Supplementary Materials

Coke deposition mechanisms of propane dehydrogenation on different sites of Al_2O_3 supported PtSn catalysts

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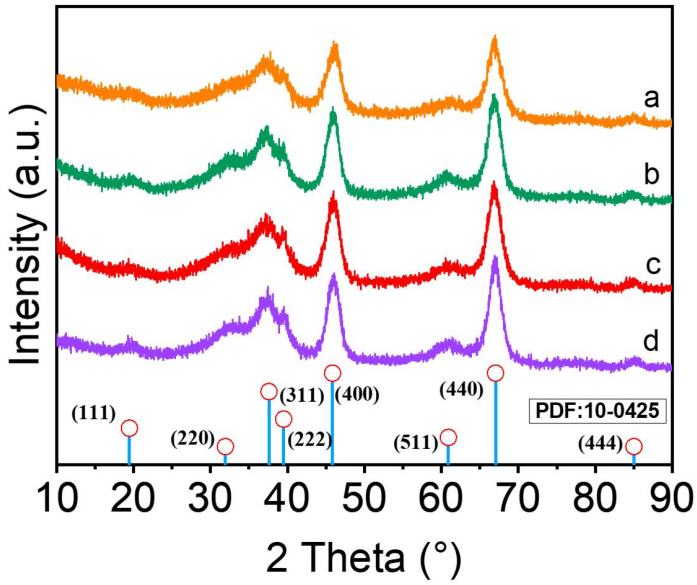
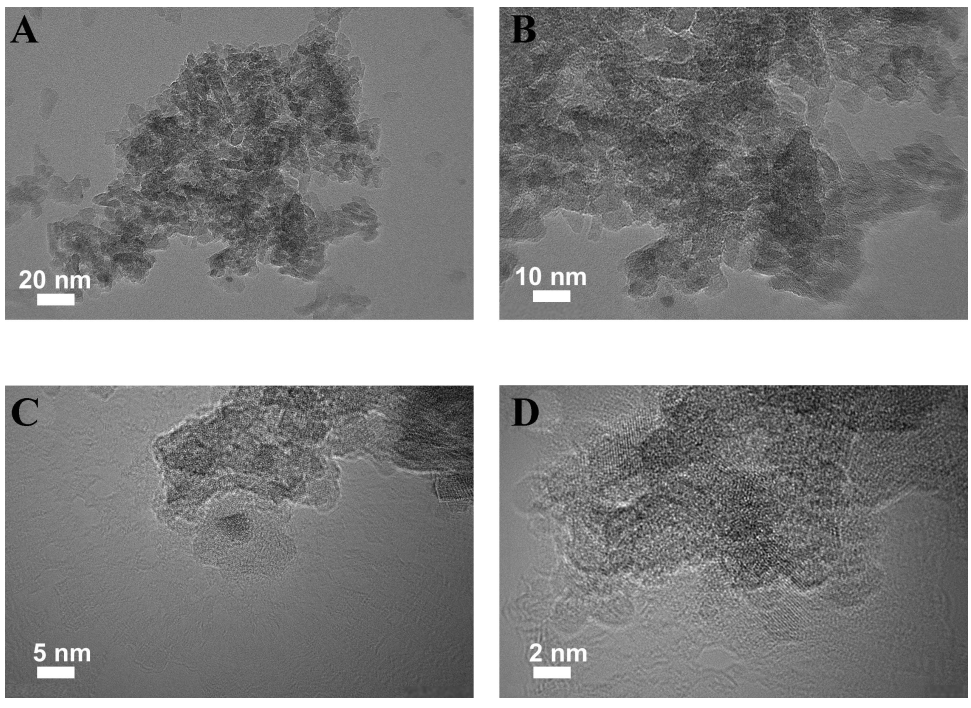
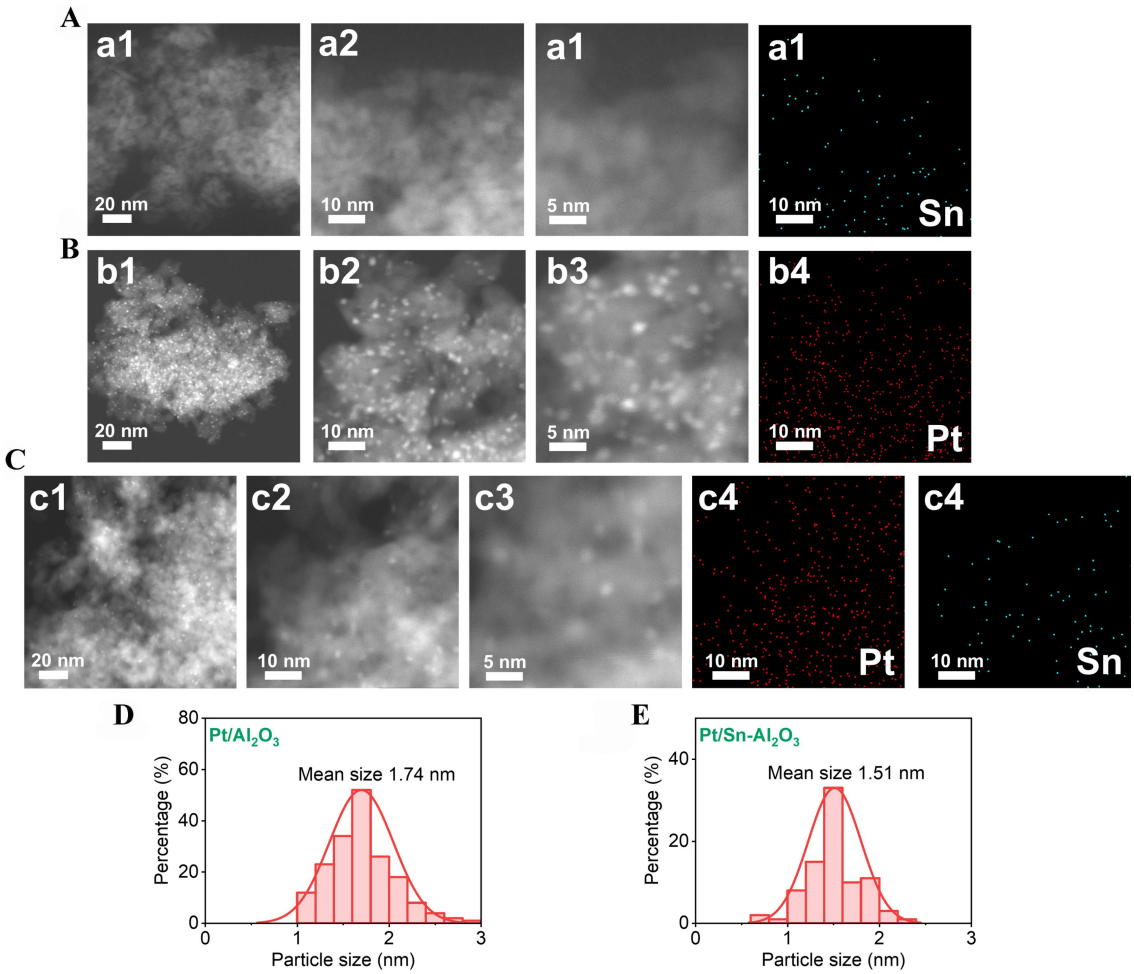


