

Supporting Information

Effects of Pt loading on the activity of Pt/ γ -Ga₂O₃ for propane dehydrogenation

Salman Khan^a, Kaijie Wang^a, Zhaoshuo Ge^a, Lixia Bao^b, Yi Dai^a, Qi Liu^c, Daxin Shi^{a*}, Qin Wu^a, Kangcheng Chen^a, Guiyuan Jiang^c, Hansheng Li^a, Yaoyuan Zhang^{a*}

^a Beijing Key Laboratory for Chemical Power Source and Green Catalysis, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing, 100081, China

^b Analysis and Testing Center, Beijing Institute of Technology, Beijing 102488, China

^c State Key Laboratory of Heavy Oil Processing, China University of Petroleum Beijing, Beijing, 102249, China

*Correspondence to: shidaxin@bit.edu.cn; yaoyuan.zhang@bit.edu.cn

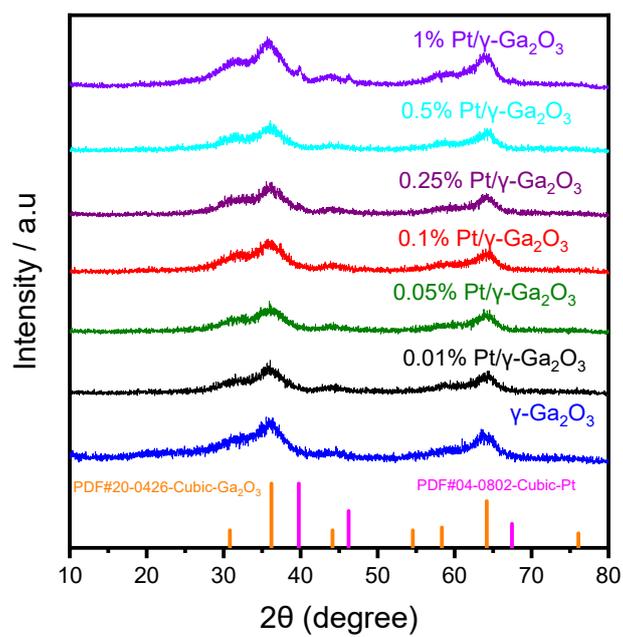


Figure S1 X-ray diffraction (XRD) patterns of different Ga₂O₃ catalyst prepared by different methods.

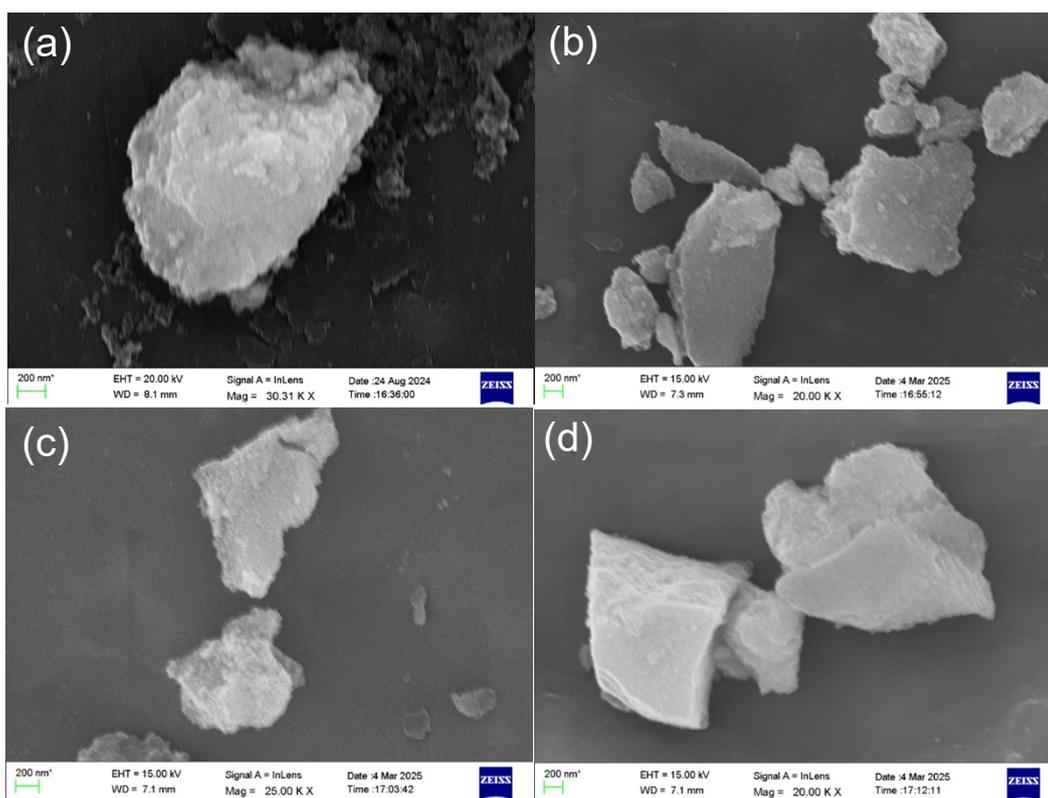


Figure S2 Scanning electron microscopy (SEM) images of (a) γ -Ga₂O₃, (b) 0.05% Pt/ γ -Ga₂O₃, (c) 0.5% Pt/ γ -Ga₂O₃, and (d) 1% Pt/ γ -Ga₂O₃.

