0.5} (1 - \theta), (F_H = (K_4 K_5 K_6 K_7 K_8 K_{10} K_{11})^{-0.5} P_{CO}^{0.5} P_{H_2O}^{0.5}) \quad (56)$$

$$\theta_{OH} = F_{OH} P_{CO_2}^{0.5} (1 - \theta), (F_{OH} = (K_4 K_5 K_6 K_7 K_8^{-1} K_{10} K_{11}^{-1})^{0.5} P_{CO}^{-0.5} P_{H_2O}^{0.5}) \quad (57)$$

$$\theta_{C_3H_7} = F_{C_3H_7} P_{C_3H_8} P_{CO_2}^{0.5} (1 - \theta) \quad (58)$$

$$(F_{C_3H_7} = (K_1^2 K_2^2 K_4 K_5 K_6 K_7 K_8 K_{10} K_{11})^{0.5} P_{CO}^{-0.5} P_{H_2O}^{-0.5})$$

$$\theta_{C_3H_8} = F_{C_3H_8} P_{C_3H_8} (1 - \theta), (F_{C_3H_8} = K_1) \quad (59)$$

377 we can use equation (35-36) to solve $(1 - \theta)$. The red-colored part in the final
 378 results at equation (50-59) can be defined as $F_i P_{C_3H_8}^{m_i} P_{CO_2}^{n_i}$, Where m_i, n_i are the
 379 indices of $P_{C_3H_8}$ and P_{CO_2} corresponding to each θ_i in equation (50-59):

$$\begin{aligned} \sum \theta_i + (1 - \theta) &= \sum F_i P_{C_3H_8}^{m_i} P_{CO_2}^{n_i} (1 - \theta) + (1 - \theta) \\ &= (1 + \sum F_i P_{C_3H_8}^{m_i} P_{CO_2}^{n_i}) (1 - \theta) \\ &= 1 \end{aligned} \quad (60)$$

380 Simplifying Equation (60) gives as follows:

$$(1 - \theta) = (1 + \sum F_i P_{C_3H_8}^{m_i} P_{CO_2}^{n_i})^{-1} \quad (61)$$

Where, the equation (15) can be regarded as a function of $P_{C_3H_8}$ or P_{CO_2} . Based on equation (61) and equation (50-59), the equation (15) can be simplified as follows:

$$\begin{aligned} r_3 &= \overrightarrow{k_3} \theta_{C_3H_7} (1 - \theta) - \overleftarrow{k_3} \theta_{C_3H_6} \theta_H \\ &\approx \frac{\overrightarrow{k_3} (K_1^2 K_2^2 K_4 K_5 K_6 K_7 K_8 K_{10} K_{11})^{0.5} P_{C_3H_8} P_{CO}^{-0.5} P_{H_2O}^{-0.5} P_{CO_2}^{0.5}}{(1 + \sum F_i P_{C_3H_8}^{m_i} P_{CO_2}^{n_i})^2} \\ &= \frac{\overrightarrow{k_3} (K_1^2 K_2^2 K_4 K_5 K_6 K_7 K_8 K_{10} K_{11})^{0.5} P_{CO}^{-0.5} P_{H_2O}^{-0.5} P_{C_3H_8} P_{CO_2}^{0.5}}{(1 + (F_{C_3H_6} + F_{CO} + F_{H_2O}) + (F_{CO_2} + F_{CO_2}^*) P_{CO_2} + F_H P_{CO_2}^{-0.5} + (F_{HCOO^-} + F_{OH}) P_{CO_2}^{0.5} + F_{C_3H_8} P_{C_3H_8} + F_{C_3H_7} P_{C_3H_8} P_{CO_2}^{0.5})^2} \\ &= \frac{\mu_3 P_{C_3H_8} P_{CO_2}^{0.5}}{(a_3 + b_3 P_{CO_2} + c_3 P_{CO_2}^{-0.5} + d_3 P_{CO_2}^{0.5} + e_3 P_{C_3H_8} + f_3 P_{C_3H_8} P_{CO_2}^{0.5})^2} \end{aligned} \quad (63)$$

$$(\mu_3 = \overrightarrow{k_3} (K_1^2 K_2^2 K_4 K_5 K_6 K_7 K_8 K_{10} K_{11})^{0.5} P_{CO}^{-0.5} P_{H_2O}^{-0.5}, a_3 = (1 + F_{C_3H_6} + F_{CO} + F_{H_2O}), b_3 = (F_{CO_2} + F_{CO_2}^*),$$

$$c_3 = F_H, d_3 = F_{HCOO^-} + F_{OH}, e_3 = F_{C_3H_8}, f_3 = F_{C_3H_7})$$

Therefore, when step (3) (2nd C-H activation) as the RDS, based on this derivation, the rate equation for the reaction is as equation (64), the reaction orders for $P_{C_3H_8}, \alpha = 1, -1, P_{CO_2}, \beta = 0.5, -1.5, 1.5, -0.5, 0.5$. $P_{C_3H_8}(\alpha)$, $P_{CO_2}(\beta)$ cannot be determined and requires further fitting and coupling with experimental data.

When assuming step (2) (1st C-H activation) as the RDS, based on the same derivation process:

$$\begin{aligned} r_2 &= \overrightarrow{k_2} \theta_{C_3H_8} (1 - \theta) - \overleftarrow{k_2} \theta_{C_3H_7} \theta_H \approx \frac{\overrightarrow{k_2} K_1 P_{C_3H_8}}{(1 + \sum A_i)^2} \\ &= \frac{\overrightarrow{k_2} K_1 P_{C_3H_8}}{(1 + (F_{C_3H_6} + F_{CO} + F_{H_2O}) + (F_{CO_2} + F_{CO_2}^*) P_{CO_2} + (F_H + F_{C_3H_7}) P_{CO_2}^{-0.5} + (F_{OH} + F_{HCOO^-}) P_{CO_2}^{0.5} + F_{C_3H_8} P_{C_3H_8})^2} \end{aligned} \quad (64)$$

the rate equation for the reaction is as equation (65), the reaction orders for $P_{C_3H_8}, \alpha = 1, -1, P_{CO_2}, \beta = 0, -2, 1, -1$, Since the value of β does not agree with the experimental results, the step (2) should not be the RDS.

When assuming step (6) (CO₂ activation) as the RDS, Based on the same derivation process:

$$r_6 = \vec{k}_6 \theta_{CO_2}^* (1 - \theta) - \vec{k}_6 \theta_{CO} \theta_O \approx \frac{\vec{k}_6 K_4 K_5 P_{CO_2}}{(1 + \sum A_i)^2} \quad (65)$$

$$= \frac{\vec{k}_6 K_4 K_5 P_{CO_2}}{1 + (F_{C_3H_6} + F_{CO} + F_{H_2O}) + F_{C_3H_8} P_{C_3H_8} + (F_{CO_2} + F_{CO_2}^*) P_{CO_2} + (F_H + F_{C_3H_7}) P_{C_3H_8}^{0.5} + (F_{OH} + F_{HCOO^-}) P_{C_3H_8}^{-0.5}}$$

the rate equation for the reaction is as equation (65), the reaction orders for $P_{C_3H_8}$, $\alpha = 0, -2, 0, -1, 1, 2$, P_{CO_2} , $\beta = 1, -1$. Since the value of β does not agree with the experimental results, the step (6) should not be the RDS.

When we substitute the experimentally measured data related to the kinetics into the formulas mathematically derived in the step (3) for fitting, we obtained the values of the relevant kinetic parameters in Eq. 63, as shown in Supplementary Table 4. Further, the fitted kinetic parameters were inserted into Eq. 63 to predict the rate of propylene formation under different conditions, and the predicted values were plotted against the actual measured values, with the horizontal coordinates being the experimentally measured true values and the vertical coordinates being the predicted values based on the kinetic equations, and the value of the linear relationship with $R^2 = 0.99$ was obtained, as shown in Fig. 4d. This fully justifies the step (3) (2nd C-H activation) as the RDS.

407 Supplementary Table 4. Kinetic equations and fitted parameter values of CO₂-PDH.

$$r_3 = \frac{\mu_3 P_{C_3H_8} P_{CO_2}^{0.5}}{(a_3 + b_3 P_{CO_2} + c_3 P_{CO_2}^{-0.5} + d_3 P_{CO_2}^{0.5} + e_3 P_{C_3H_8} + f_3 P_{C_3H_8} P_{CO_2}^{0.5})^2} \quad (63)$$

μ_3	58.04	a_3	2.23
b_3	0.03	c_3	0.67
d_3	-2.83	e_3	-0.48
f_3	0.12		

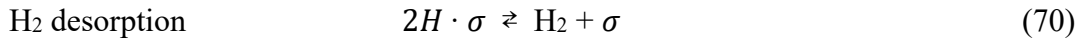
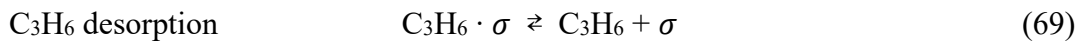
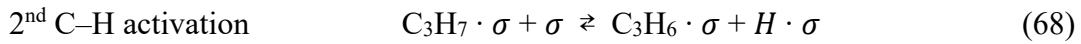
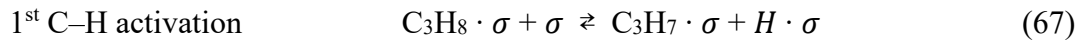
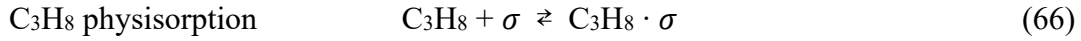
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Kinetic analysis of PDH

(A) Kinetic modeling of PDH on Pt₁Sn₇/CeO_x-Al₂O₃

As with CO₂-PDH, we derived the kinetic equation for the PDH on Pt₁Sn₇/CeO_x-Al₂O₃ reaction based on the same principle.



