

Supplementary information

Highly Efficient Catalytic Propane Dehydrogenation Driven by MFI Zeolite Defect Sites

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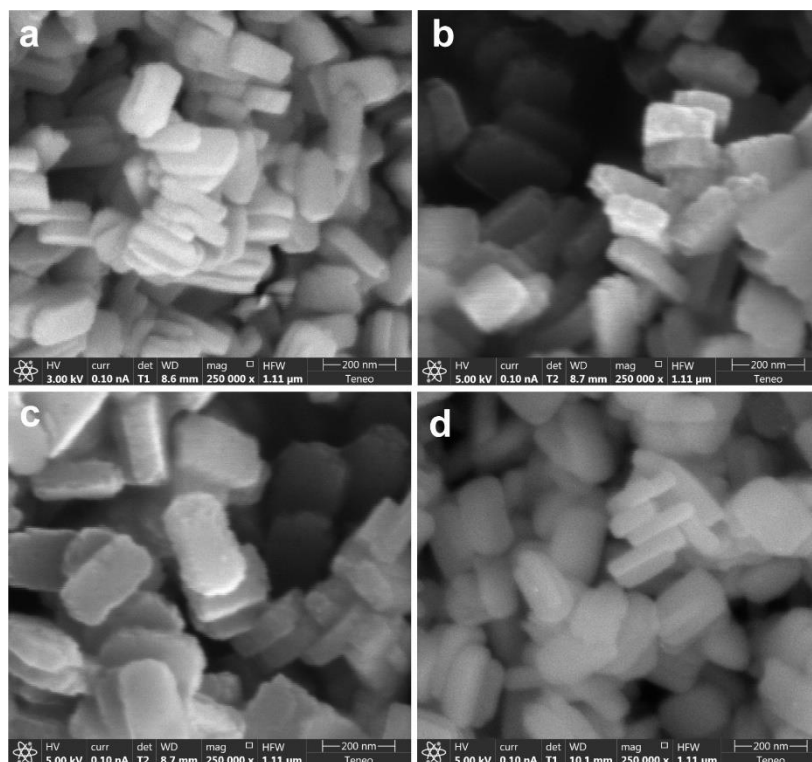
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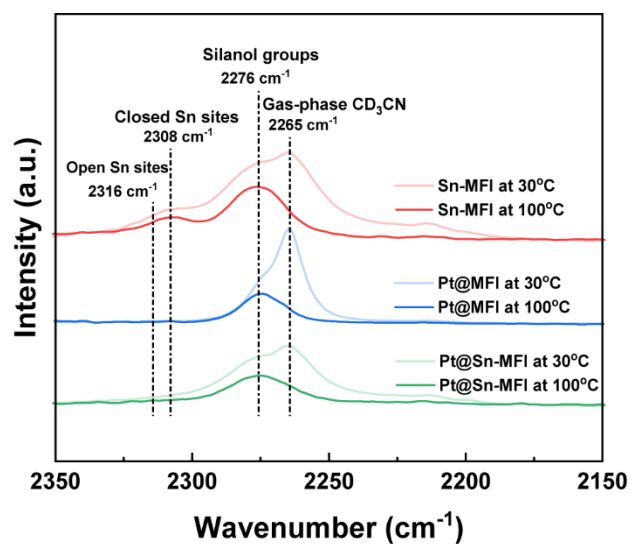
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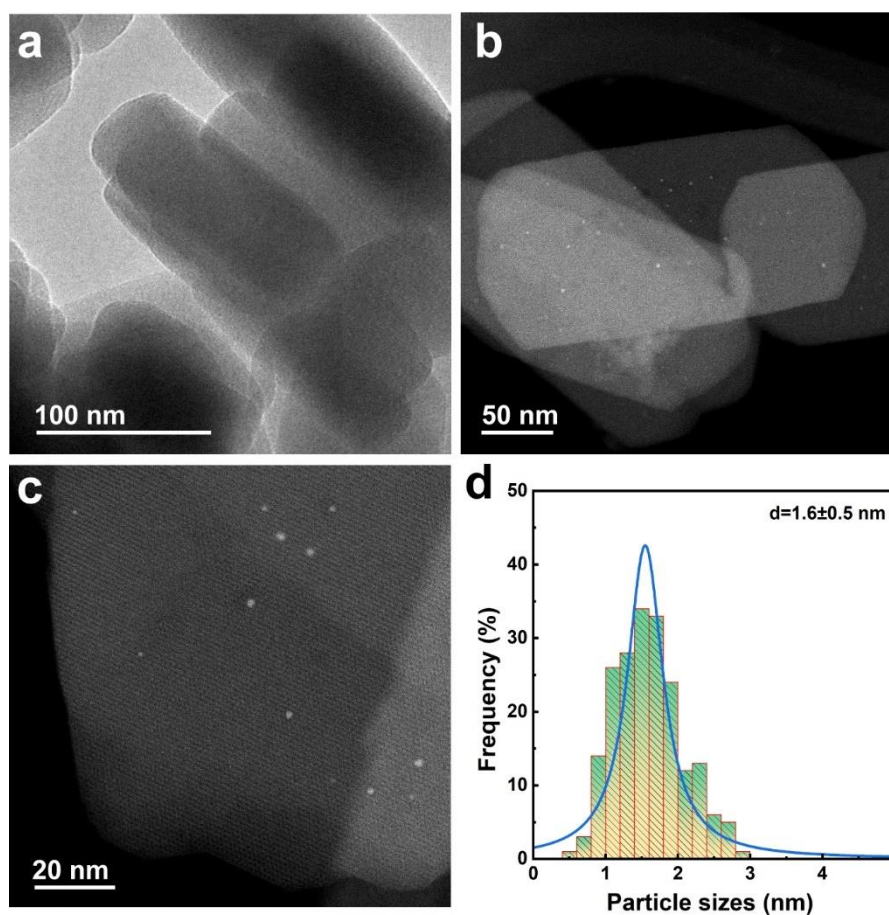
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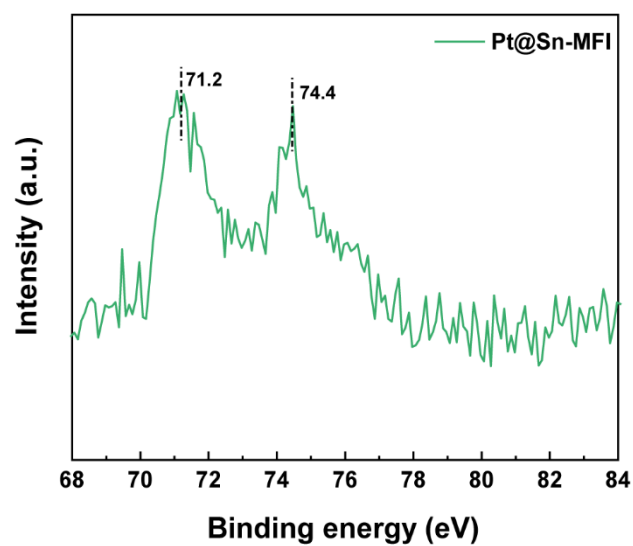
Supplementary Fig. 1 | SEM images of various catalysts. a, Pt@MFI. b, Sn-MFI. c, Pt@Sn-MFI. d, PtSn/MFI.