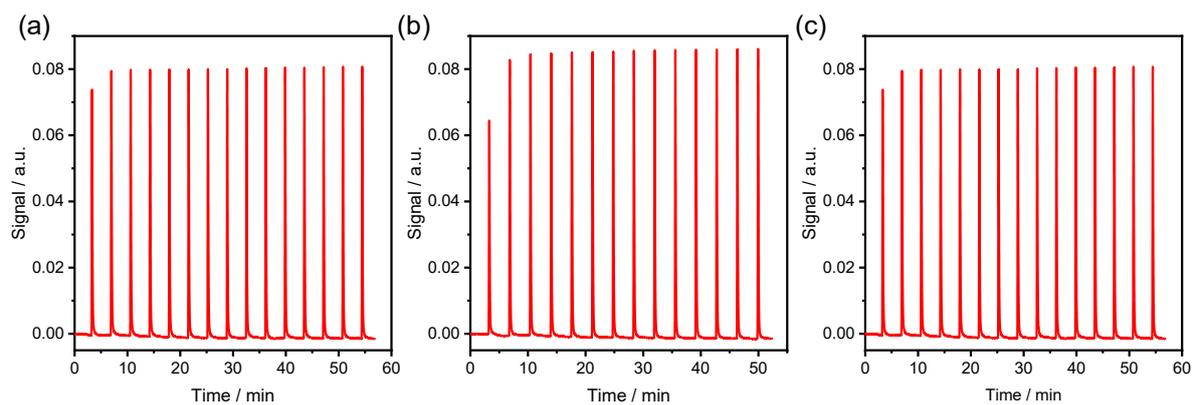


Figure S3 CO-pulse measurement of (a) 0.05% Pt/γ-Ga₂O₃, (b) 0.5% Pt/γ-Ga₂O₃, and (c) 1% Pt/γ-Ga₂O₃.

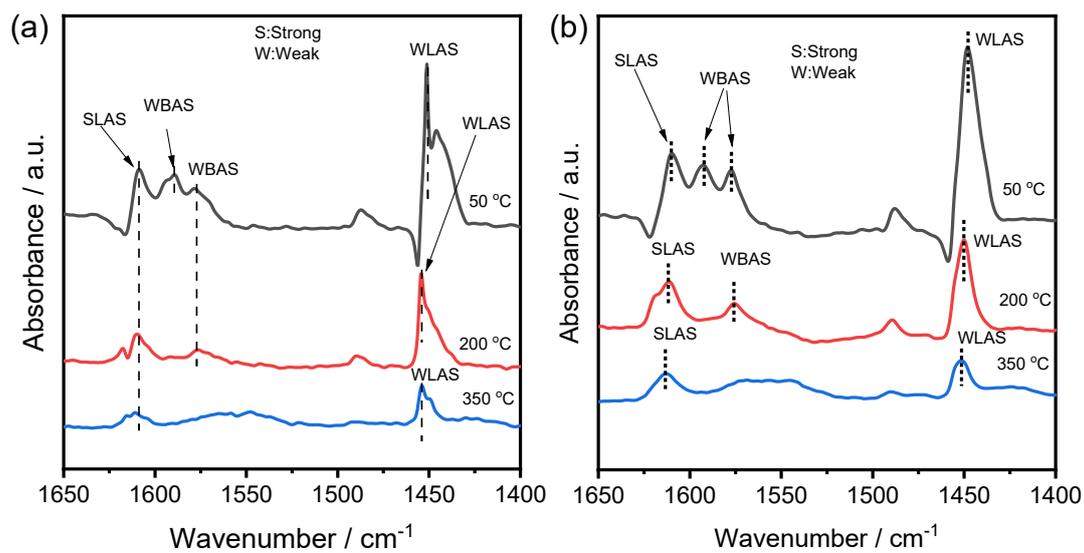


Figure S4 Pyridine-IR profiles obtained for (a) $\gamma\text{-Ga}_2\text{O}_3$ and (b) 1% Pt/ $\gamma\text{-Ga}_2\text{O}_3$.