The elementary steps for propane dehydrogenation are shown in equation (66-70), which establish the surface concentrations of all intermediates involved. The conservation of the number of adsorption site is considered as follows:

$$\sum \theta_i + (1 - \theta) = 1 \quad (35)$$

The specific representation of each reaction rate is shown below:

$$r_1^{PDH} = \bar{k}_1 P_{\text{C}_3\text{H}_8} (1 - \theta) - \bar{k}_1 \theta_{\text{C}_3\text{H}_8} \quad (71) \quad r_2^{PDH} = \bar{k}_2 \theta_{\text{C}_3\text{H}_8} (1 - \theta) - \bar{k}_2 \theta_{\text{C}_3\text{H}_7} \theta_{\text{H}} \quad (72)$$

$$r_3^{PDH} = \bar{k}_3 \theta_{\text{C}_3\text{H}_7} (1 - \theta) - \bar{k}_3 \theta_{\text{C}_3\text{H}_6} \theta_{\text{H}} \quad (73) \quad r_4^{PDH} = \bar{k}_4 \theta_{\text{C}_3\text{H}_6} - \bar{k}_4 P_{\text{C}_3\text{H}_6} (1 - \theta) \quad (74)$$

$$r_5^{PDH} = \bar{k}_5 \theta_{\text{H}}^2 - \bar{k}_5 P_{\text{H}_2} (1 - \theta)^2 \quad (75)$$

(B) Kinetic Analysis based on quasi-stationary approximation

According to the quasi-stationary approximation, when a certain step is considered as the rate-determining step, other steps can be regarded to be in equilibrium. Therefore, the equilibrium constants are provided as follows:

$$K_1 = \frac{\theta_{\text{C}_3\text{H}_8}}{P_{\text{C}_3\text{H}_8} (1 - \theta)} \quad (76) \quad K_2 = \frac{\theta_{\text{C}_3\text{H}_7} \theta_{\text{H}}}{\theta_{\text{C}_3\text{H}_8} (1 - \theta)} \quad (77) \quad K_3 = \frac{\theta_{\text{C}_3\text{H}_6} \theta_{\text{H}}}{\theta_{\text{C}_3\text{H}_7} (1 - \theta)} \quad (78)$$

$$K_4 = \frac{P_{\text{C}_3\text{H}_6} (1 - \theta)}{\theta_{\text{C}_3\text{H}_6}} \quad (79) \quad K_5 = \frac{P_{\text{H}_2} (1 - \theta)^2}{\theta_{\text{H}}^2} \quad (80)$$

The kinetics of propane dehydrogenation has been widely reported in previous studies, The kinetics of propane dehydrogenation has been extensively reported in previous studies, and the first or second C-H bond activation is the RDS in this reaction.

Assuming step (2) as the RDS:

When step (2) (1st C–H activation) as the RDS, the site coverages of surface species are:

$$\theta_{C_3H_8} = K_1 P_{C_3H_8} (1 - \theta) \quad (81)$$

$$\theta_{C_3H_6} = K_4^{-1} P_{C_3H_6} (1 - \theta) \quad (82)$$

$$\theta_H = K_5^{-0.5} P_{H_2}^{0.5} (1 - \theta) \quad (83)$$

$$\theta_{C_3H_7} = K_3^{-1} K_4^{-1} K_5^{-0.5} P_{C_3H_6} P_{H_2}^{0.5} (1 - \theta) \quad (84)$$

We were able to notice that each equation (81-84) have $(1 - \theta)$ in its final result, and in this kinetic reaction conditions, where $P_{C_3H_8} \gg P_{C_3H_6}, P_{H_2}$. Meanwhile, the equation (72) can be regarded as a function of $P_{C_3H_8}$ and/or P_{H_2} . So, based on equation (81-84), each red-colored part is decomposed into $P_{H_2}, P_{C_3H_8}$ and a constant F_i as follows:

$$\theta_{C_3H_8} = F_{C_3H_8} P_{C_3H_8} (1 - \theta), \quad (F_{C_3H_8} = K_1) \quad (81)$$

$$\theta_{C_3H_6} = F_{C_3H_6} (1 - \theta), \quad (F_{C_3H_6} = K_4^{-1} P_{C_3H_6}) \quad (82)$$

$$\theta_H = F_H P_{H_2}^{0.5} (1 - \theta), \quad (F_H = K_5^{-0.5}) \quad (83)$$

$$\theta_{C_3H_7} = F_{C_3H_7} P_{H_2}^{0.5} (1 - \theta), \quad (F_{C_3H_7} = K_3^{-1} K_4^{-1} K_5^{-0.5} P_{C_3H_6}) \quad (84)$$

We can use equation (35-36) to solve $(1 - \theta)$. The red-colored part in the final results at equation (81-84) can be defined as $F_i P_{C_3H_8}^{m_i} P_{H_2}^{n_i}$, Where m_i, n_i are the indices of $P_{C_3H_8}$ and P_{H_2} corresponding to each θ_i in equation (81-84):

$$\begin{aligned} \sum \theta_i + (1 - \theta) &= \sum F_i P_{C_3H_8}^{m_i} P_{H_2}^{n_i} (1 - \theta) + (1 - \theta) \\ &= (1 + \sum F_i P_{C_3H_8}^{m_i} P_{H_2}^{n_i}) (1 - \theta) \\ &= 1 \end{aligned} \quad (85)$$

Simplifying Equation (85) gives as follows:

$$(1 - \theta) = (1 + \sum F_i P_{C_3H_8}^{m_i} P_{H_2}^{n_i})^{-1} \quad (86)$$

437 Based on equation (86), the equation (72) can be expressed as follows:

$$\begin{aligned}
 r_2^{PDH} &= \overrightarrow{k_2} \theta_{C_3H_8} (1 - \theta) - \overleftarrow{k_2} \theta_{C_3H_7} \theta_H \\
 &\approx \frac{\overrightarrow{k_2} K_1 P_{C_3H_8}}{(1 + K_1 P_{C_3H_8} + K_4^{-1} P_{C_3H_6} + K_5^{-0.5} P_{H_2}^{0.5} + K_3^{-1} K_4^{-1} K_5^{-0.5} P_{C_3H_6} P_{H_2}^{0.5})^2}
 \end{aligned} \tag{87}$$

438 The experiments were carried out under rather low conversions. The site coverage
 439 of propylene and other intermediates are expected to be rather small, which can be
 440 ignored. Assuming that hydrogen is the most abundant intermediates, the forward
 441 dehydrogenation reaction rates equation (87) can be simplified to equation (88).

$$\begin{aligned}
 r_2^{PDH} &= \overrightarrow{k_2} \theta_{C_3H_8} (1 - \theta) - \overleftarrow{k_2} \theta_{C_3H_7} \theta_H \\
 &\approx \frac{\overrightarrow{k_2} K_1 P_{C_3H_8}}{(1 + K_1 P_{C_3H_8} + K_4^{-1} P_{C_3H_6} + K_5^{-0.5} P_{H_2}^{0.5} + K_3^{-1} K_4^{-1} K_5^{-0.5} P_{C_3H_6} P_{H_2}^{0.5})^2} \\
 &\approx \frac{\overrightarrow{k_2} K_1 P_{C_3H_8}}{(1 + K_5^{-0.5} P_{H_2}^{0.5})^2} \\
 &= \frac{\mu_2^{PDH} P_{C_3H_8}}{(1 + K_5^{-0.5} P_{H_2}^{0.5})^2} \\
 (\mu_2^{PDH} &= \overrightarrow{k_2} K_1)
 \end{aligned} \tag{88}$$

442 Assuming step (3) as the RDS:

443 When step (3) (2nd C–H activation) as the RDS, the site coverages of surface
 444 species are:

$$\theta_{C_3H_8} = K_1 P_{C_3H_8} (1 - \theta) \tag{89}$$

$$\theta_{C_3H_6} = K_4^{-1} P_{C_3H_6} (1 - \theta) \tag{90}$$

$$\theta_H = K_5^{-0.5} P_{H_2}^{0.5} (1 - \theta) \tag{91}$$

$$\theta_{C_3H_7} = K_1 K_2 K_5^{0.5} P_{H_2}^{-0.5} P_{C_3H_8} (1 - \theta) \tag{92}$$

445 the equation (73) can be expressed as follows:

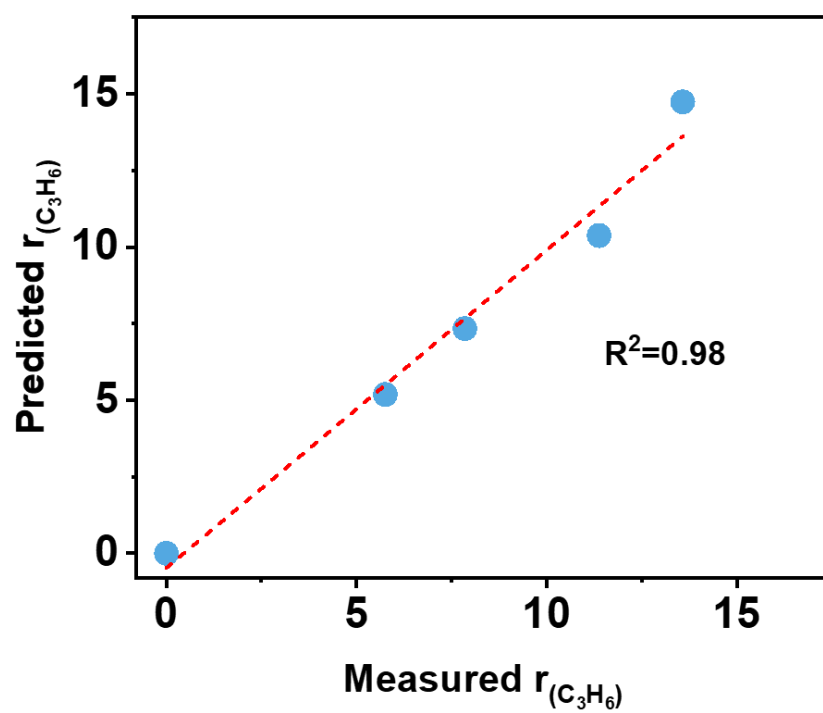
$$\begin{aligned}
r_3^{PDH} &= \overrightarrow{k_3} \theta_{C_3H_7} (1 - \theta) - \overleftarrow{k_3} \theta_{C_3H_6} \theta_H \\
&\approx \frac{\overrightarrow{k_3} K_1 K_2 K_5^{0.5} P_{H_2}^{-0.5} P_{C_3H_8}}{(1 + K_1 P_{C_3H_8} + K_4^{-1} P_{C_3H_6} + K_5^{-0.5} P_{H_2}^{0.5} + K_3^{-1} K_4^{-1} K_5^{-0.5} P_{C_3H_6} P_{H_2}^{0.5})^2} \\
&\approx \frac{\overrightarrow{k_3} K_1 K_2 K_5^{0.5} P_{H_2}^{-0.5} P_{C_3H_8}}{(1 + K_5^{-0.5} P_{H_2}^{0.5})^2} = \frac{\mu_3^{PDH} P_{H_2}^{-0.5} P_{C_3H_8}}{(1 + K_5^{-0.5} P_{H_2}^{0.5})^2} \\
(\mu_3^{PDH} &= \overrightarrow{k_3} K_1 K_2 K_5^{0.5})
\end{aligned} \tag{93}$$