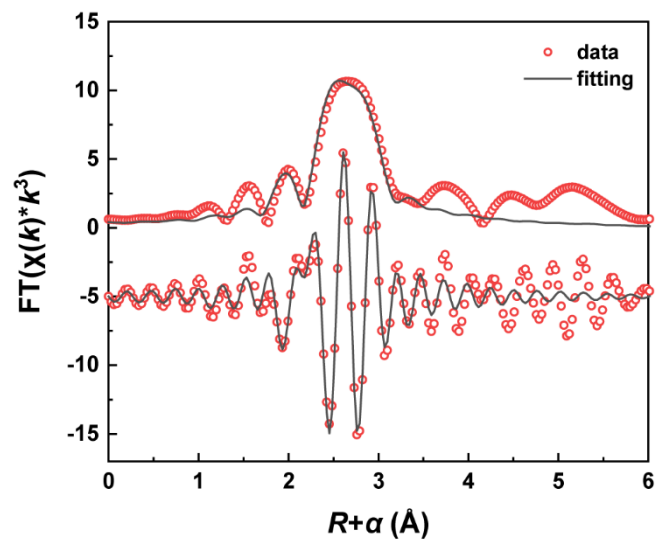
Supplementary Fig. 2 | *In-situ* DRIFTS spectra of Sn-MFI, Pt@MFI and Pt@Sn-MFI using CD_3CN as probe molecular at different temperatures (30 and 100°C).