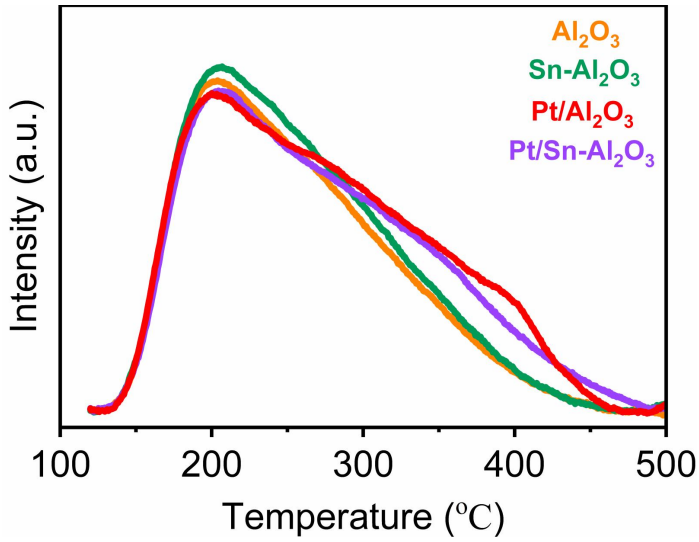
Supplementary Figure 1. XRD patterns of the Al_2O_3 (a), Sn-Al_2O_3 (b), Pt/Al_2O_3 (c), Pt/Sn-Al_2O_3 (d) catalysts.



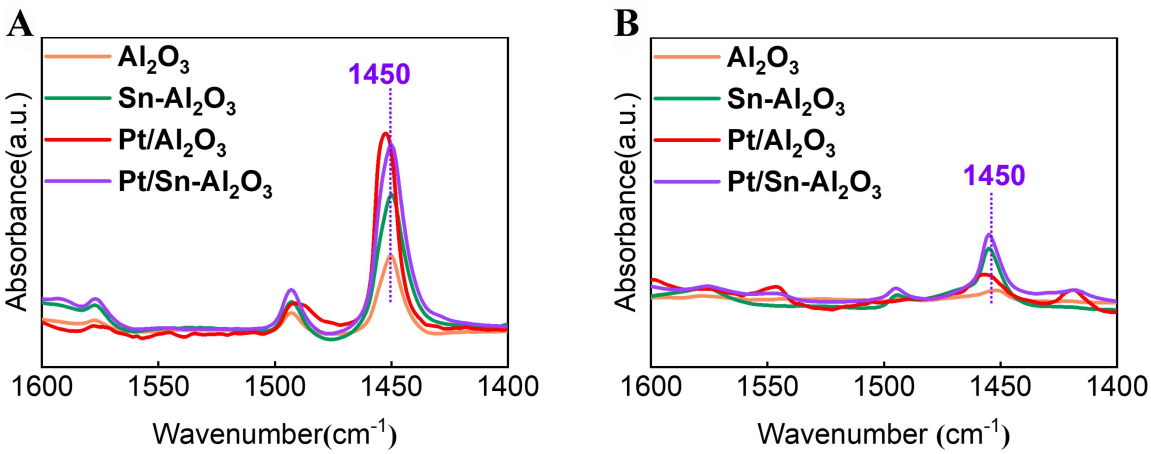
Supplementary Figure 2. TEM images of the Pt/Sn-Al_2O_3 sample. Scale bars: 20 nm (A); 10 nm (B); 5 nm (C); 2 nm (D).