When we substitute the experimentally measured data related to the kinetics into the formulas mathematically derived in the step (2) and step (3) for fitting, we obtained the values of the relevant kinetic parameters in Eq. 88 and Eq. 93, as shown in Supplementary Table 5. Further, the fitted kinetic parameters were inserted into Eq. 88 and Eq. 93 to predict the rate of propylene formation under different conditions, and the predicted values were plotted against the actual measured values, with the horizontal coordinates being the experimentally measured true values and the vertical coordinates being the predicted values based on the kinetic equations. When step (2) (1st C–H activation) as the RDS, large differences between projected and actual values. But when step (3) (2nd C–H activation) as the RDS, the value of the linear relationship with $R^2 = 0.99$ was obtained, as shown in Fig. S17. This fully justifies the step (3) (2nd C–H activation) as the RDS.

458 Supplementary Table 5. Kinetic equations and fitted parameter values of PDH.

$r_2^{PDH} = \frac{\mu_2^{PDH} P_{C_3H_8}}{(1 + K_5^{-0.5} P_{H_2}^{0.5})^2}$		(88)
μ_2^{PDH}		2.0
$K_5^{-0.5}$		30.41
$r_3^{PDH} = \frac{\mu_3^{PDH} P_{H_2}^{-0.5} P_{C_3H_8}}{(1 + K_5^{-0.5} P_{H_2}^{0.5})^2}$		(93)
μ_3^{PDH}		2.47
$K_5^{-0.5}$		3.93×10^{16}

459



460

461 Supplementary Figure 24 | Comparison of predicted (from Eq. (93)) and experimental

462 C_3H_6 formation rates (obtained under differential reactor).

Kinetic analysis of RWGS

I Mars-van Krevelen (MvK) mechanism

The elementary step:



Where the H*, O_{lattice} and $\square_{\text{vac}}$ represent H* coverage, lattice oxygen and oxygen vacancies respectively.

The rate equation expression for each elementary step is:

Step 1	$H_2 + 2^* \rightleftharpoons 2H^*$	$r_1 = k_1^+ P_{H_2} (1 - \theta_H)^2 - k_1^- \theta_H^2$	M4
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Step 2	$2H^* + O_{\text{lattice}} \rightleftharpoons H_2O + \square_{\text{vac}} + 2^*$	$r_2 = k_2^+ \theta_H^2 (1 - \theta_{\square}) - k_2^- P_{H_2O} \theta_{\square} (1 - \theta_H)^2$	M5
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Step 3	$CO_2 + \square_{\text{vac}} \rightleftharpoons CO + O_{\text{lattice}}$	$r_3 = k_3^+ P_{CO_2} \theta_{\square} - k_3^- P_{CO} (1 - \theta_{\square})$	M6
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Key Simplification: For most metal oxides (e.g., CeO₂), the catalytic sites for lattice oxygen and oxygen vacancies are distinct from those for H₂ adsorption, therefore:

$$\theta_* + \theta_H = 1 \quad \text{M7}$$

$$\theta_O + \theta_{\square} = 1 \quad \text{M8}$$

When the consumption of lattice oxygen by H₂ is the RDS (step 2).

Assumptions:

1. The dissociative adsorption of H₂ reaches rapid equilibrium.

$$K_1 = \frac{\theta_H^2}{P_{H_2}(1 - \theta_H)^2} \quad \text{M9}$$

474 Simplified, we obtain:

$$\theta_H = \frac{K_1^{\frac{1}{2}} P_{H_2}^{\frac{1}{2}}}{1 + K_1^{\frac{1}{2}} P_{H_2}^{\frac{1}{2}}} \quad \text{M10}$$

475 Under most experimental conditions, since $K_1^{\frac{1}{2}} P_{H_2}^{\frac{1}{2}} \ll 1$, therefore:

$$\theta_H = K_1^{\frac{1}{2}} P_{H_2}^{\frac{1}{2}} \quad \text{M11}$$

476 2. The CO₂ adsorption and dissociation reaches rapid equilibrium.

$$K_3 = \frac{P_{CO}(1 - \theta_{\square})}{P_{CO_2} \theta_{\square}} \quad \text{M12}$$

$$\theta_{\square} = \frac{P_{CO}}{K_3 P_{CO_2} + P_{CO}} \quad \text{M13}$$

477 Using M11 and M13, simplify M5 to obtain:

$$\begin{aligned} r_2 &= k_2^+ \theta_H^2 (1 - \theta_{\square}) - k_2^- P_{H_2O} \theta_{\square} (1 - \theta_H)^2 \approx k_2^+ \theta_H^2 (1 - \theta_{\square}) \\ &= \frac{k_2^+ K_1 K_3^2 P_{H_2} P_{CO_2}^2}{(K_3 P_{CO_2} + P_{CO})^2} \end{aligned} \quad \text{M14}$$

478 Since the $P_{CO} \ll P_{CO_2}, P_{H_2}$, here we can let $P_{CO} \approx 0$, the M14 allow to express:

$$r_2 = k_2^+ \theta_H^2 (1 - \theta_{\square}) = k_2^+ K_1 P_{H_2} \quad \text{M15}$$

479 **When the CO₂ adsorption and dissociation is the RDS (step 3).**

$$K_2 = \frac{P_{H_2O} \theta_{\square} (1 - \theta_H)^2}{\theta_H^2 (1 - \theta_{\square})} \quad \text{M16}$$

$$\theta_{\square} = \frac{K_1 K_2 P_{H_2}}{P_{H_2O} (1 - \sqrt{K_1 P_{H_2}})^2 + K_1 K_2 P_{H_2}} \quad \text{M17}$$

480 Using M11 and M17, simplify M6 to obtain:

$$\begin{aligned} r_3 &= k_3^+ P_{CO_2} \theta_{\square} - k_3^- P_{CO} (1 - \theta_{\square}) \approx k_3^+ P_{CO_2} \theta_{\square} \\ &= \frac{k_3^+ P_{CO_2} K_1 K_2 P_{H_2}}{P_{H_2O} (1 - \sqrt{K_1 P_{H_2}})^2 + K_1 K_2 P_{H_2}} \end{aligned} \quad \text{M18}$$

481 Since the $P_{H_2O} \ll P_{CO_2}, P_{H_2}$, here we can let $P_{H_2O} \approx 0$, the M18 allow to express:

$$r_3 = k_3^+ P_{CO_2} \theta_{\square} = k_3^+ P_{CO_2} \quad \text{M19}$$

482 **When the H_2 adsorption and dissociation is the RDS (step 1).**

$$K_2 = \frac{P_{H_2O} \theta_{\square} (1 - \theta_H)^2}{\theta_H^2 (1 - \theta_{\square})} \quad \text{M20}$$

$$K_3 = \frac{P_{CO} (1 - \theta_{\square})}{P_{CO_2} \theta_{\square}} \quad \text{M21}$$

483 Using M20 and M21, the θ_H allow to express:

$$\theta_H = \frac{\sqrt{P_{H_2O} P_{CO}}}{\sqrt{K_2 K_3 P_{CO_2}} + \sqrt{P_{H_2O} P_{CO}}} \quad \text{M22}$$

484 Using M22, simplify M4 to obtain:

$$\begin{aligned} r_1 &= k_1^+ P_{H_2} (1 - \theta_H)^2 - k_1^- \theta_H^2 \approx k_1^+ P_{H_2} (1 - \theta_H)^2 \\ &= \frac{k_1^+ P_{H_2} K_2 K_3 P_{CO_2}}{(\sqrt{K_2 K_3 P_{CO_2}} + \sqrt{P_{H_2O} P_{CO}})^2} \end{aligned} \quad \text{M22}$$

485 Since the $P_{H_2O}, P_{CO} \ll P_{CO_2}, P_{H_2}$, here we can let $P_{H_2O}, P_{CO} \approx 0$, the M22 allow
486 to express:

$$r_1 = k_1^+ P_{H_2} (1 - \theta_H)^2 = k_1^+ P_{H_2} \quad \text{M22}$$

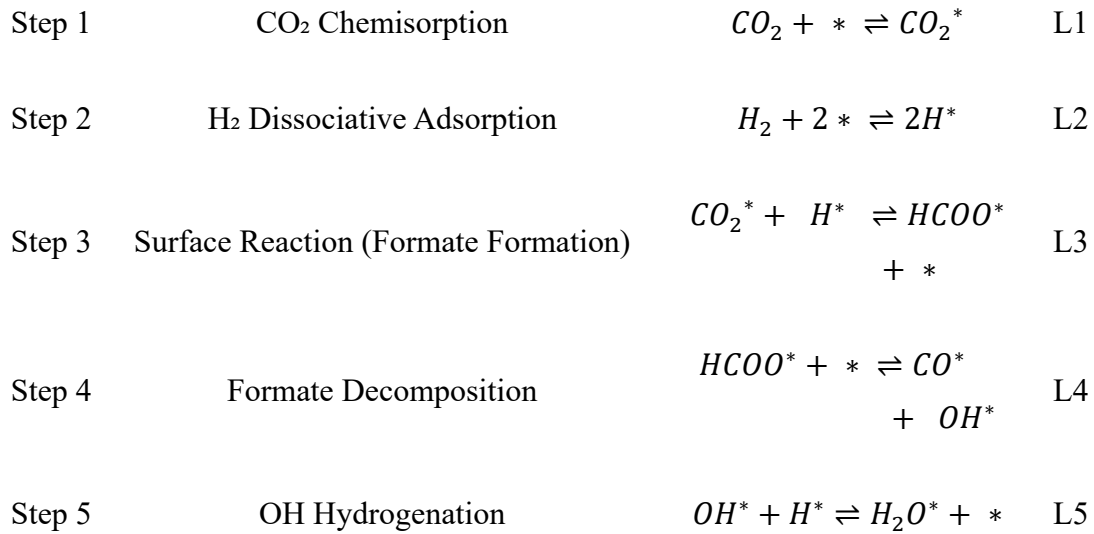
Based on the preceding mechanistic formulations, the reaction orders for components CO₂ and H₂ under different rate-determining step (RDS) assumptions are derived as follows:

Supplementary Table 6. The reaction orders for RWGS derived from the Mars-van Krevelen (MvK) mechanism.