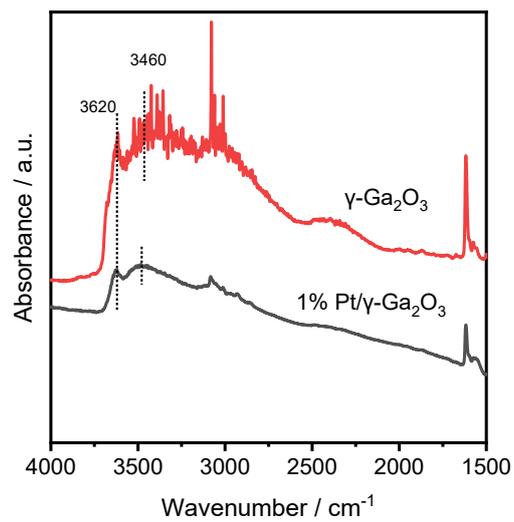


Figure S5 Fourier transform infrared spectroscopy (FTIR) spectra obtained for $\gamma\text{-Ga}_2\text{O}_3$ and 1% Pt/ $\gamma\text{-Ga}_2\text{O}_3$.

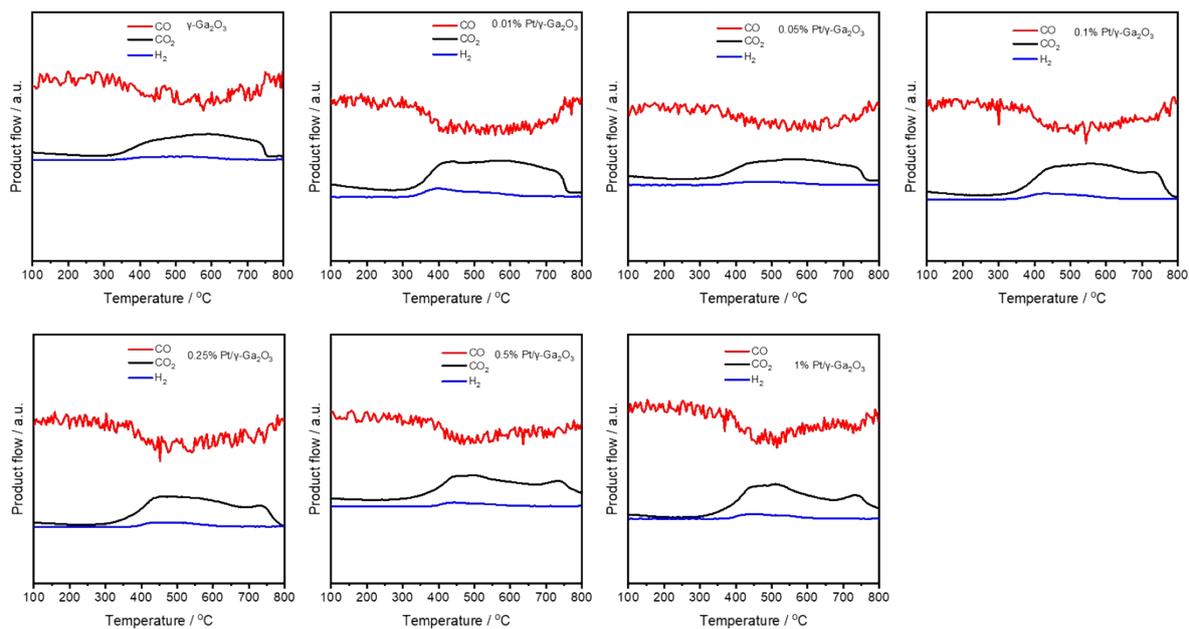


Figure S6 CO temperature-programmed reduction (CO-TPR) tests of different x% Pt/ γ -Ga₂O₃ catalysts. OH concentration was calculated from CO-TPR based on $(\text{CO} + \text{OH} \rightarrow \text{CO}_2 + 1/2\text{H}_2)$ using $n(\text{OH}) = 2 \times n(\text{H}_2)$.

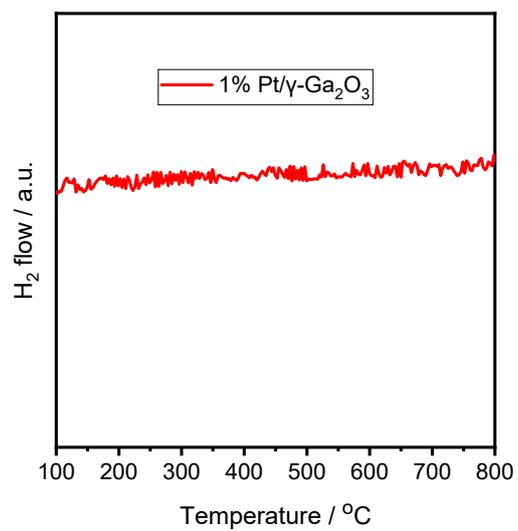


Figure S7 H₂ temperature-programmed reduction (H₂-TPR) test of 1% Pt/γ-Ga₂O₃.