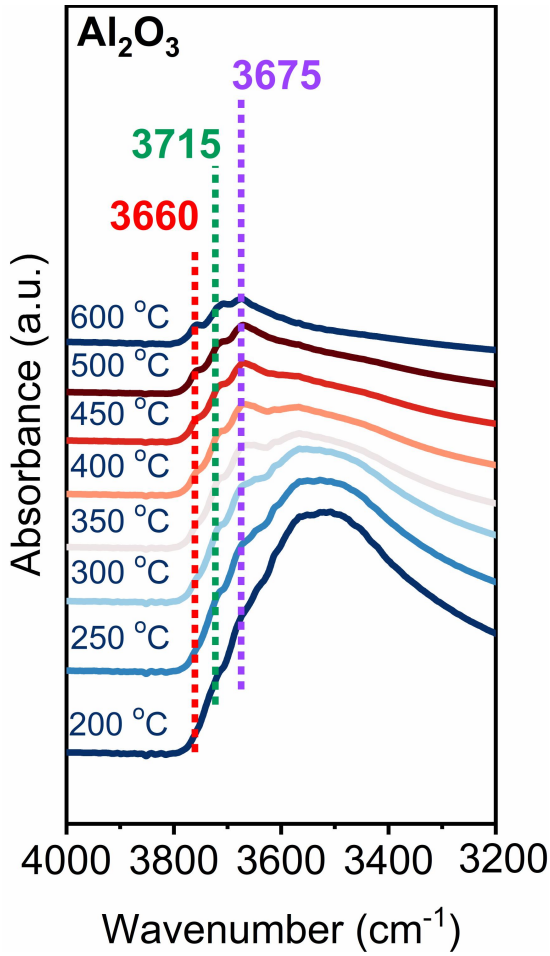
Supplementary Figure 3. STEM images and EDX element-mapping analysis of $Sn\text{-}Al_2O_3$ (A), Pt/Al_2O_3 (B) and $Pt/Sn\text{-}Al_2O_3$ (C) samples and particle size distributions of Pt/Al_2O_3 (D) and $Pt/Sn\text{-}Al_2O_3$ (E) samples.



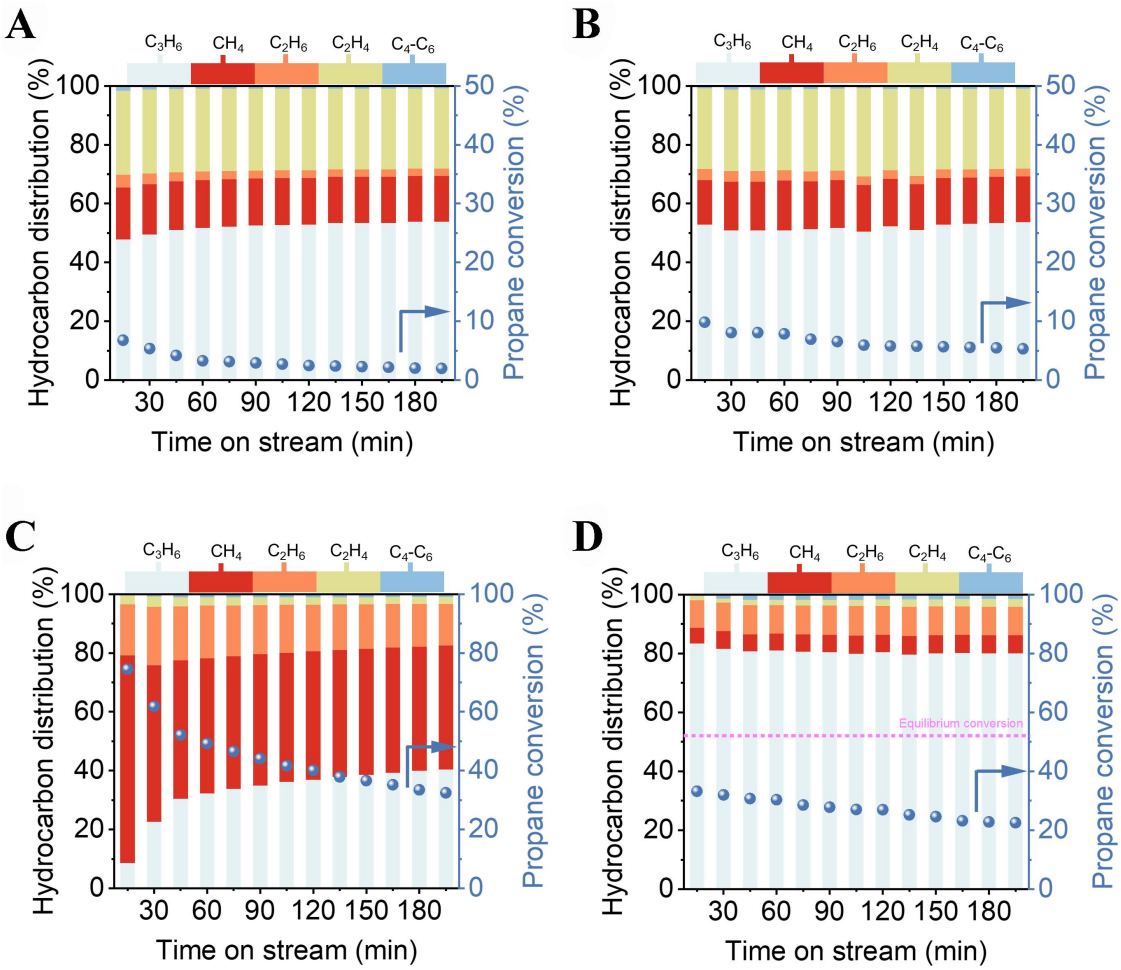
Supplementary Figure 4. NH_3-TPD curves of Al_2O_3, Sn-Al_2O_3, Pt/Al_2O_3 and Pt/Sn-Al_2O_3 samples.



