

Supporting Information

Stabilizing Pd/In₂O₃ on Zeolite Silicalite-1: A Route to Durable and Selective CO₂ Hydrogenation to Methanol

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Supplementary Figures

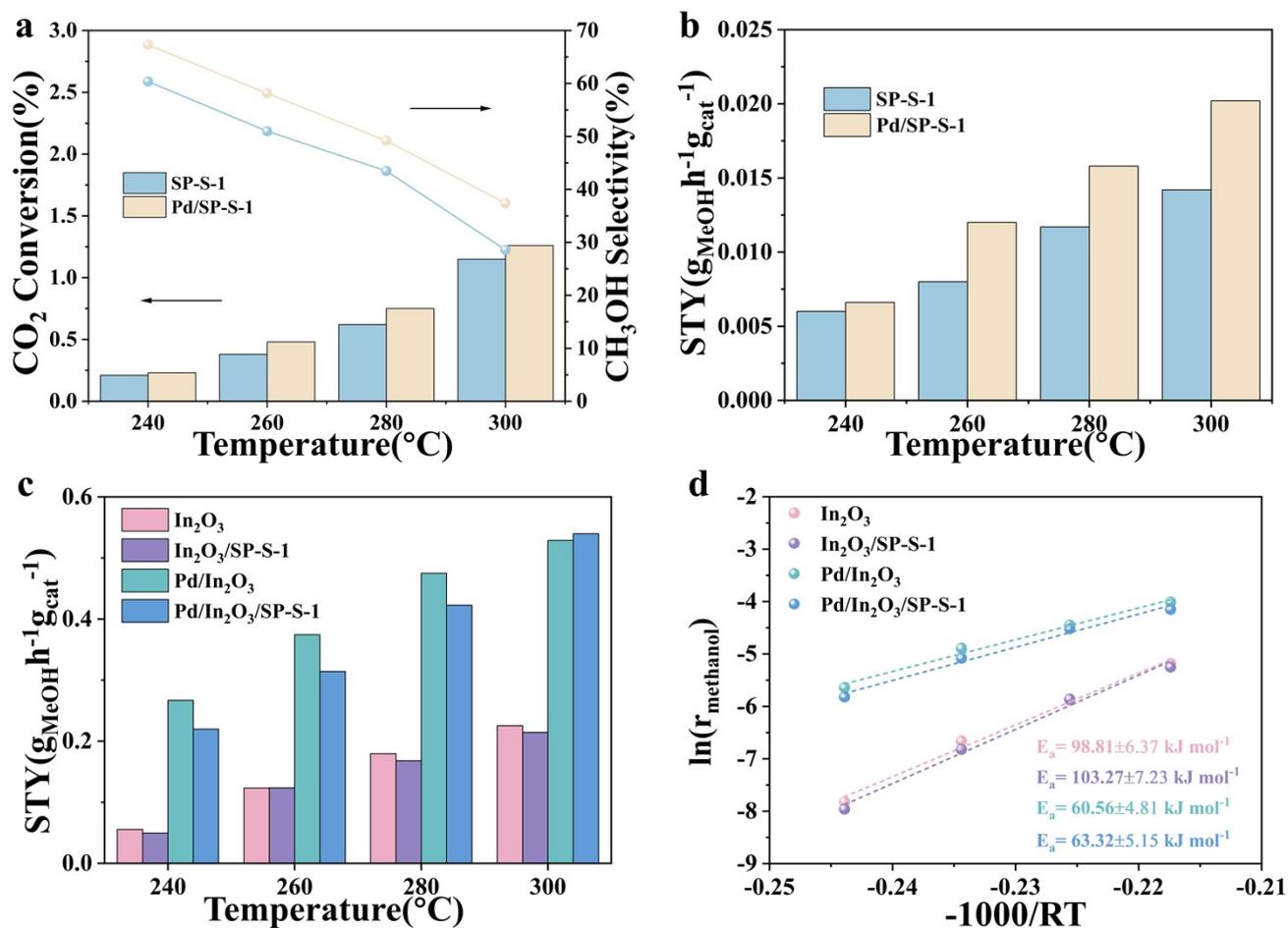


Figure S1 Catalytic activity tests of the SP-S-1 and Pd/SP-S-1 catalysts: (a) CO₂ conversion and methanol selectivity, (b) methanol STY. (c) Methanol STY of In₂O₃, In₂O₃/SP-S-1, Pd/In₂O₃, and Pd/In₂O₃/SP-S-1 catalysts normalized by total catalyst mass. (d) The apparent activation energy of CH₃OH formation. Reaction conditions: 5 MPa, H₂/CO₂ = 4/1, GHSV = 15000 cm³ g_{cat}⁻¹ h⁻¹.