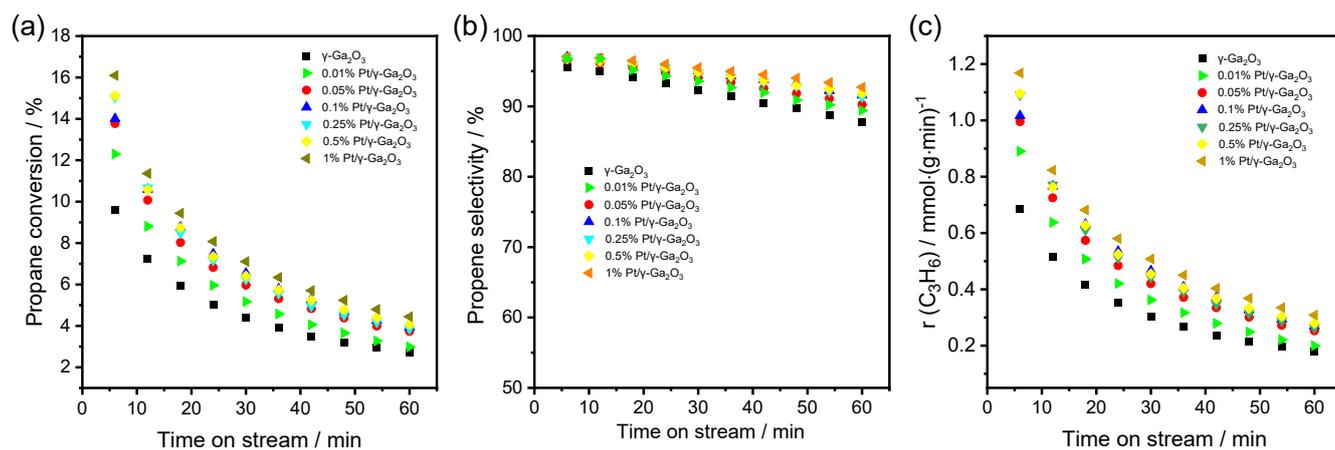


Figure S8 The dependence of (a) propane conversion, (b) propene selectivity, (c) rate of propene formation ($r(\text{C}_3\text{H}_6)$) and time on stream over x% Pt/ γ -Ga₂O₃ catalysts in PDH reaction. Reaction temperature: 550°C, feed composition: 40% C₃H₈ in N₂.

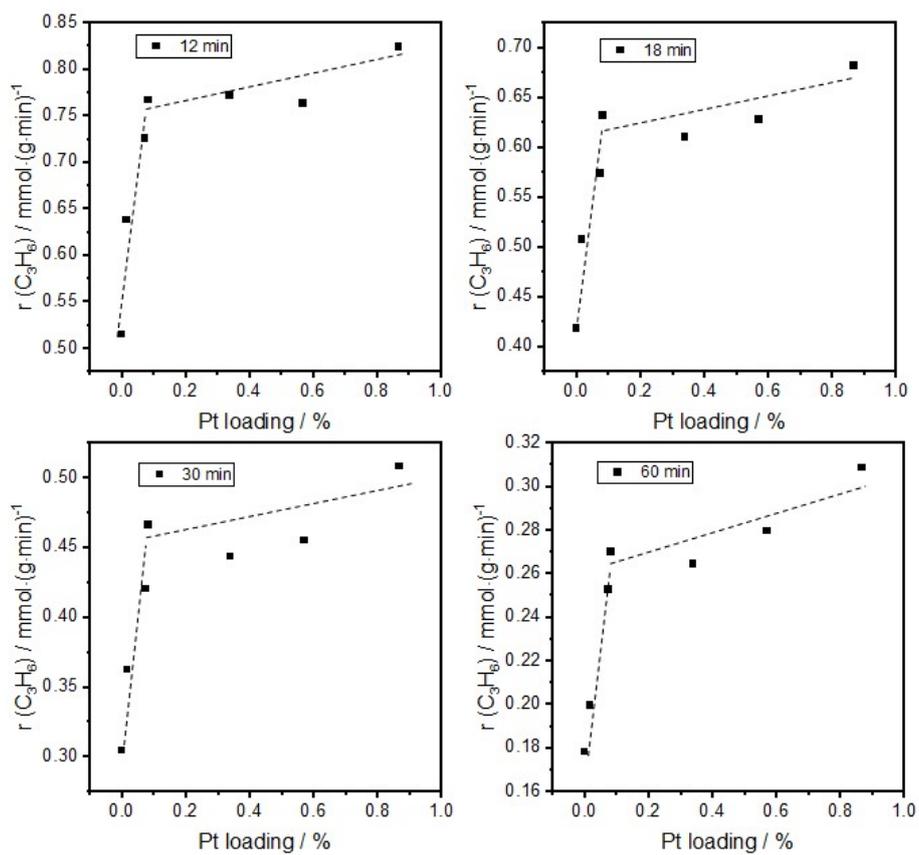


Figure S9 The relationship between the rate of propene formation ($r(\text{C}_3\text{H}_6)$) and Pt loading on different time on stream.