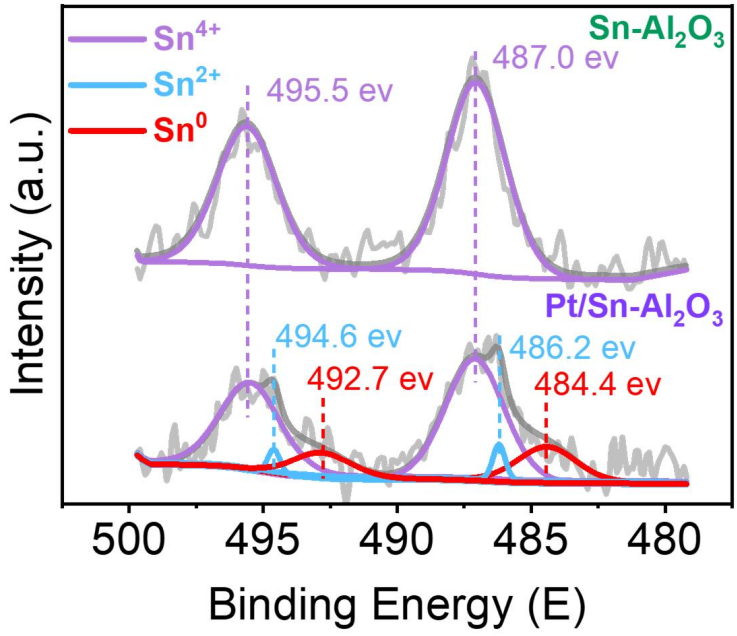
Supplementary Figure 5. FTIR spectra of pyridine adsorption on Al_2O_3, Sn-Al_2O_3, Pt/Al_2O_3 and Pt/Sn-Al_2O_3 samples after desorption at 150 °C (A) and 400 °C (B) for 0.5 h.



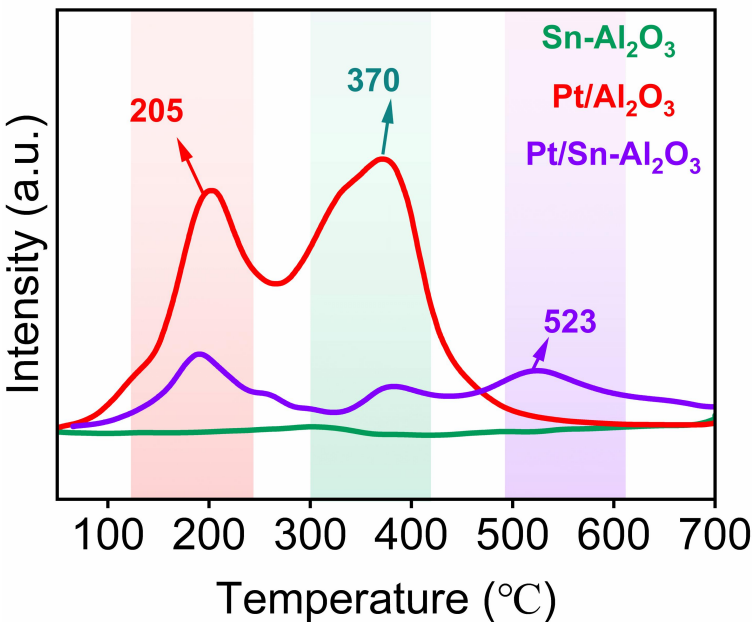
Supplementary Figure 6. FTIR spectra acquired during dehydration of the Al_2O_3 sample at various temperatures.