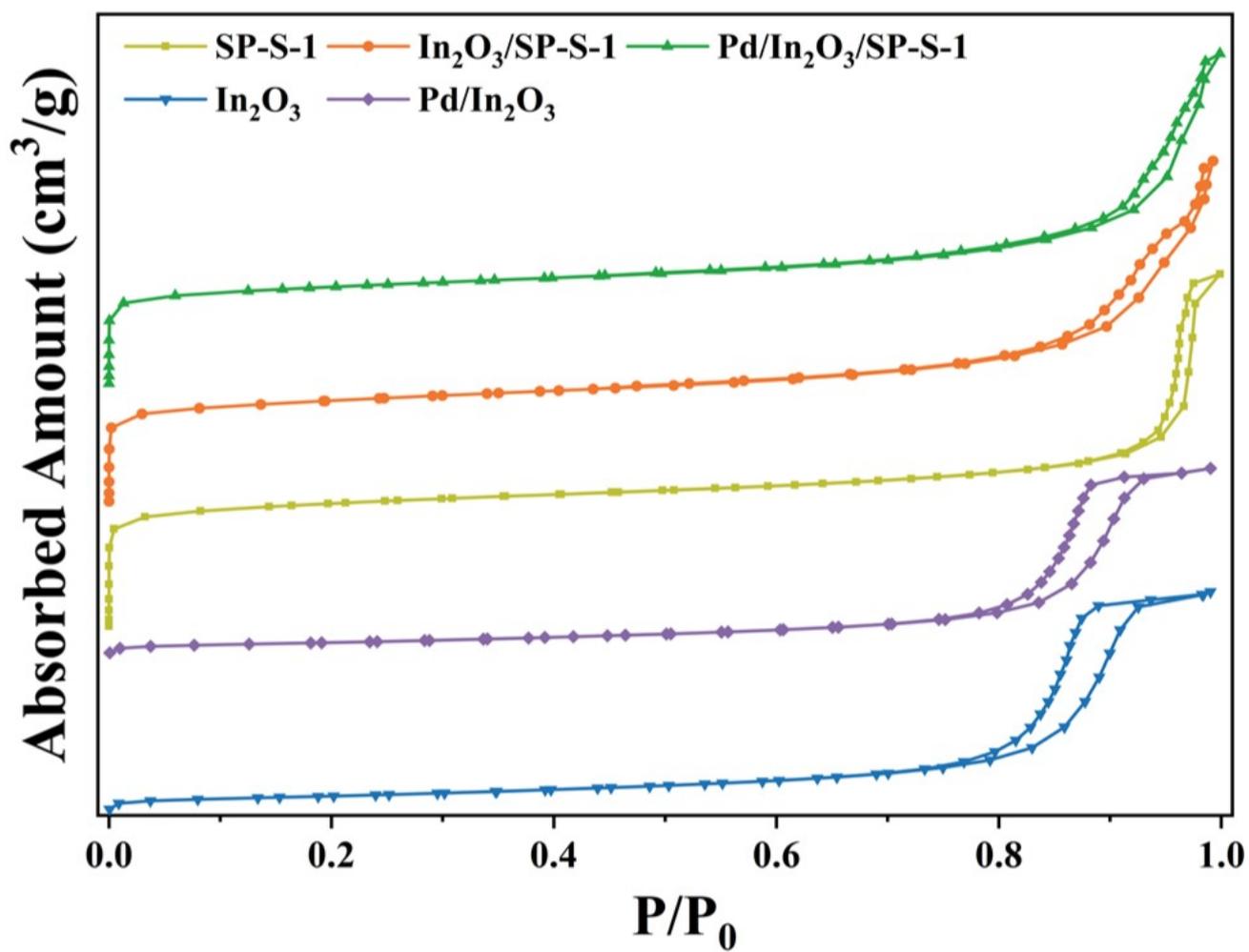


Figure S2 N₂ adsorption-desorption isotherms of catalysts.

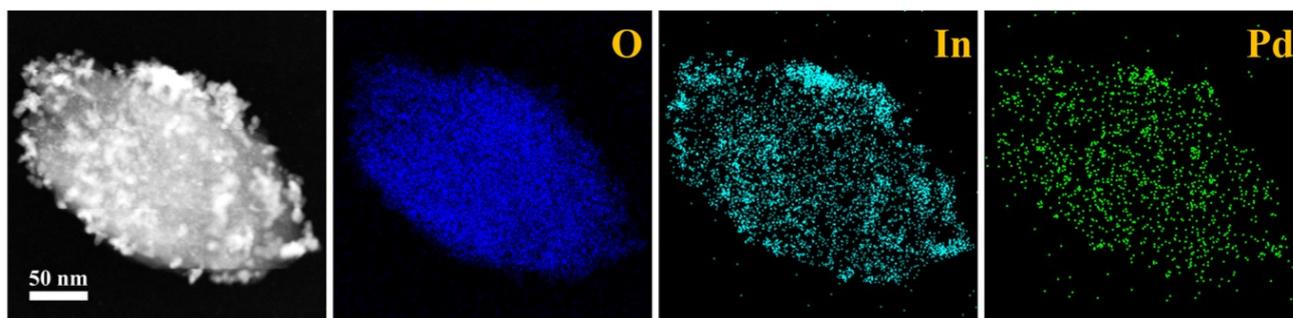


Figure S3 HAADF-STEM images and corresponding EDX elemental mapping images of the fresh Pd/In₂O₃/SP-S-1 catalyst.