RDS Scenario	Rate Equation	Reaction Orders ($P_{CO_2}^\alpha$ or $P_{H_2}^\beta$)	
		α	β
H ₂ adsorption and dissociation	$r_1 = k_1^+ P_{H_2}$	0	1
Lattice oxygen depletion	$r_2 = k_2^+ K_1 P_{H_2}$	1	0
CO ₂ adsorption and dissociation	$r_3 = k_3^+ P_{CO_2}$	0	1

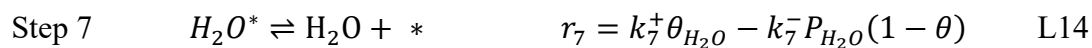
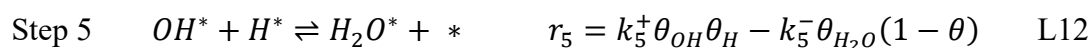
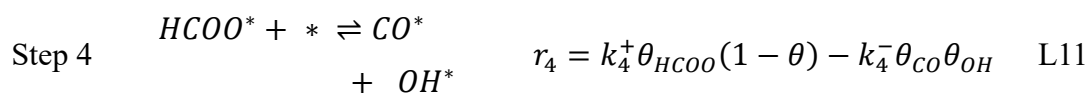
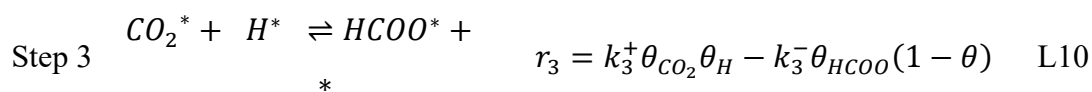
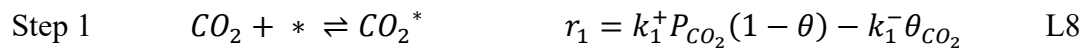
II Langmuir-Hinshelwood (L-H) mechanism

The elementary step:





494 The rate equation expression for each elementary step is:



495 According to the quasi-stationary approximation, when a certain step is considered
496 as the rate-determining step, other steps can be regarded to be in equilibrium. Therefore,
497 the equilibrium constants are provided as follows:



$$\text{Step 6} \quad CO^* \rightleftharpoons CO + * \quad K_6 = \frac{k_6^+}{k_6^-} = \frac{P_{CO}(1-\theta)}{\theta_{CO}} \quad \text{L20}$$

$$\text{Step 7} \quad H_2O^* \rightleftharpoons H_2O + * \quad K_7 = \frac{k_7^+}{k_7^-} = \frac{P_{H_2O}(1-\theta)}{\theta_{H_2O}} \quad \text{L21}$$

Note that K_i cannot be defined when the step i is considered as the RDS (six equilibrium constants can be used). Besides, the conservation of the number of adsorption site is considered as follows:

$$\theta_H + \theta_{CO_2} + \theta_{HCOO} + \theta_{OH} + \theta_{CO} + \theta_{H_2O} + (1-\theta) = 1 \quad \text{L22}$$

Each θ_i except $(1-\theta)$ is expressed as a function of K_i , P_j , and $(1-\theta)$, then the site conservation equation is solved for $(1-\theta)$. Thus, each coverage and reaction rate can be expressed as a function of K_i , and P_j :

$$\theta_L = f_L(K_i, P_j) \quad \text{L23}$$

$$r_L = \overrightarrow{r_L} - \overleftarrow{r_L} = \overrightarrow{k_m} \prod_m \overrightarrow{P_m} \prod_j f_m(K_i, P_j) - \overleftarrow{k_m} \prod_m \overleftarrow{P_j} \prod_m g_m(K_i, P_j) \quad \text{L24}$$

Then, K_i and P_j except P_{CO_2} and P_{H_2} which makes r_L a function of P_{CO_2} or P_{H_2} are regarded as constants in a series of catalytic experiments, which makes r_L a function of P_{CO_2} or P_{H_2} . This function can be approximated to a simplified form at a certain limit of coefficients included in the equation as follows:

$$r_L = k \cdot P_{CO_2}^\alpha \cdot P_{H_2}^\beta \quad \text{L25}$$

where, k is an apparent rate constant. α , and β represent kinetic parameters that can be obtained by regressing the measured rate data to these rate equations.

Assuming step (3) as the RDS:

$$\theta_{CO_2} = K_1 P_{CO_2} (1-\theta) = L_{CO_2} P_{CO_2} (1-\theta) \quad (L_{CO_2} = K_1) \quad \text{L26}$$

$$\theta_H = K_2^{0.5} P_{H_2}^{0.5} (1-\theta) = L_{H_2} P_{H_2}^{0.5} (1-\theta) \quad (L_H = K_2^{0.5}) \quad \text{L27}$$

$$\begin{aligned} \theta_{HCOO} &= K_2^{-0.5} K_4^{-1} K_5^{-1} K_6^{-1} K_7^{-1} P_{CO} P_{H_2O} P_{H_2}^{-0.5} (1-\theta) \\ &= L_{HCOO} P_{H_2}^{-0.5} (1-\theta) \end{aligned} \quad \begin{aligned} (L_{HCOO} &= K_2^{-0.5} K_4^{-1} K_5^{-1} K_6^{-1} K_7^{-1} P_{CO} P_{H_2O}) \end{aligned} \quad \text{L28}$$

$$\begin{aligned} \theta_{OH} &= K_2^{-0.5} K_5^{-1} K_7^{-1} P_{H_2O} P_{H_2}^{-0.5} (1-\theta) \\ &= L_{OH} P_{H_2}^{-0.5} (1-\theta) \end{aligned} \quad (L_{OH} = K_2^{-0.5} K_5^{-1} K_7^{-1} P_{H_2O}) \quad \text{L29}$$

$$\theta_{CO} = K_6^{-1} P_{CO} (1 - \theta) \quad (L_{CO} = K_6^{-1}) \quad L30$$

$$\theta_{H_2O} = K_7^{-1} P_{H_2O} (1 - \theta) \quad (L_{H_2O} = K_7^{-1}) \quad L31$$

511 we can use equation L22 to solve $(1 - \theta)$. Equation (L26-L31) can be defined as
 512 $L_i P_{CO_2}^{m_i} P_{H_2}^{n_i}$, Where m_i , n_i are the indices of P_{CO_2} and P_{H_2} corresponding to each θ_i
 513 in equation (L26-L31):

$$\begin{aligned} \sum \theta_i + (1 - \theta) &= \sum F_i P_{CO_2}^{m_i} P_{H_2}^{n_i} (1 - \theta) + (1 - \theta) \\ &= (1 + \sum F_i P_{CO_2}^{m_i} P_{H_2}^{n_i}) (1 - \theta) \\ &= 1 \end{aligned} \quad L32$$

514 Simplifying Equation L32 gives as follows:

$$(1 - \theta) = (1 + \sum F_i P_{CO_2}^{m_i} P_{H_2}^{n_i})^{-1} \quad L33$$

515 Where, the equation (15) can be regarded as a function of P_{CO_2} or P_{H_2} . Based on
 516 equation L33 and equation L26-L31, the equation L10 can be simplified as follows:

$$\begin{aligned} r_3 &= k_3^+ \theta_{CO_2} \theta_H - k_3^- \theta_{HCOO} (1 - \theta) \\ &\approx k_3^+ \theta_{CO_2} \theta_H \end{aligned} \quad L34$$

$$= \frac{k_3^+ P_{CO_2} P_{H_2}^{0.5}}{[(1 + L_{CO} + L_{H_2O}) + L_{CO_2} P_{CO_2} + L_H P_{H_2}^{0.5} + (L_{HCOO} + L_{OH}) P_{H_2}^{-0.5}]^2}$$

517 Therefore, when step (3) (Surface Reaction (Formate Formation)) as the RDS,
 518 based on this derivation, the rate equation for the reaction is as equation L34.

519 When assuming that $(1 + L_{CO} + L_{H_2O}) \gg L_{CO_2}, L_H$ and $(L_{HCOO} + L_{OH})$, the
 520 reaction orders are determined as follows: $\alpha = 1$, $\beta = 0.5$;

521 When assuming that $L_{CO_2} \gg (1 + L_{CO} + L_{H_2O}), L_H$ and $(L_{HCOO} + L_{OH})$, the
 522 reaction orders are determined as follows: $\alpha = -1$, $\beta = 0.5$;

523 When assuming that $L_H \gg (1 + L_{CO} + L_{H_2O}), L_{CO_2}$ and $(L_{HCOO} + L_{OH})$, the
 524 reaction orders are determined as follows: $\alpha = 1$, $\beta = -0.5$;

When assuming that $(L_{HCOO} + L_{OH}) \gg (1 + L_{CO} + L_{H_2O}), L_{CO_2}$ and L_H , the reaction orders are determined as follows: $\alpha = 1, \beta = 1.5$.