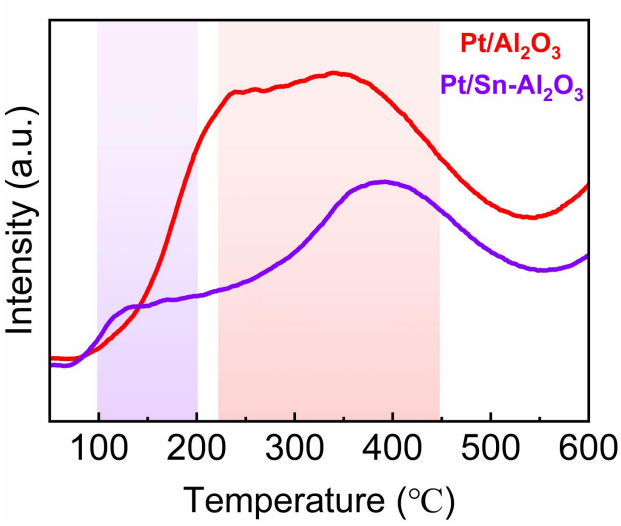
Supplementary Figure 7. Product distribution of different catalysts as a function of time on stream during propane dehydrogenation for Al_2O_3 (A), Sn-Al_2O_3 (B), Pt/Al_2O_3 (C), and Pt/Sn-Al_2O_3 (D) samples. Dehydrogenation conditions: $m_{catalyst}$ = 100 mg, C_3H_8/H_2 = 1/1 (2.3 mL min^{-1} of propane and 2.3 mL min^{-1} of H_2), $T_{reduction}$= 500 °C, $T_{reaction}$= 600 °C, GHSV= 1,000.



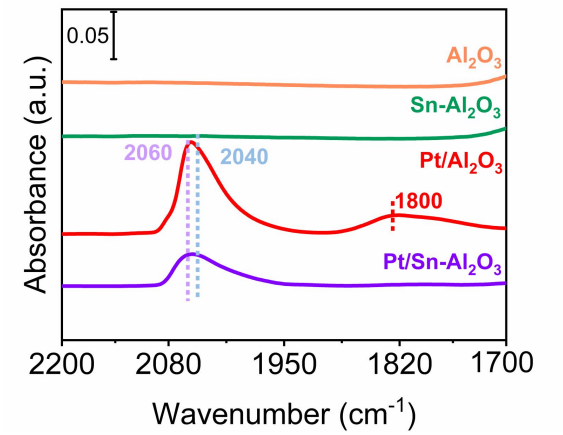
Supplementary Figure 8. Sn 3d XPS spectra of Sn-Al_2O_3 and Pt/Sn-Al_2O_3 samples.



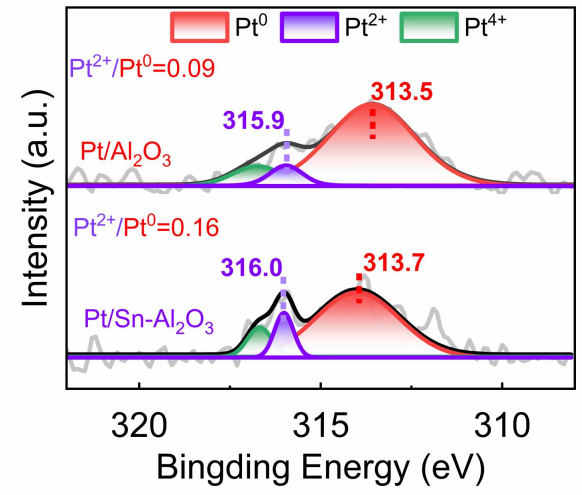
Supplementary Figure 9. H_2-TPR profiles of Sn-Al_2O_3, Pt/Al_2O_3 and Pt/Sn-Al_2O_3 samples.