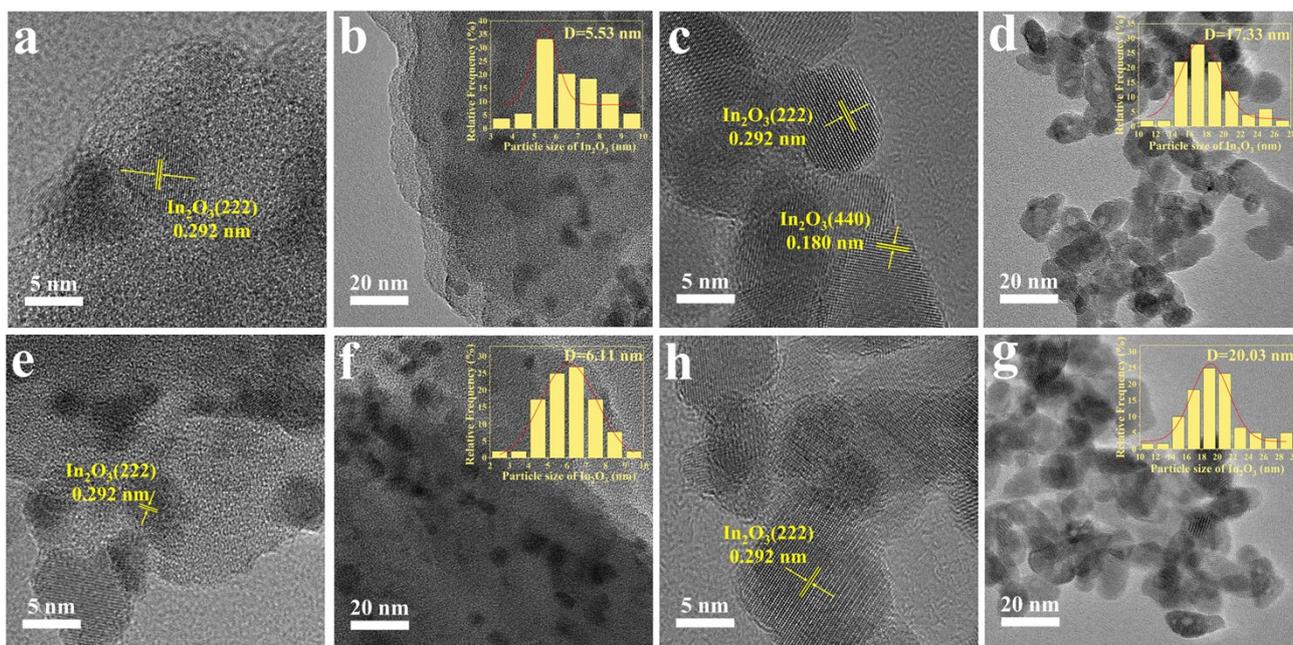


Figure S4 (a) – (b) HRTEM and TEM images with particle size distribution of the fresh $\text{In}_2\text{O}_3/\text{SP-S-1}$ catalyst, (c) – (d) HRTEM and TEM images with particle size distribution of the fresh In_2O_3 catalyst, (e) – (f) HRTEM and TEM images with particle size distribution of the spent $\text{In}_2\text{O}_3/\text{SP-S-1}$ catalyst, (g) – (h) HRTEM and TEM images with particle size distribution of the spent In_2O_3 catalyst after reaction.