Thus, the possible reaction orders for CO_2 (α) include: -1, 1; and possible reaction orders for H_2 (β) include: -0.5, 0.5, 1.5.

Assuming step (4) as the RDS:

We can derive the rate expression when Step 4 is the rate-determining step using the same methodology, as demonstrated in L35:

$$\begin{aligned} r_4 &= k_4^+ \theta_{HCOO} (1 - \theta) - k_4^- \theta_{CO} \theta_{OH} \\ &\approx k_4^+ \theta_{HCOO} (1 - \theta) \\ &= \frac{k_4^+ K_1 K_2^{0.5} K_3 P_{CO_2} P_{H_2}^{0.5}}{[(1 + L_{CO} + L_{H_2O}) + L_{CO_2} P_{CO_2} + L_H P_{H_2}^{0.5} + L_{OH} P_{H_2}^{-0.5} + L_{HCOO} P_{CO_2} P_{H_2}^{0.5}]} \end{aligned} \quad \begin{array}{l} \text{L3} \\ 5 \end{array}$$

Therefore, when step (4) (Formate Decomposition) as the RDS, based on this derivation, the rate equation for the reaction is as equation L35.

When assuming that $(1 + L_{CO} + L_{H_2O}) \gg L_{CO_2}, L_H, L_{OH}$ and L_{HCOO} , the reaction orders are determined as follows: $\alpha = 1, \beta = 0.5$;

When assuming that $L_{CO_2} \gg (1 + L_{CO} + L_{H_2O}), L_H, L_{OH}$ and L_{HCOO} , the reaction orders are determined as follows: $\alpha = -1, \beta = 0.5$;

When assuming that $L_H \gg (1 + L_{CO} + L_{H_2O}), L_{CO_2}, L_{OH}$ and L_{HCOO} , the reaction orders are determined as follows: $\alpha = 1, \beta = -0.5$;

When assuming that $L_{OH} \gg (1 + L_{CO} + L_{H_2O}), L_{CO_2}, L_H$ and L_{HCOO} , the reaction orders are determined as follows: $\alpha = 1, \beta = 1.5$;

When assuming that $L_{HCOO} \gg (1 + L_{CO} + L_{H_2O}), L_{CO_2}, L_H$ and L_{OH} , the reaction orders are determined as follows: $\alpha = -1, \beta = -0.5$;

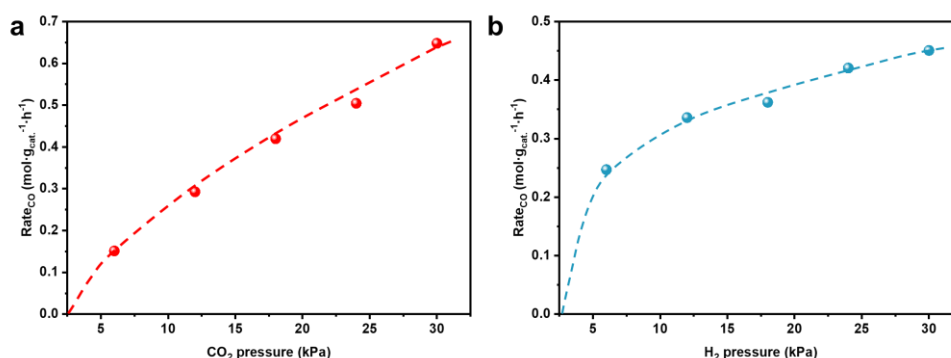
Thus, the possible reaction orders for CO_2 (α) include: -1, 1; and possible reaction orders for H_2 (β) include: -0.5, 0.5, 1.5.

We have compiled the reaction order analysis for scenarios where both Step 3 and Step 4 serve as rate-determining steps (RDS) into Supplementary Table 6 when use L-H mechanism, as listed below:

Supplementary Table 7. The reaction orders for RWGS derived from the Langmuir-Hinshelwood (L-H) mechanism.

RDS Scenario	Rate Equation	Reaction Orders ($P_{CO_2}^\alpha$ or $P_{H_2}^\beta$)	
		α	β
Formate Formation	$r_3 = \frac{k_3^+ P_{CO_2} P_{H_2}^{0.5}}{[(1 + L_{CO} + L_{H_2O}) + L_{CO_2} P_{CO_2} + L_H P_{H_2}^{0.5} + (L_{HCOO} + L_{OH}) P_{H_2}^{-0.5}]^2}$	1	0.5
		-1	0.5
		1	-0.5
		1	1.5
Formate Decomposition	$r_4 = \frac{k_4^+ K_1 K_2^{0.5} K_3 P_{CO_2} P_{H_2}^{0.5}}{[(1 + L_{CO} + L_{H_2O}) + L_{CO_2} P_{CO_2} + L_H P_{H_2}^{0.5} + L_{OH} P_{H_2}^{-0.5} + L_{HCOO} P_{CO_2} P_{H_2}^{0.5}]^2}$	1	0.5
		-1	0.5
		1	-0.5
		1	1.5
		-1	-0.5

To validate CO₂ activation kinetics on CeO₂, we conducted RWGS kinetic experiments over Pt₁Sn₇/CeO_x-Al₂O₃. As detailed below, the reaction exhibits non-zero-order dependence for both CO₂ (0.89) and H₂ (0.48) across varied partial pressures, excluding the Mars-van Krevelen (MvK) mechanism for CO₂ activation on CeO_x in the tandem system. Based on the derivation from the Langmuir-Hinshelwood (L-H) mechanism, we obtain reaction orders (e.g., $\alpha = 1$, $\beta = 0.5$) that closely align with experimental values ($\alpha = 0.89$, $\beta = 0.48$). Therefore, the L-H mechanism provides a more appropriate description for the catalytic system studied herein.



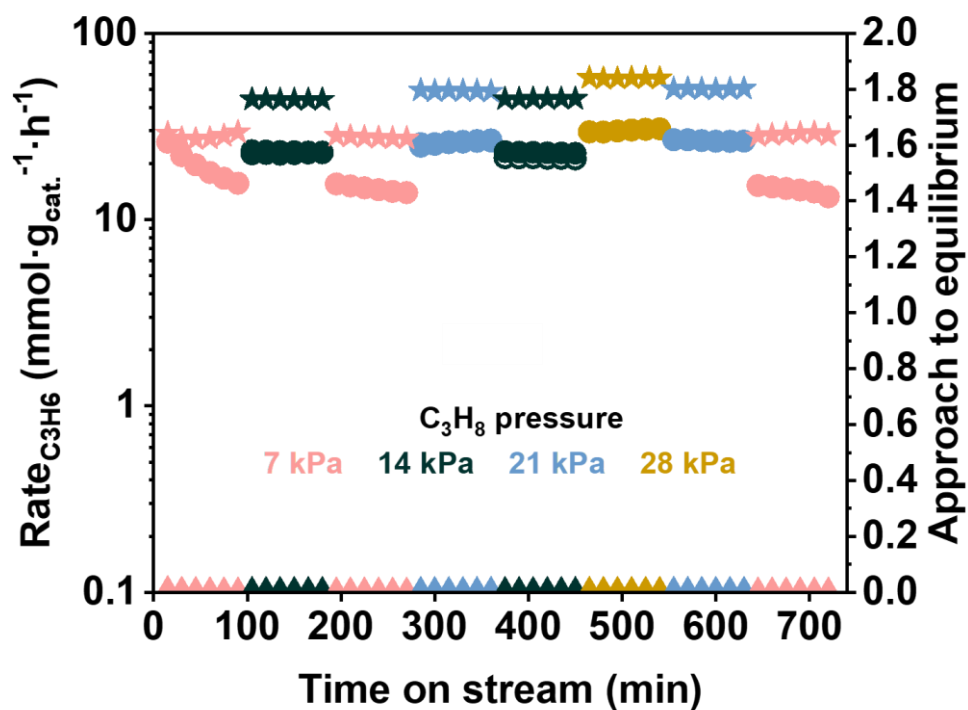
Supplementary Figure 25 | Kinetic experiments for RWGS with different CO₂ or H₂ partial pressures on Pt₁Sn₇/CeO_x-Al₂O₃. Test conditions: differential reactor, $T = 500$ °C, 100 kPa, 0.05 g. For different CO₂ partial pressure, CO₂ : H₂ : N₂ = x : 14.2 : (85.8-x) kPa; For different H₂ partial pressure, CO₂ : H₂ : N₂ = 14.2 : x : (85.8-x) kPa. x =

564 6/12/18/24/30 kPa. Total flow rate: 70 mL·min⁻¹.

565 Supplementary Table 8. Apparent reaction orders measured under varying P_{CO_2} and
566 P_{H_2} for Pt₁Sn₇/CeO_x-Al₂O₃ at RWGS reaction.