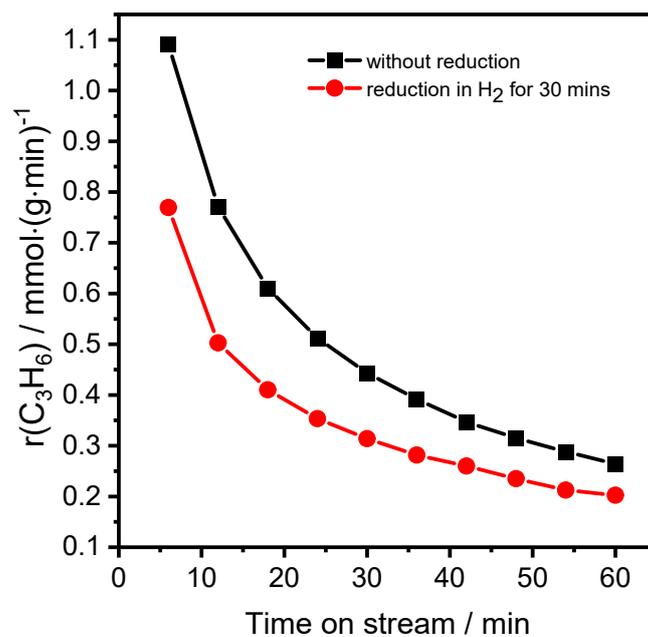


Figure S10 The relationship between the rate of propene formation and time on stream over 0.25% Pt/ γ -Ga₂O₃ under different reduction treatments. Reaction temperature: 550 °C, feed composition: 40% C₃H₈ in N₂.

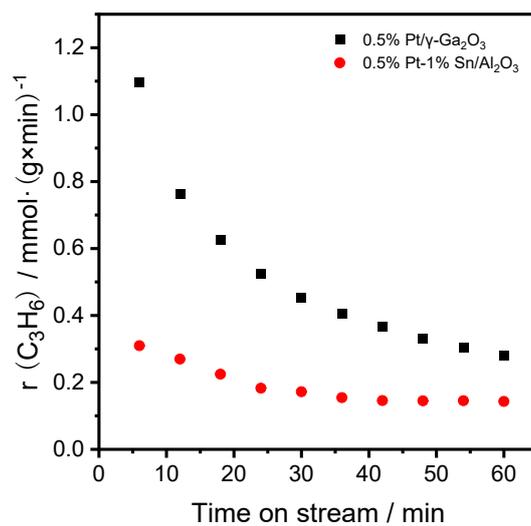


Figure S11 .Comparison of time-on-stream propene formation rates during propane dehydrogenation over 0.5 wt.% Pt/ γ - Ga_2O_3 and 0.5 wt.% Pt-1 wt.% Sn/ Al_2O_3 . Reaction temperature: 550 °C, feed composition: 40% C_3H_8 in N_2 .

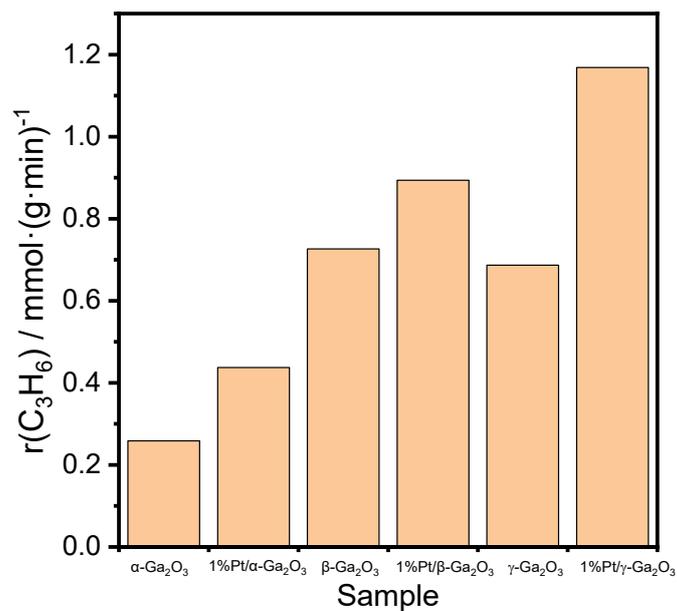


Figure S12 The rate of propene formation over $\alpha\text{-Ga}_2\text{O}_3$, $\beta\text{-Ga}_2\text{O}_3$ and $\gamma\text{-Ga}_2\text{O}_3$ their corresponding Pt-supported catalysts.