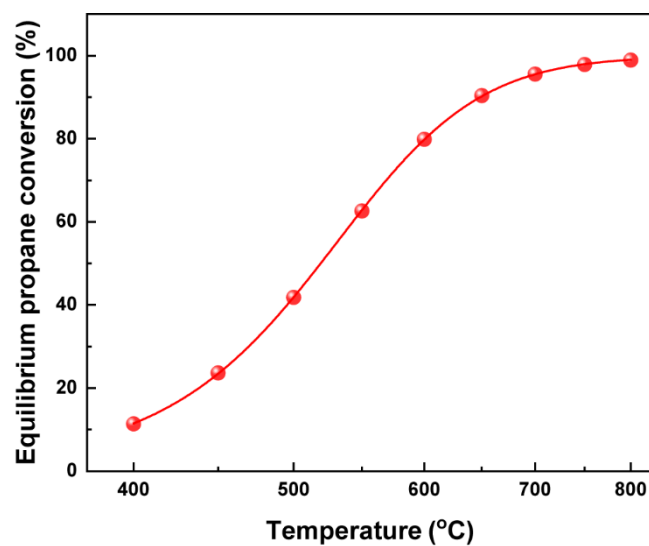
Supplementary Fig. 3 | Pt dispersion of Pt@MFI. a, TEM image. b and c, HAADF-STEM images. d, Corresponding Pt cluster size distribution.



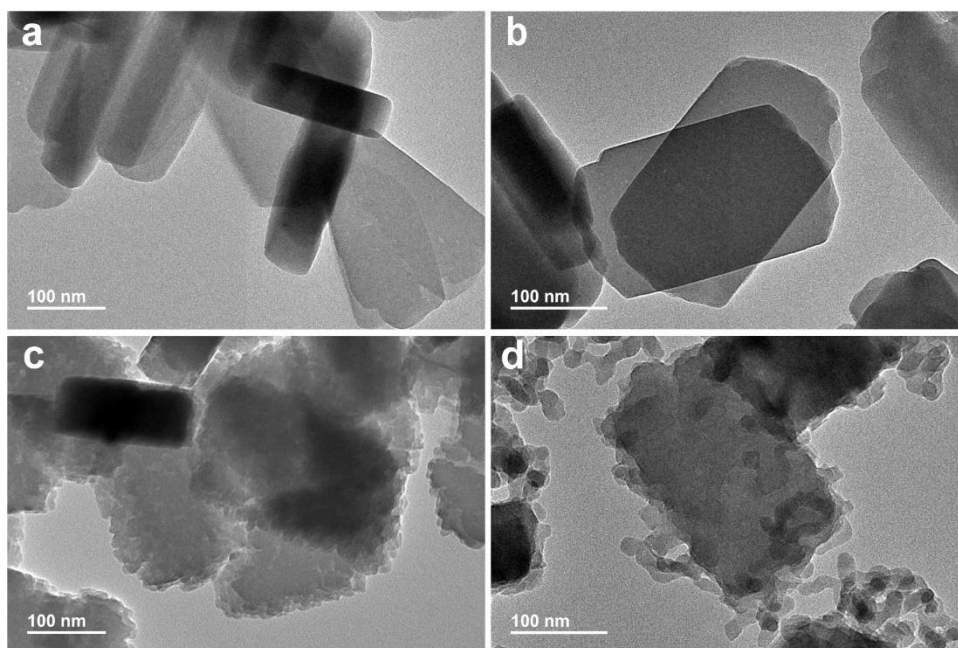
Supplementary Fig. 4 | *Quasi-in situ* Pt 4f XPS spectrum of Pt@Sn-MFI.