	Reaction Orders	
Variables	$P_{CO_2} : \alpha$	$P_{H_2} : \beta$
Value	0.89	0.48

567



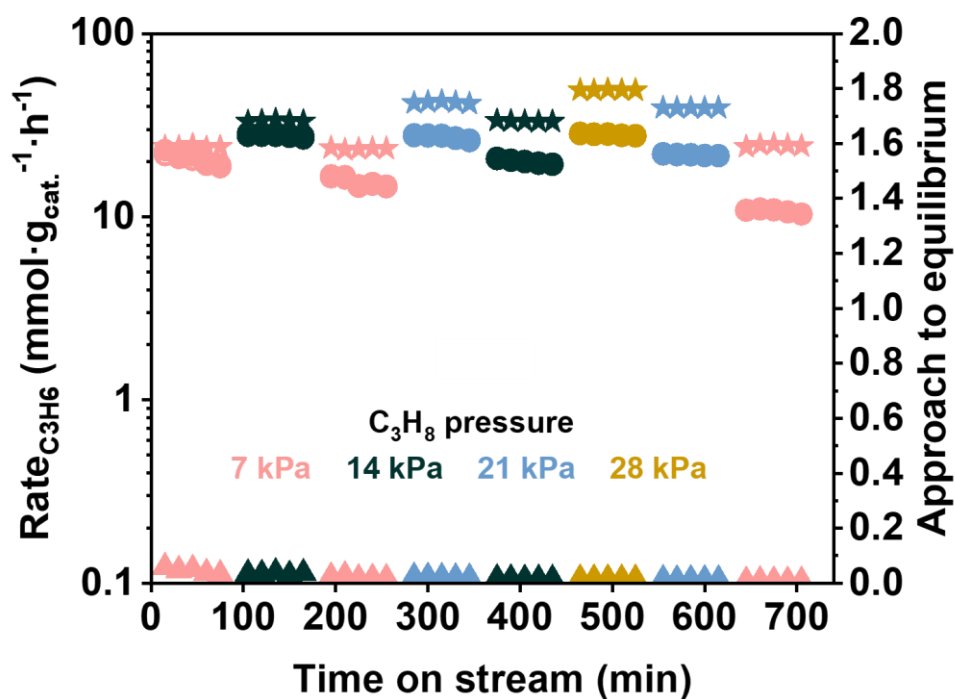
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569 Supplementary Figure 26 | Kinetic experiments with different propane partial pressures

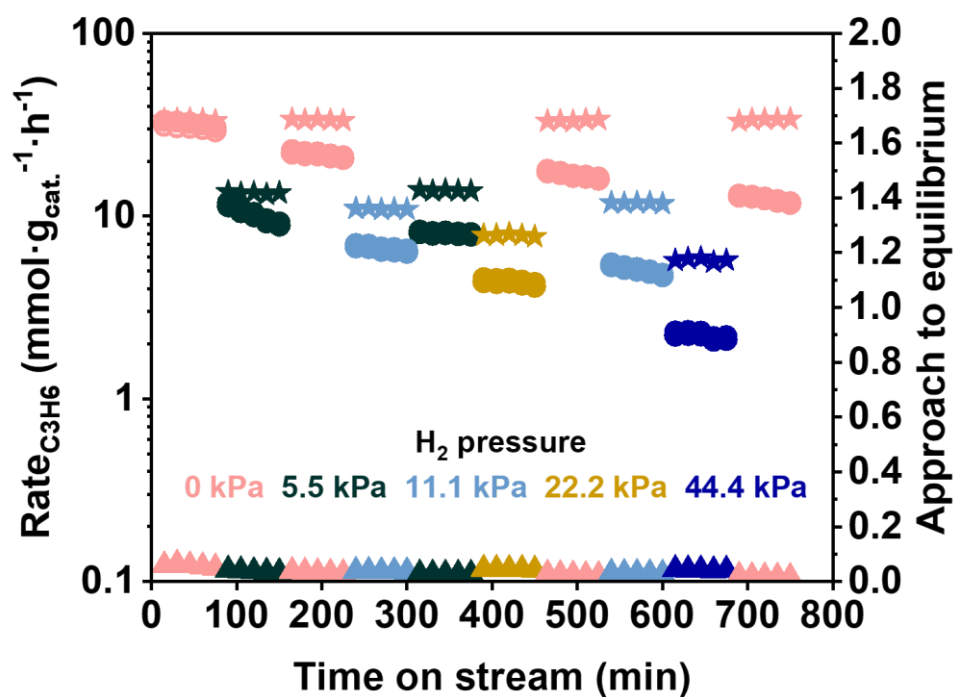
570 on Pt₁Sn₇/CeO_x-Al₂O₃. Rate of C₃H₆ production, hollow circle: r_m , triangular: η , solid

571 circle: r_f , pentagram: r_c . Test conditions: differential reactor, $T = 500$ °C, 100 kPa, CO₂-

572 PDH: 0.05 g, CO₂ : C₃H₈ : N₂ = 8.6 : x : (77.4-x) kPa, Total flow rate: 35 mL·min⁻¹.



Supplementary Figure 27 | Kinetic experiments with different propane partial pressures on Pt₁Sn₇/CeO_x-Al₂O₃. Rate of C₃H₆ production, hollow circle: r_m , triangular: η , solid circle: r_f , pentagram: r_c . Test conditions: differential reactor, $T = 500\text{ }^\circ\text{C}$, 100 kPa, PDH: 0.05 g, C₃H₈ : N₂ = $x : (86-x)$ kPa, Total flow rate: 35 mL·min⁻¹.



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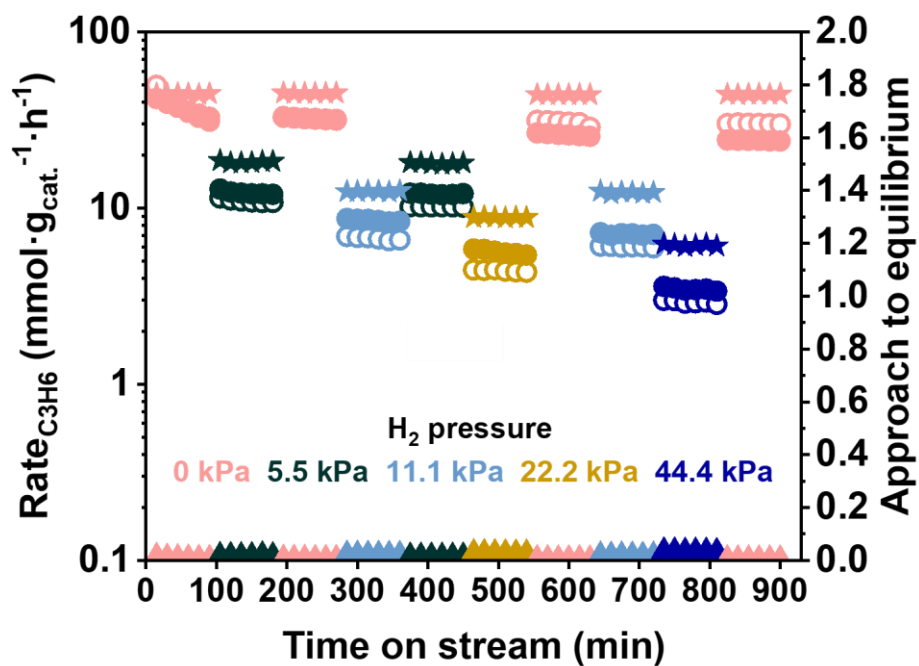
580 Supplementary Figure 28 | Kinetic experiments with different hydrogen partial

581 pressures on Pt₁Sn₇/CeO_x-Al₂O₃. Rate of C₃H₆ production, hollow circle: r_m , triangular:

582 η , solid circle: r_f , pentagram: r_c . Test conditions: differential reactor, $T = 500\text{ }^\circ\text{C}$, 100

583 kPa, PDH: 0.05 g, C₃H₈ : H₂ : N₂ = 14 : x : (86-x) kPa, Total flow rate: 35 mL·min⁻¹.

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586 Supplementary Figure 29 | Kinetic experiments with different hydrogen partial

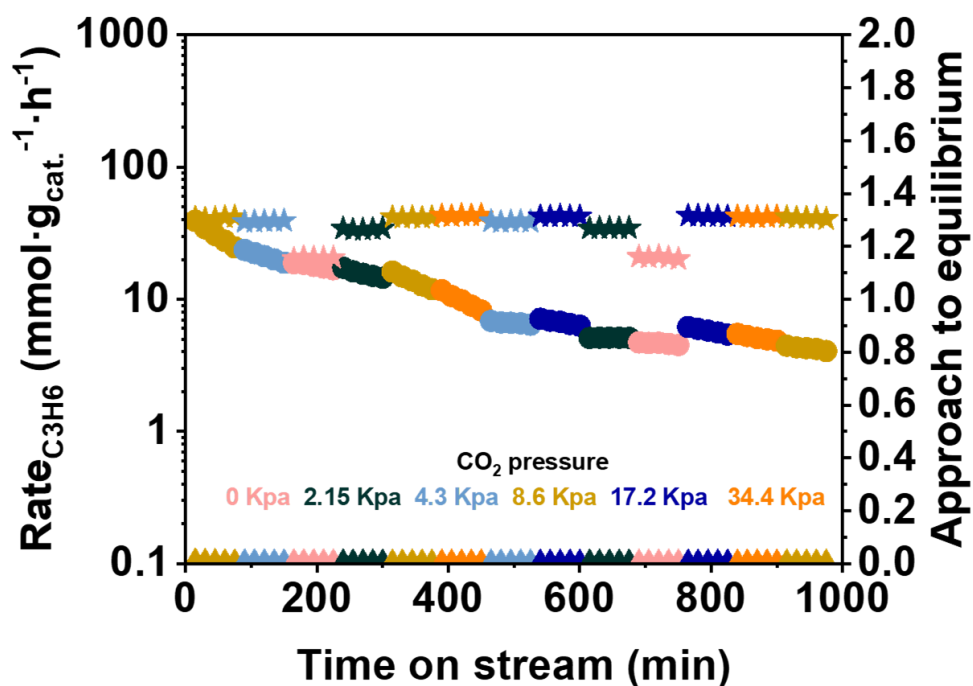
587 pressures on Pt₁Sn₇/CeO_x-Al₂O₃. Rate of C₃H₆ production, hollow circle: r_m, triangular:

588 η, solid circle: r_f, pentagram: r_c. Test conditions: differential reactor, T = 500 °C, 100

589 kPa, CO₂-PDH: 0.05 g, CO₂ : C₃H₈ : H₂ : N₂ = 8.6 : 14 : x : (77.4-x) kPa, Total flow

590 rate: 35 mL·min⁻¹.