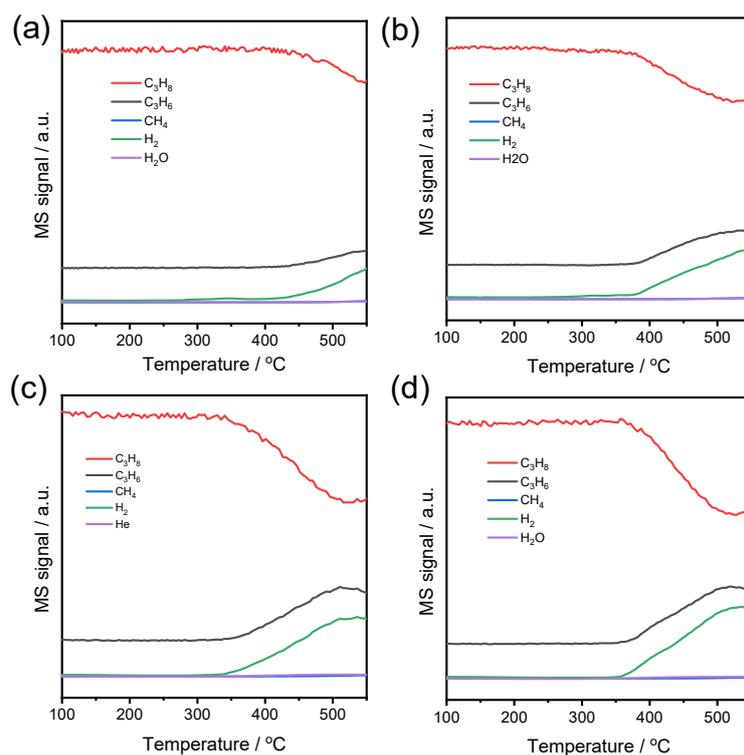


Figure S13 The MS signal intensity of C₃H₈, H₂, and H₂O recorded in propane temperature-programmed surface reaction (C₃H₈-TPSR) tests over (a) γ -Ga₂O₃, (b) 0.05%Pt/ γ -Ga₂O₃, (c) 0.5%Pt/ γ -Ga₂O₃, and (d) 1%Pt/ γ -Ga₂O₃.

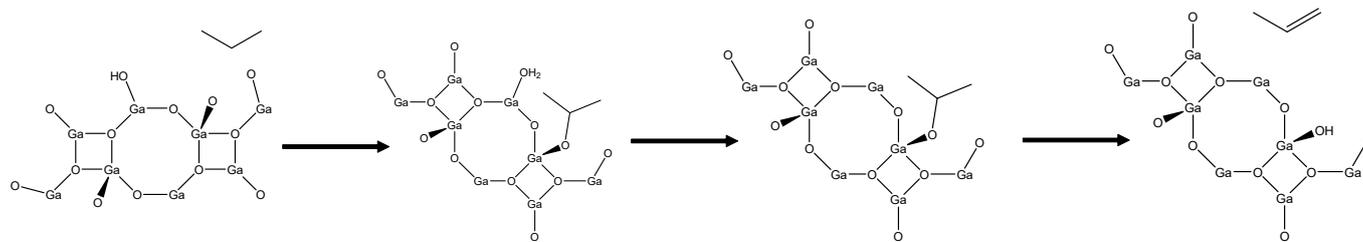


Figure S14 The closed PDH reaction cycle over $\gamma\text{-Ga}_2\text{O}_3\text{-OH}$ surface.

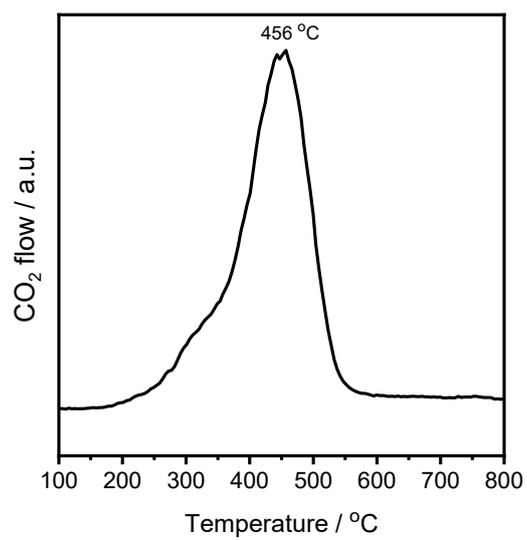


Figure S15 Temperature-programmed oxidation (TPO) tests of the spent 1% Pt/ γ -Ga₂O₃ from activity test in PDH.

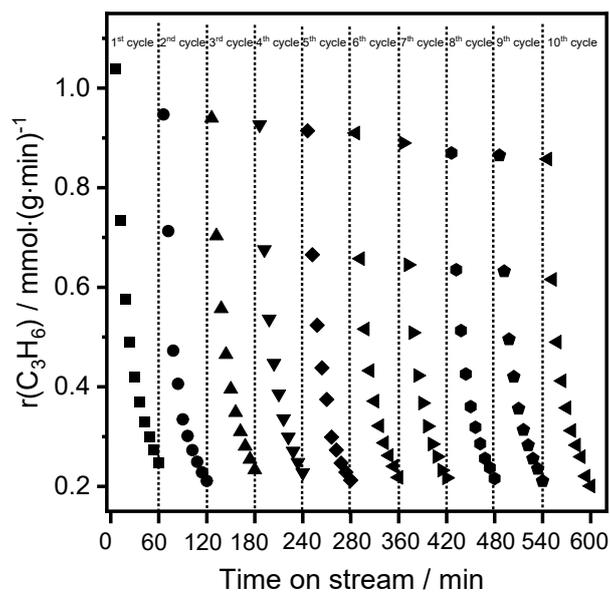


Figure S16 Reaction-regeneration stability of 1%Pt/ γ -Ga₂O₃ in the PDH reaction.