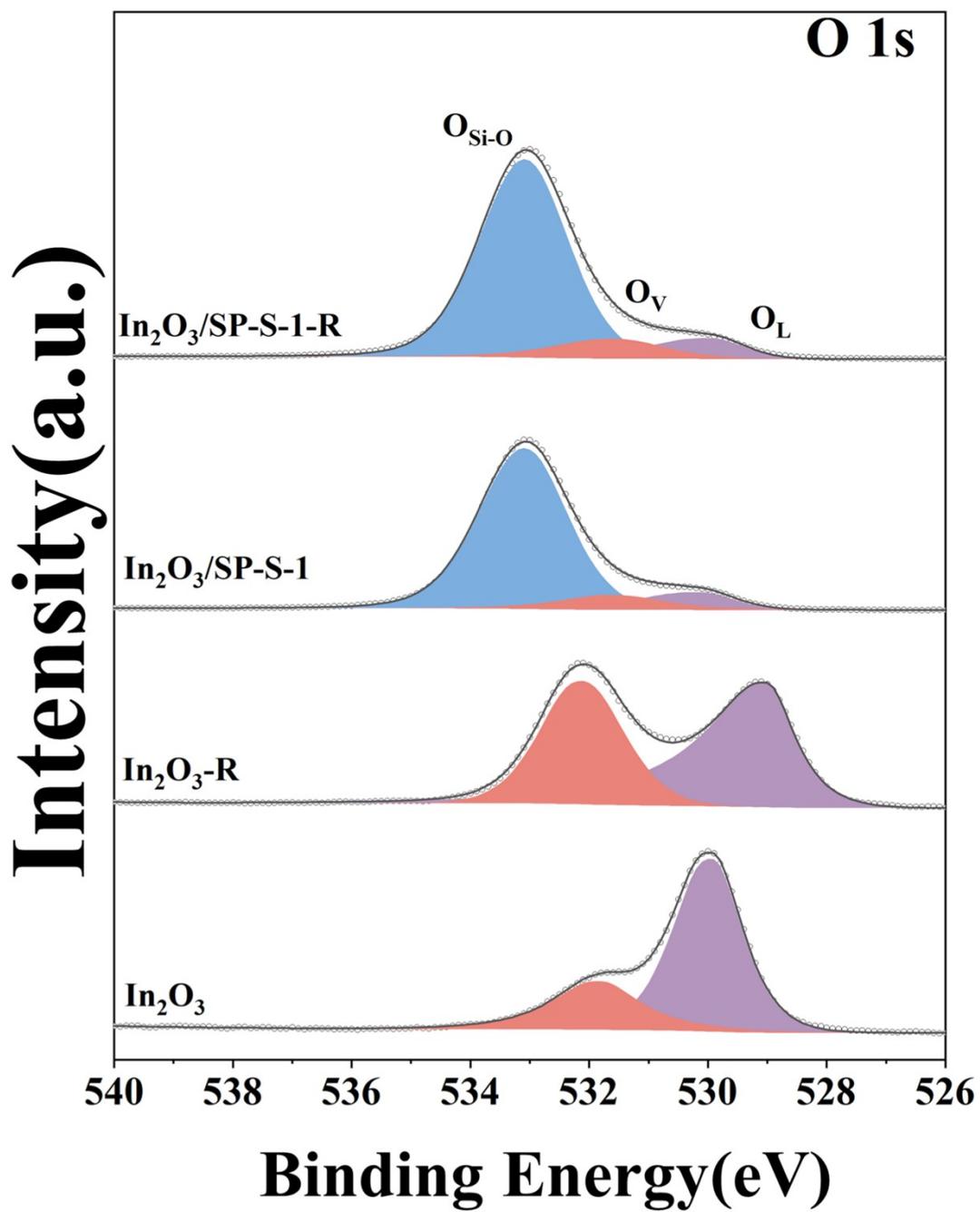


Figure S5 The XPS spectra of fresh and spent In_2O_3 and $\text{In}_2\text{O}_3/\text{SP-S-1}$ catalysts: O 1s