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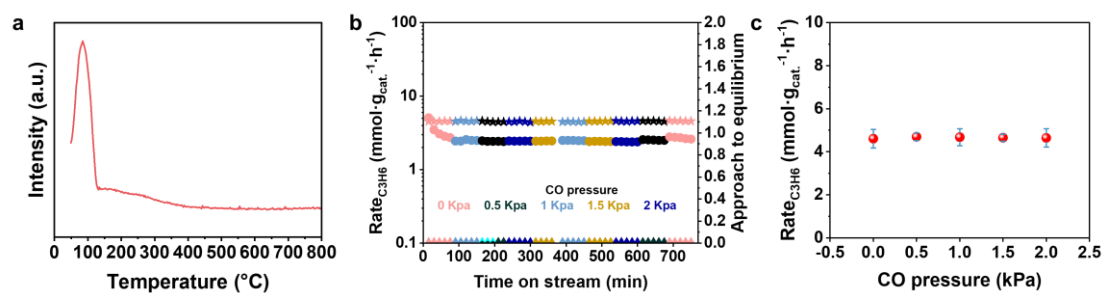
593 Supplementary Figure 30 | Kinetic experiments with different carbon dioxide partial

594 pressures on Pt₁Sn₇/CeO_x-Al₂O₃. Rate of C₃H₆ production, hollow circle: r_m , triangular:

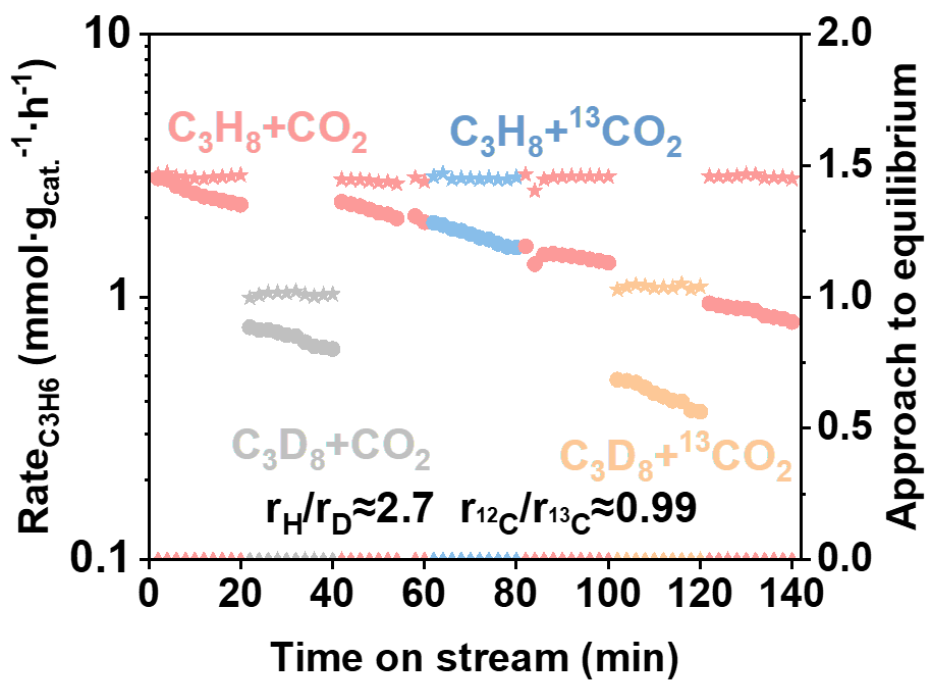
595 η , solid circle: r_f , pentagram: r_c . Test conditions: differential reactor, $T = 500$ °C, 100

596 kPa, CO₂-PDH: 0.05 g, CO₂ : C₃H₈ : N₂ = x : 9 : (91- x) kPa, Total flow rate: 35 mL·min⁻¹

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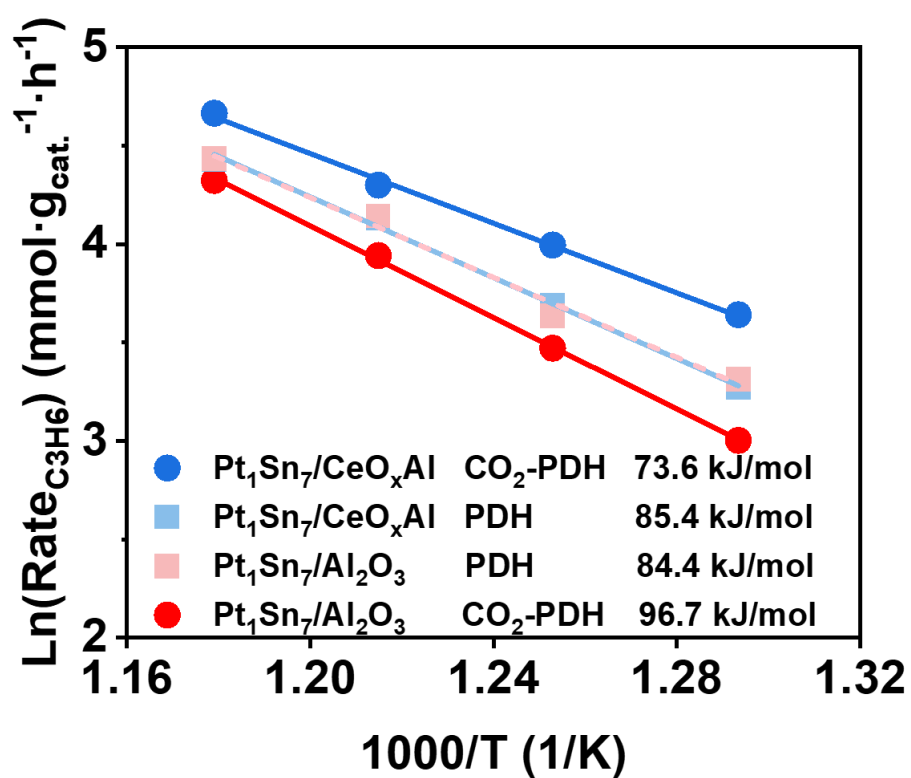
Supplementary Figure 31 | (a) CO-TPD on Pt₁Sn₇/CeO_x-Al₂O₃, and (b-c) kinetic experiments with different carbon monoxide partial pressures on Pt₁Sn₇/CeO_x-Al₂O₃. Rate of C₃H₆ production, hollow circle: r_m , triangular: η , solid circle: r_f , pentagram: r_c . Test conditions: differential reactor, $T = 500$ °C, 100 kPa, CO₂-PDH: 0.05 g, CO : CO₂ : C₃H₈ : N₂ = x : 8.6 : 14 : (77.4-x) kPa, , Total flow rate: 35 mL·min⁻¹.



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606 Supplementary Figure 32 | KIEs obtained under differential reactor of CO₂-PDH on

607 Pt₁Sn₇/CeO_x-Al₂O₃.

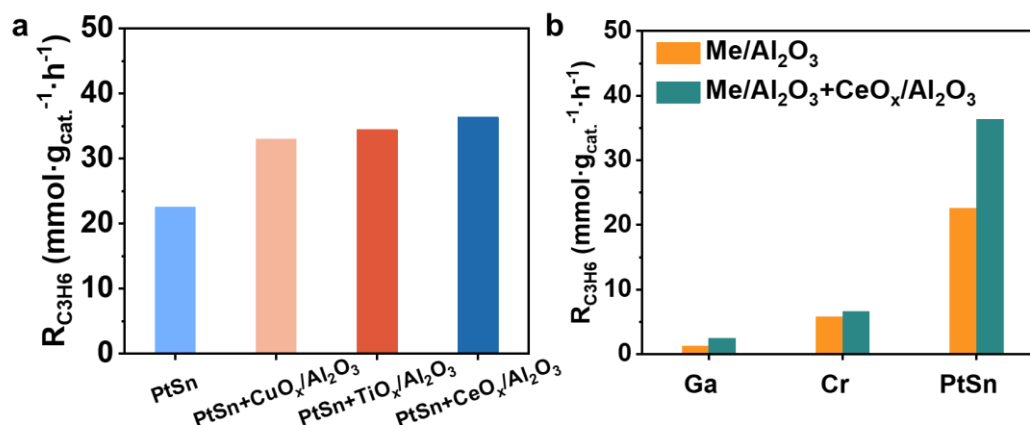


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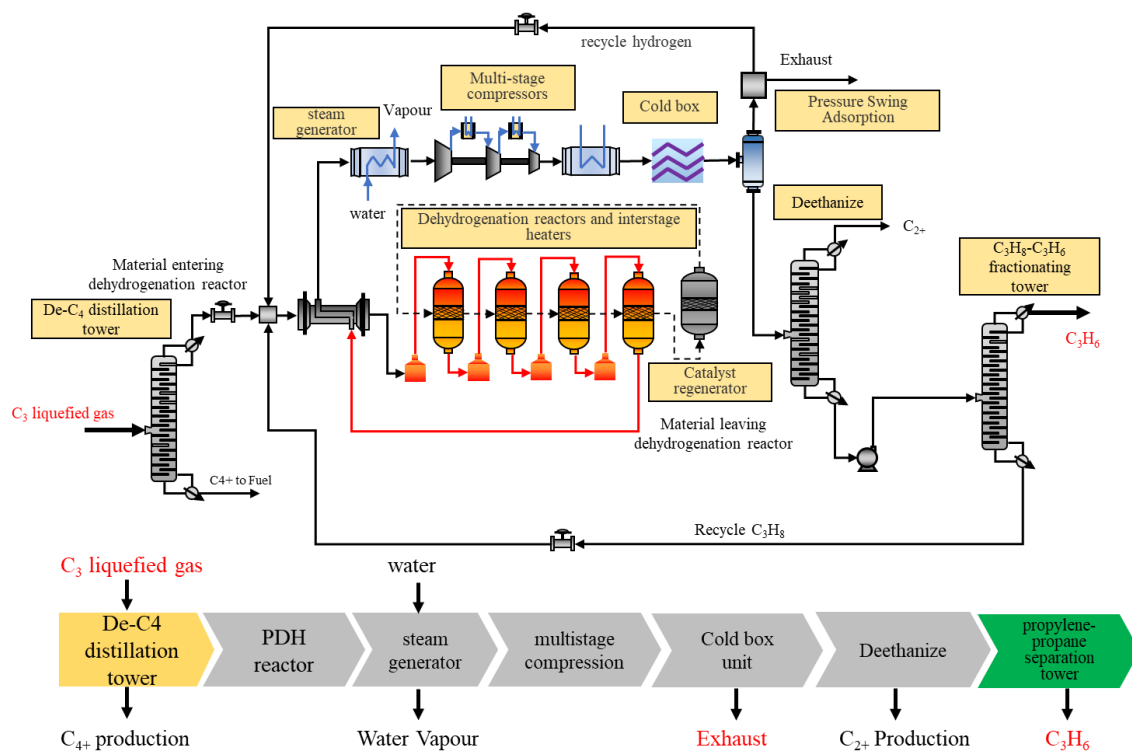
609 Supplementary Figure 33 | Arrhenius plots of propylene formation in PDH and CO_2 -