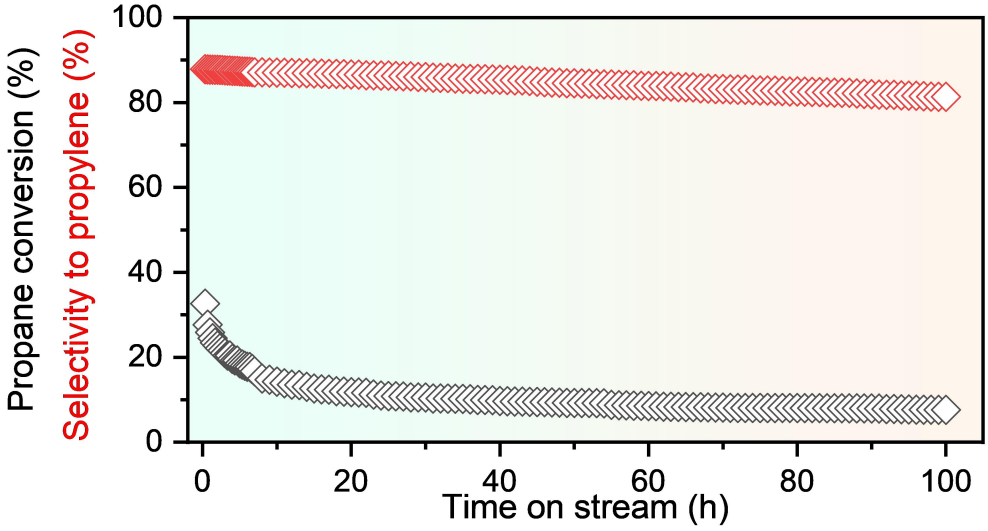
Supplementary Figure 10. H_2-TPD profiles of the Pt/Al_2O_3 and $Pt/Sn\text{-}Al_2O_3$ samples.



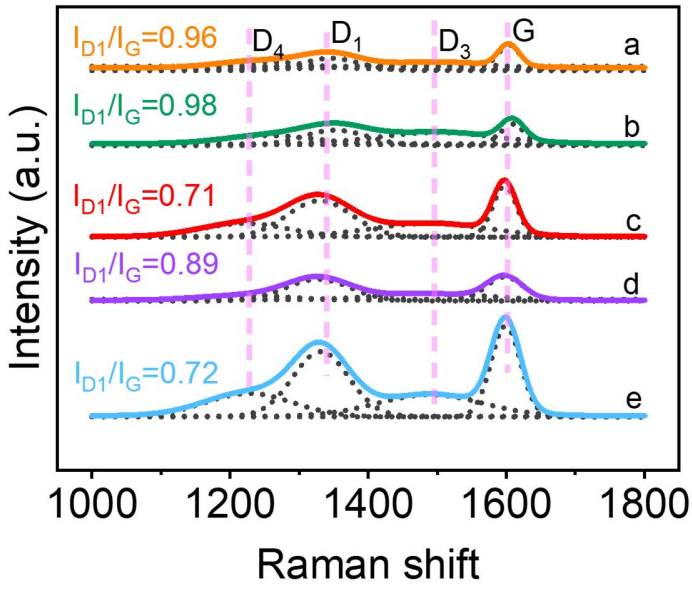
Supplementary Figure 11. FTIR spectra of CO adsorption on the fresh Al_2O_3, $Sn\text{-}Al_2O_3$, Pt/Al_2O_3 and $Pt/Sn\text{-}Al_2O_3$ catalysts.



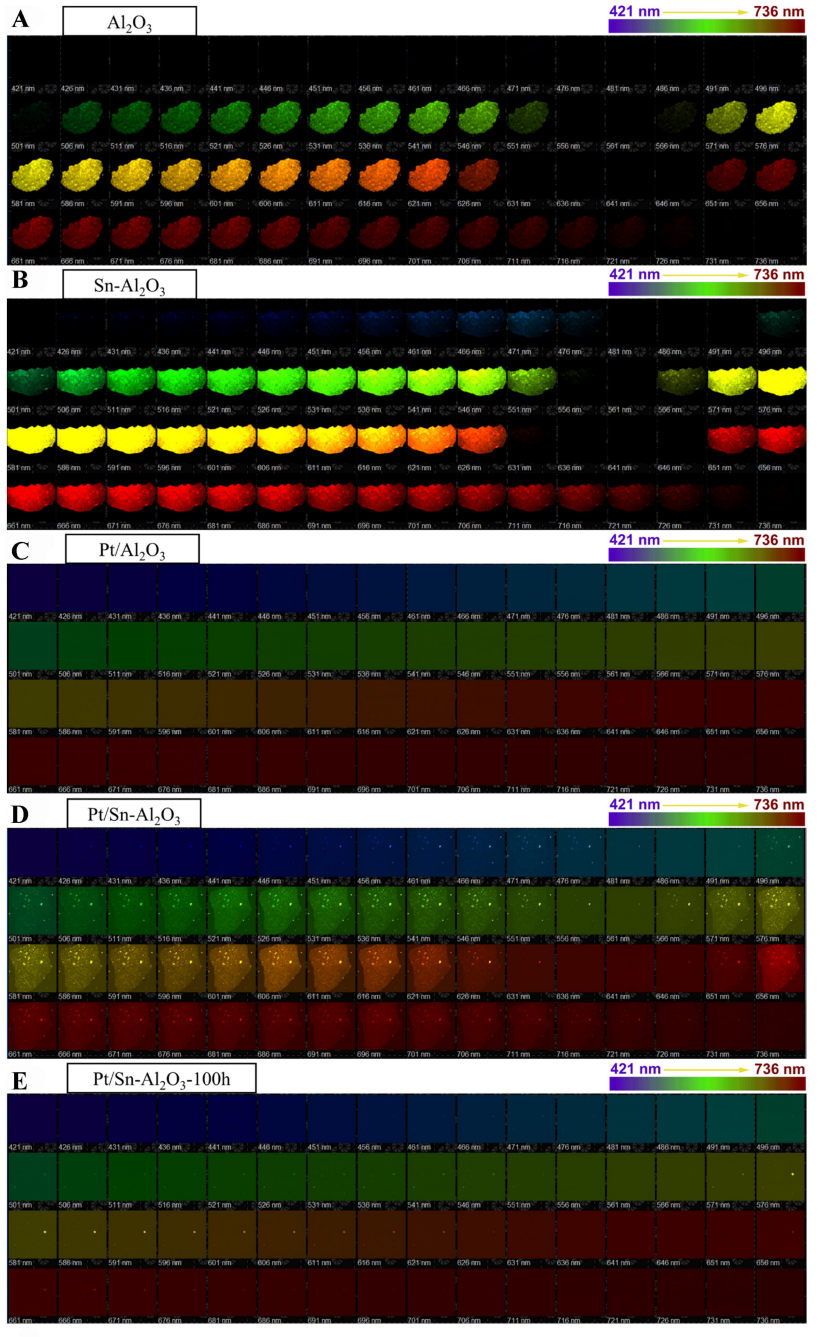
Supplementary Figure 12. Pt 4d XPS spectra of Pt/Al_2O_3 and $Pt/Sn\text{-}Al_2O_3$ samples.