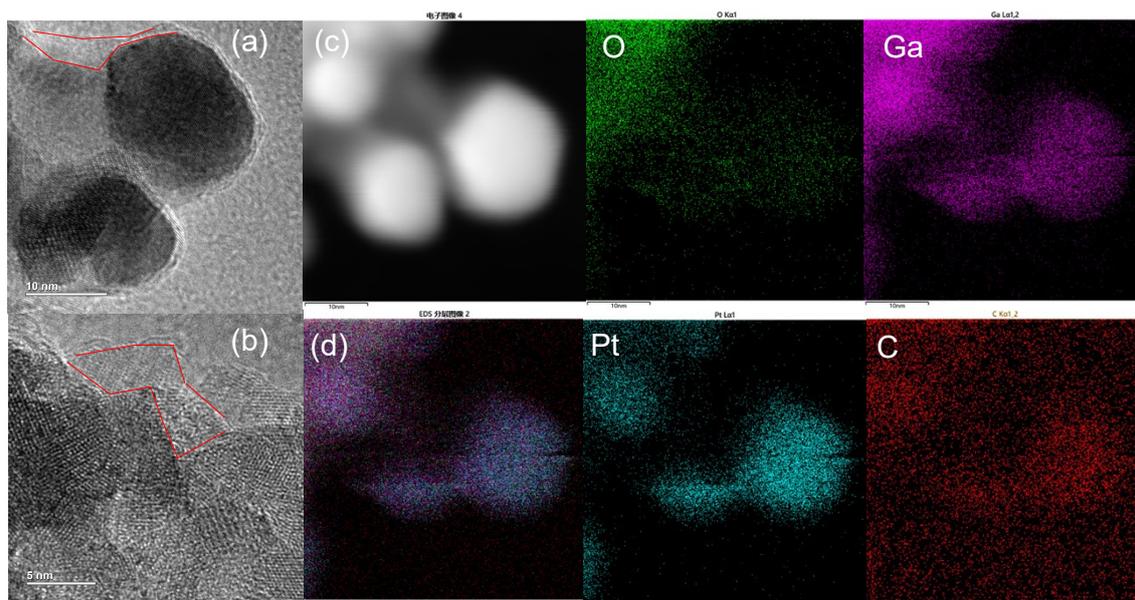


Figure S17 HRTEM images (a-b) of 1%Pt/ γ -Ga₂O₃ to identify coke, and (c and d) EDS mapping of 1%Pt/ γ -Ga₂O₃.

Table S1 The physiochemical properties including surface area, Pt content, and Pt dispersion degree, and the rate of propene formation, Y_{Pt} and TOF for different Pt/ γ -Ga₂O₃ catalysts.

Catalysts	$S_{BET} / m^2 \cdot g^{-1}$	Pt content / wt. %	Dispersion degree / %	$r(C_3H_6) / mmol \cdot g^{-1} \cdot min^{-1}$	Y_{Pt} / min^{-1}	TOF / min^{-1}
γ -Ga ₂ O ₃	89	/	/	0.69	/	
0.01% Pt/ γ -Ga ₂ O ₃	78	0.016	/	0.89	10.85	
0.05% Pt/ γ -Ga ₂ O ₃	78	0.074	35.7	0.99	2.62	7.35
0.1% Pt/ γ -Ga ₂ O ₃	79	0.083	/	1.02	2.38	
0.25% Pt/ γ -Ga ₂ O ₃	82	0.340	/	1.09	0.62	
0.5% Pt/ γ -Ga ₂ O ₃	83	0.570	26.0	1.10	0.37	1.44
1% Pt/ γ -Ga ₂ O ₃	83	0.870	6.1	1.20	0.26	4.29

Estimated uncertainties: BET surface area ± 1 -2%; Pt content (ICP) ± 1 %; Pt dispersion (CO chemisorption) ± 0.5 -1%; propene formation rate ± 1 -3%; Y_{Pt} and TOF uncertainties follow from rate and dispersion uncertainties.

Table S2 The calculated acid density of different Pt/ γ -Ga₂O₃ catalysts as obtained from NH₃-TPD tests. Estimated uncertainty: ± 0.5 -1%.