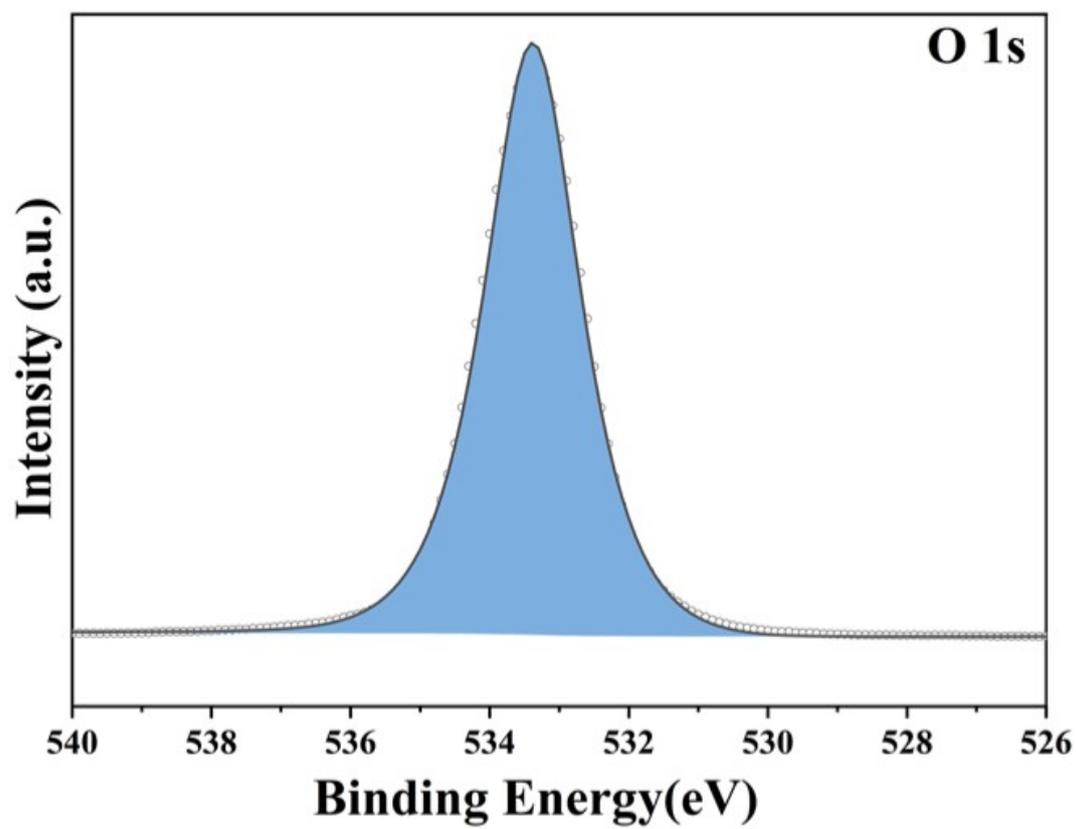


Figure S6 The XPS spectra of SP-S-1: O 1s.

Supplementary Tables

Table S1 Metal loadings of the prepared catalysts determined by ICP-OES.

Catalyst samples	Pd (wt %)	In (wt %)
Pd/In ₂ O ₃	0.97	79.47
In ₂ O ₃ /SP-S-1	-	15.93
Pd/In ₂ O ₃ /SP-S-1	0.98	15.87
Pd/SP-S-1	0.98	-

Table S2 Comparison of CO₂ hydrogenation to methanol with reported catalysts.

Catalyst	H ₂ : CO ₂ ratio	T (°C)	P (MPa)	X _{CO2} (%)	S _{MeOH} (%)	GHSV (cm ³ g _{cat} ⁻¹ h ⁻¹)	STY (g _{MeOH} g _{cat} ⁻¹ h ⁻¹)	STY (g _{MeOH} g _{In+Pd} ⁻¹ h ⁻¹)	Ref
Pd/In ₂ O ₃ /SP-S-1	4:1	300	5	15.98	78.7	15000	0.539	2.569	This work
In ₂ O ₃ /SP-S-1	4:1	300	5	7.7	68.1	15000	0.225	1.071	This work
Pd/In ₂ O ₃	4:1	300	5	20	>70	21000	0.890	0.890	1
In ₂ O ₃	4:1	300	5	6.0	70	21000	0.350	0.350	1