610 PDH obtained under differential reactors.

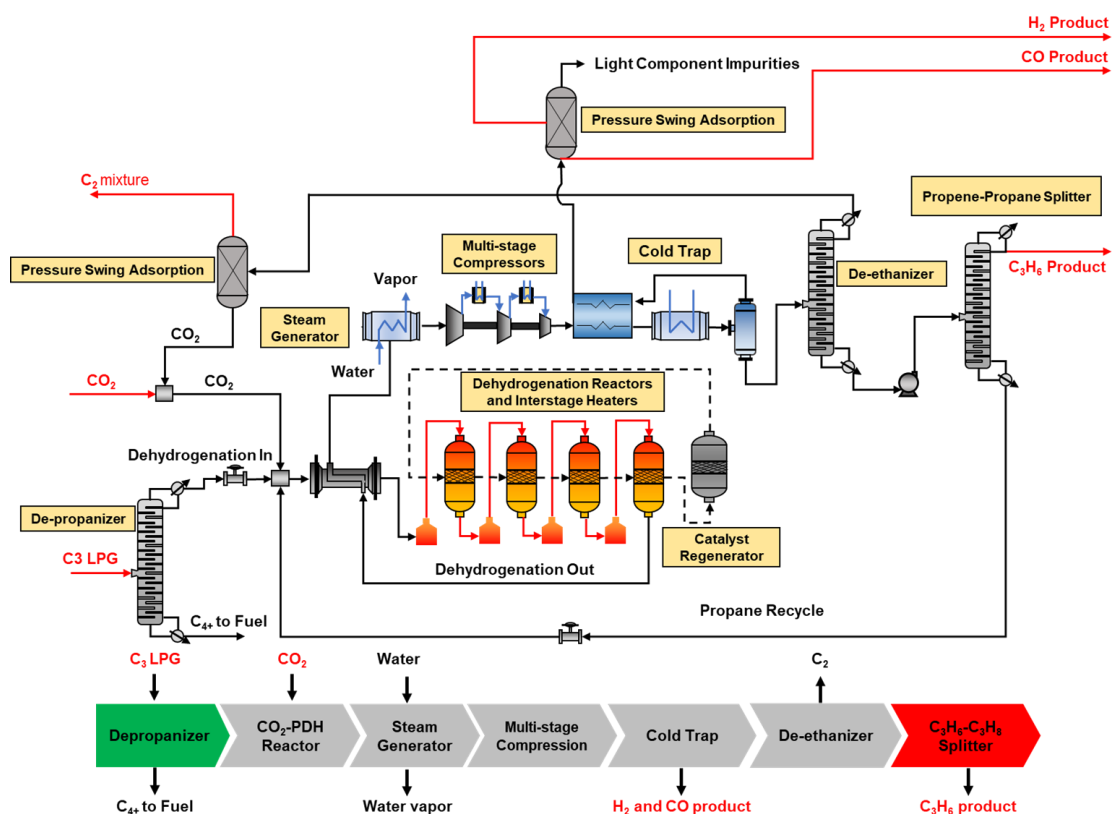
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Supplementary Figure 34 | Tandem mode of different catalysts performance obtained by integral reactor. (a) Pt₁Sn₇/Al₂O₃ + C=O bond activated catalysts (CeO_x/Al₂O₃, CuO_x/Al₂O₃, TiO_x/Al₂O₃) and (b) C-H bond activated catalysts (PtSn/Al₂O₃, Ga₂O₃/Al₂O₃, Cr₂O₃/Al₂O₃) + CeO_x/Al₂O₃. To extend the coupling of PDH and RWGS through hydrogen spillover, the tandem catalysts are investigated from two perspectives, as expected, we observed the intensified propylene production rates compared to the apparent ones. These results support the such hydrogen spillover-mediated coupling mechanism in a tandem fashion with proximity.



Supplementary Figure 35 | The scheme of Oleflex technology (PDH) by ASPEN Plus simulation. It was reproduced with permission from [1]. Copyright © 2022 American Chemical Society.



Supplementary Figure 36 | The scheme of PDH-CO₂R by ASPEN Plus simulation. It was reproduced with permission from [1]. Copyright © 2022 American Chemical Society.

632 Supplementary Table 9. Simulation Settings (modules and methods) by ASPEN plus.

Aspen Plus modules, databanks and methods	
Stream class	CONVEN
Databank	PURE, SOLIDS, INORGANIC
Property method	SRK, STEAMNBS
Unit operation models	
Reactor	Rstoic
Pressure changers	Pump, MCompr & Valve
Heat exchangers	Heater,HeaterX
Distillation columns	RadFrac
Separator, regenerator	Sep
Flash unit	Flash2

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Supplementary Table 10. Simulation conditions and assumptions by ASPEN plus.

Ambient condition		T=25 °C, p=1 atm	
Reaction unit		Oleflex process	Reacting at 550 °C
		CO ₂ -PDH process	Reacting at 550 °C
Compression & refrigeration unit	Compressor	3 stages with outlet pressure at 14.5 bar Isentropic efficiency 0.72	
	Cold box	Refrigeration temperature at -95 °C	
Separation unit	Debutanizer	80 stages at 15 bar Distillate feed ratio 0.98	
	Deethanizer	Oleflex process	70 stages at 12 bar Distillate feed ratio 0.043
		CO ₂ -PDH process	70 stages at 13.5 bar Distillate feed ratio 0.341
	Propylene tower	Oleflex process	150 stages at 17 bar Distillate feed ratio 0.41
		CO ₂ -PDH process	150 stages at 17 bar Distillate feed ratio 0.438
	Pressure swing Adsorption (PSA)	Oleflex process	Hydrogen recovery 4327.2 kmol·h ⁻¹
		CO ₂ -PDH process	Hydrogen separation efficiency: 85% Carbon monoxide separation efficiency: 90%
	Carbon dioxide capture operations	CO ₂ -PDH process	Carbon dioxide separation efficiency: 85%
others	By-product steam generator	Byproduct Steam Pressure :10 bar	

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638 Supplementary Table 11. Simulation Settings (feeds and yields).

	Oleflex process	CO ₂ -PDH process
Factory feed wt%	3455.3 kmol·h ⁻¹ (96 propane, 2 ethane, 2 butane)	3455.3 kmol·h ⁻¹ (96 propane, 2 ethane, 2 butane) 2622.9 kmol·h ⁻¹ Carbon dioxide
React1 feed wt%	12566.5 kmol·h ⁻¹ (65 propane, 34 hydrogen, 1 other hydrocarbons)	12180.3 kmol/h (59 propane, 40 carbon dioxide, 1 other hydrocarbons)
Carbon yield mole flow (kmol·h ⁻¹)		
Propane	4815.56	3889.94
Propylene	3058.31	2907.59
Methane	197.49	235.41
Ethylene	97.28	115.00
Ethane	169.31	189.51
Carbon monoxide	0	2306.57
Carbon dioxide	0	2764.80
Coke(graphite)	296.23	353.12
Carbon yield mole%		
Propane	55.77	30.48
Propylene	35.42	22.78
Methane	2.29	1.84
Ethylene	1.13	0.90
Ethane	1.96	1.48
Carbon monoxide	0	18.07
Carbon dioxide	0	21.66
Coke(graphite)	3.43	2.77
Hydrogen yield mole flow (kmol·h ⁻¹)		
Hydrogen	7617.18	1488.63
Water	0	1974.99
Hydrogen yield mole%		
Hydrogen	100	42.98
Water	0	57.02

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Supplementary Table 12. Comparison of energy consumption and net CO₂ emission of PDH and CO₂-PDH.

section	Oleflex process			CO ₂ -PDH process		
	Total MW	Unit GJ/ton product	CO ₂ emission ton/ton product	Total MW	Unit GJ/ton product	CO ₂ emission ton/ton product
Reaction	176.2	5.07	0.333	203.7	6.02	0.396
Compression	43.3	1.25	0.120	37.3	1.10	0.106
Separation	399.5	11.49	0.737	464.5	13.72	0.911
Heat exchangers	43.1	1.24	0.082	45.4	1.34	0.088
By-product steam generator	-44.1	-1.27	-0.047	-36.7	-1.09	-0.033
Reaction CO ₂ emission	0	0	0	0	0	-0.773
Total	618.10	17.78	1.23	714.18	21.09	0.694

645 Supplementary Table 13. Comparison of economics of PDH and CO₂-PDH.

section	Oleflex process		CO ₂ -PDH process	
	Total \$/h	Unit (\$/h)/ton product	Total \$/h	Unit (\$/h)/ton product
Reaction	-2696	-21.55	-3117	-25.57
Compression	-3422	-27.34	-2944	-24.15
Separation	-4503	-35.98	-7754	-63.61
Heat exchangers	-523	-4.18	-585	-4.80
By-product steam generator	171	1.37	119	0.97
Propane raw material	-92943	-742.73	-92943	-762.46
Propylene Products	137650	1100	134089	1100
Total	33735	269.58	26864	220.38

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References

- [1] Qin, J., Pei, C., Zhao, C., Lu, Z. & Sun, G. *et al.* Techno-economic analysis of a hybrid process for propylene and ammonia production. *ACS Sustain. Chem. Eng.* **10**, 6999-7009 (2022).