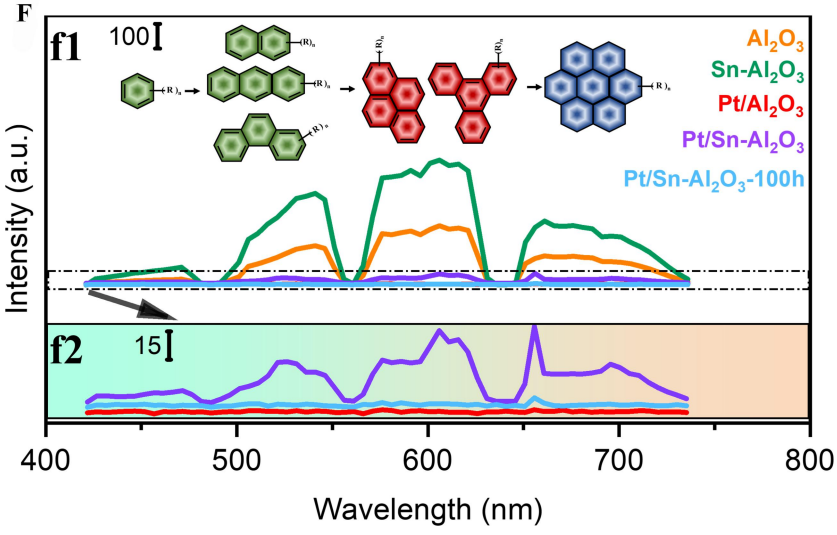


Supplementary Figure 13. Conversion and selectivity as a function of time during propane dehydrogenation for Pt/Sn-Al_2O_3 samples. Dehydrogenation conditions: $m_{catalyst}$ = 100 mg, C_3H_8/H_2 = 1/1 (2.3 mL min^{-1} of propane and 2.3 mL min^{-1} of H_2), $T_{reduction}$= 500 °C, $T_{reaction}$= 600 °C, GHSV= 1,000.

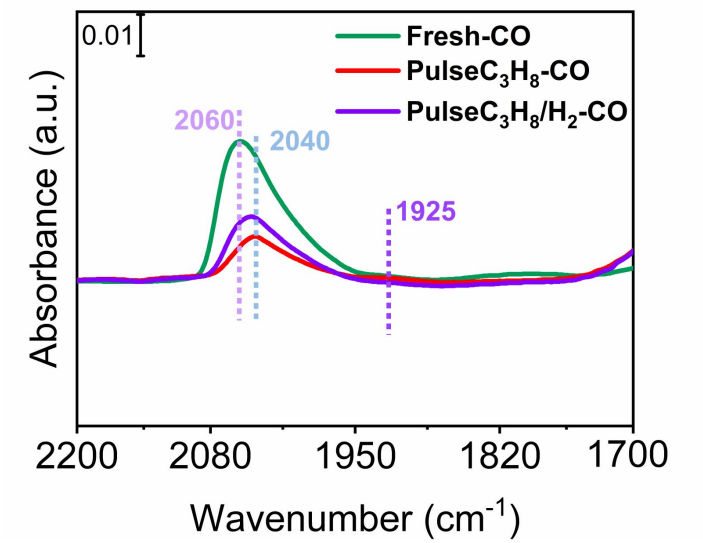


Supplementary Figure 14. Raman spectra of the Al_2O_3 (a), Sn- Al_2O_3 (b), Pt/Al_2O_3 (c), Pt/Sn-Al_2O (d) catalyst after 3.3 h of reaction and Pt/Sn-Al_2O-100h (e) catalyst after 100 h of reaction.