Pd-Pt/In ₂ O ₃	4:1	300	5	17.7	70	21000	0.730	0.730	2
Pd/In ₂ O ₃	4:1	280	5	10	78	48000	1.010	1.040	3
Pd/In ₂ O ₃	4:1	280	5	12	75	24000	0.600	0.600	3
Pd-In ₂ O ₃ -SBA-15	4:1	260	5	12.6	84	15000	0.352	1.760	4
Pd-12In ₂ O ₃ -Al ₂ O ₃	4:1	300	3	8.4	63	40800	0.518	4.317	5
Pd/In ₂ O ₃ -600	3:1	300	5	9.2	63.5	15000	0.387	0.387	6
Pd-In ₂ O ₃ -ZrO ₂	4:1	280	5	12.0	87	48000	1.290	25.8	7
In ₂ O ₃ /ZSM-5-35	3:1	300	4	3.2	68.6	21000	0.154	1.100	8

Table S3 Surface properties of the samples.

Catalyst samples	S_{BET} (m ² /g)	V_{P} (cm ³ /g)	D_{P} (nm)
SP-S-1	472.81	0.66	7.77
In ₂ O ₃ /SP-S-1	402.92	0.62	7.09
Pd/In ₂ O ₃ /SP-S-1	393.62	0.61	7.04
Pd/In ₂ O ₃	66.62	0.34	6.63
In ₂ O ₃	81.59	0.41	6.87

References

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