Catalysts	NH ₃ desorbed (mmol·g ⁻¹)
γ -Ga ₂ O ₃	0.089
0.01% Pt / γ -Ga ₂ O ₃	0.075
0.05% Pt / γ -Ga ₂ O ₃	0.083
0.1% Pt / γ -Ga ₂ O ₃	0.075
0.25% Pt / γ -Ga ₂ O ₃	0.056
0.5% Pt / γ -Ga ₂ O ₃	0.062
1% Pt / γ -Ga ₂ O ₃	0.062

Table S3 The calculated amount of CO consumption, CO₂ formation, H₂ formation and OH concentration over different Pt/ γ -Ga₂O₃ catalysts in CO-TPR tests. Estimated uncertainty: ± 0.2 - 0.5% .

Catalysts	CO consumption (mmol·g ⁻¹)	CO ₂ (mmol·g ⁻¹)	H ₂ (mmol·g ⁻¹)	OH concentration (mmol·g ⁻¹)
γ -Ga ₂ O ₃	0.32	0.26	0.027	0.054
0.01%Pt/ γ -Ga ₂ O ₃	0.31	0.29	0.039	0.078
0.05% Pt / γ -Ga ₂ O ₃	0.26	0.24	0.026	0.052
0.1% Pt / γ -Ga ₂ O ₃	0.26	0.25	0.030	0.060
0.25% Pt / γ -Ga ₂ O ₃	0.29	0.28	0.025	0.050
0.5% Pt / γ -Ga ₂ O ₃	0.25	0.24	0.025	0.051
1% Pt / γ -Ga ₂ O ₃	0.30	0.24	0.027	0.055

Note: OH concentration was calculated from CO-TPR based on $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + 1/2\text{H}_2$ using $n(\text{OH}) = 2 \times n(\text{H}_2)$.

Table S4. The binding energies of Ga2p_{3/2}, Pt4f_{5/2} and Pt4f_{7/2}, and the ratio of different Pt species (Pt⁰, Pt²⁺, and Pt⁴⁺) over Pt/ γ -Ga₂O₃ catalysts obtained from XPS results. Estimated uncertainty: ± 0.1 eV.

Catalysts	Binding energy (Ga2p _{3/2}) / eV	Binding energy (Pt4f _{5/2}) / eV	Binding energy (Pt4f _{7/2}) / eV	Species	Ratio / %
γ -Ga ₂ O ₃	1117.4				
0.05% Pt / γ -Ga ₂ O ₃	1117.8	71.1	74.5	Pt ⁰	62.49
		72.6	75.9	Pt ²⁺	24.43
		73.8	77.2	Pt ⁴⁺	13.08
0.5% Pt / γ -Ga ₂ O ₃	1118.0	70.1	73.4	Pt ⁰	31.61
		71.3	74.6	Pt ²⁺	45.51
		72.8	76.2	Pt ⁴⁺	22.88
1% Pt / γ -Ga ₂ O ₃	1117.7	69.6	72.9	Pt ⁰	32.19
		70.6	73.9	Pt ²⁺	52.84
		72.3	75.6	Pt ⁴⁺	14.97

Note: XPS peak fitting were performed using MultiPak software with the Direct Fit routine. All spectra were calibrated to C 1s = 284.8 eV. A Shirley-type background was applied prior to curve fitting. Peaks were fitted using an asymmetric line-shape function. The Pt 4f region was analyzed using the double fitting option, which generates the Pt 4f_{7/2} and Pt 4f_{5/2} components simultaneously and applies physically meaningful constraints, including fixed spin-orbit splitting and fixed area ratio between the two components. Separate doublets corresponding to Pt⁰, Pt²⁺, and Pt⁴⁺ were included based on literature-reported binding energies and optimized to minimize residual error. The Ga 2p region was treated using the same fitting strategy. The fitted peak areas were used to calculate the Pt⁰/Pt²⁺/Pt⁴⁺ ratios reported in Table S4. The uncertainty in fitted binding-energy positions is ± 0.05 – 0.10 eV after charge correction (C 1s = 284.8 eV).

Table S5 The products selectivity including methane, ethane, ethene, and propene for all prepared Ga₂O₃ catalysts during the PDH reaction. Estimated uncertainty: ±0.5%.

Catalysts	S(CH ₄) / %	S(C ₂ H ₆) / %	S(C ₂ H ₄) / %	S(C ₃ H ₆) / %
γ-Ga ₂ O ₃	1.62	0.29	2.5	95.59
0.01% Pt /γ-Ga ₂ O ₃	0	1.60	1.70	96.70
0.05% Pt /γ-Ga ₂ O ₃	1.26	0.38	1.79	96.57
0.1% Pt /γ-Ga ₂ O ₃	1.08	0.33	1.61	96.98
0.25% Pt /γ-Ga ₂ O ₃	1.12	0.43	1.57	96.88
0.5% Pt /γ-Ga ₂ O ₃	1.10	0.44	1.66	96.80
1% Pt /γ-Ga ₂ O ₃	1.05	0.47	1.48	97.01