A
Al2O3
421 nm
736 nm
B
Sn-Al2O3
421 nm
736 nm
C
Pt/Al2O3
421 nm
736 nm
D
Pt/Sn-Al2O3
421 nm
736 nm
E
Pt/Sn-Al2O3-100h
421 nm
736 nm


F
f1
100
f2
15
Al2O3
Sn-Al2O3
Pt/Al2O3
Pt/Sn-Al2O3
Pt/Sn-Al2O3-100h
Intensity (a.u.)
400
500
600
700
800
Wavelength (nm)

Supplementary Figure 15. Confocal fluorescence intensity maps of the Al_2O_3 (A), Sn-Al_2O_3 (B), Pt/Al_2O_3 (C), Pt/Sn-Al_2O (D) catalysts after 3.3 h of reaction and Pt/Sn-Al_2O-100h (E) after 100 h of reaction, (F) The applied laser excitation wavelengths are 405 nm, 488 nm, 561 nm, and 640 nm. The inset is the enlarged profiles (f2). The detection area is full spectrum detection. Minor adjustments in the saturation level have been made to decrease the overexposure level.



Supplementary Figure 16. FTIR spectra of CO adsorption on the fresh Pt/Sn-Al_2O_3 sample and the Pt/Sn-Al_2O_3 sample after pulse C_3H_8 and pulse C_3H_8/H_2 mixture (volume ratio=1:1).

Supplementary Table 1. Study on coke composition and location of different Pt-based catalysts

Samples	Characterize	Highlights
Reacted Pt-Sn/Al_2O_3[1]	GC-MS, IR, Raman	The coke mainly consists of three kind of species: aliphatics, aromatics, and pregraphite
Reacted Pt-Sn/Al_2O_3[2]	TPO	The coke is located on the metal, in the vicinity of the metal, and on the carrier
Pt-Sn/Al_2O_3[3]	Transient experiments	Identified the reversible and irreversible coke on the catalysts
Reacted Pt/Al_2O_3[4]	GC-MS, IR	The coke is pyrene and methyl pyrene are the main components.
Reacted Pt-Sn/Al_2O_3[5]	XRD, XPS, TPO	The pregraphite-like carbon is the main component of coke
Pt-Sn/Al_2O_3，Pt/Al_2O_3[6,7]	Operando Raman	The physicochemical properties of the coke change with time on stream and regeneration times
Pt/Al_2O_3[8]	DFT	Revealing the Janus character of the coke precursor in the propane direct dehydrogenation on Pt catalysts from a kMC simulation

Supplementary Table 2. Curve-Fitting Parameters for Pt $4d_{5/2}$ XPS Spectra of Fresh Catalysts

	binding energy (eV)			
Sample	**Pt^0**	**Pt^{2+}**	**Pt^{4+}**	**Pt^{2+}/Pt^0**
Pt/Al_2O_3	313.5 (81.1%)	315.9 (7.5%)	316.8 (11.3%)	0.09
$Pt/Sn\text{-}Al_2O_3$	313.7 (76.6%)	316.0 (12.2%)	316.8(11.2%)	0.16

Supplementary Table 3. Curve-Fitting Parameters for Sn 3d XPS Spectra of Fresh Catalysts

	binding energy (eV)		
Sample	**Sn^{4+}**	**Sn^{2+}**	**Sn^0**
$Pt/Sn\text{-}Al_2O_3$	495.5, 487.0 (74.0%)	494.6, 486.2 (4.4%)	492.7,484.4 (21.5%)

Supplementary Table 4. Compositions of the Coke on Catalysts

Samples	C (wt %)	H (wt %)	H/C (mol ratio)
Al_2O_3	0.89	1.17	15.85
Sn-Al_2O_3	0.65	1.06	19.59
Pt/Al_2O_3	15.2	1.10	0.87
Pt/Sn-Al_2O_3	3.06	1.0	3.96
Pt/Sn-Al_2O_3-100h	12.5	0.94	0.91

Supplementary Table 5. Catalytic properties of propane dehydrogenation over catalysts used in this work[a]

Sample	Conversion [%]			K_d[b] [h^{-1}]	τ[c] [h]
	0.5h	3.3h	100h		
Al_2O_3	6.8	2.0		0.053	19
Sn-Al_2O_3	9.8	5.3		0.028	36
Pt/Al_2O_3	74.5	32.5		0.075	13
Pt/Sn-Al_2O_3	32.6	19.3		0.029	34
Pt/Sn-Al_2O_3-100h	32.6		7.6	0.073	14

[a]Reaction temperature, 600℃; 50.5 kPa C_3H_8, 50.5 kPa H_2. [b]k_d, deactivation rate constant, calculated from $\ln[(1-X_{final})/-X_{final}]=k_d*t+\ln[(1--X_{final})/-X_{final}]$. [c]Time required for rates to decrease by e^{-1}, $\tau=1/k_d$.

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