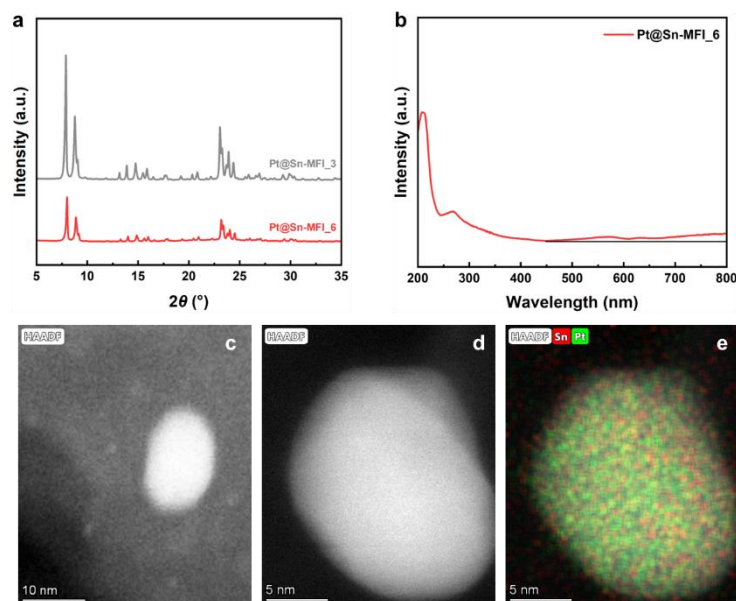
Supplementary Fig. 5 | Fitting EXAFS curve of Pt@Sn-MFI. Only one Pt-Pt path was considered in the fitting process. In each panel, the upper and lower lines are the FT magnitude and imaginary components, respectively.



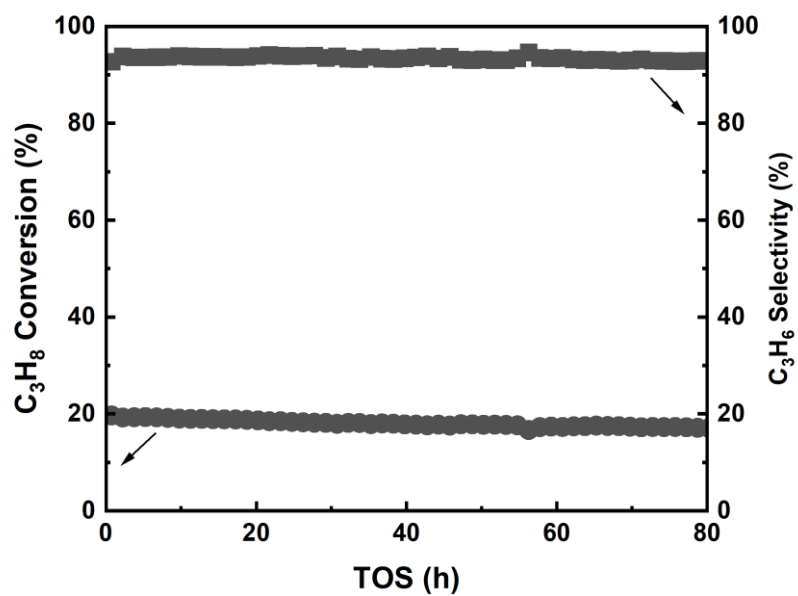
Supplementary Fig. 6 | Equilibrium propane conversion as a reaction temperature function calculated using Aspen Plus software. The partial pressure of propane is fixed at 0.10. Equilibrium conversion improves with increasing reaction temperature.



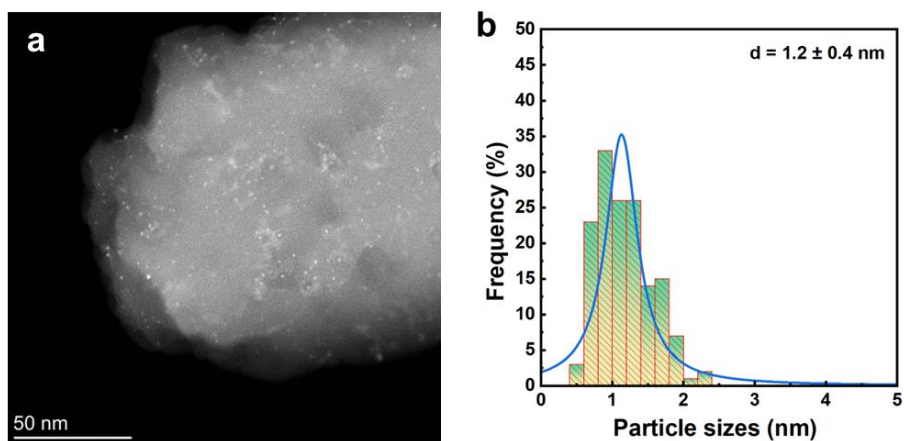
Supplementary Fig. 7 | TEM images. a, 1/3Pt@Sn-MFI_3. **b,** Pt@Sn-MFI_1. **c,** Pt@Sn-MFI_3 (i.e., Pt@Sn-MFI). **d,** Pt@Sn-MFI_6.



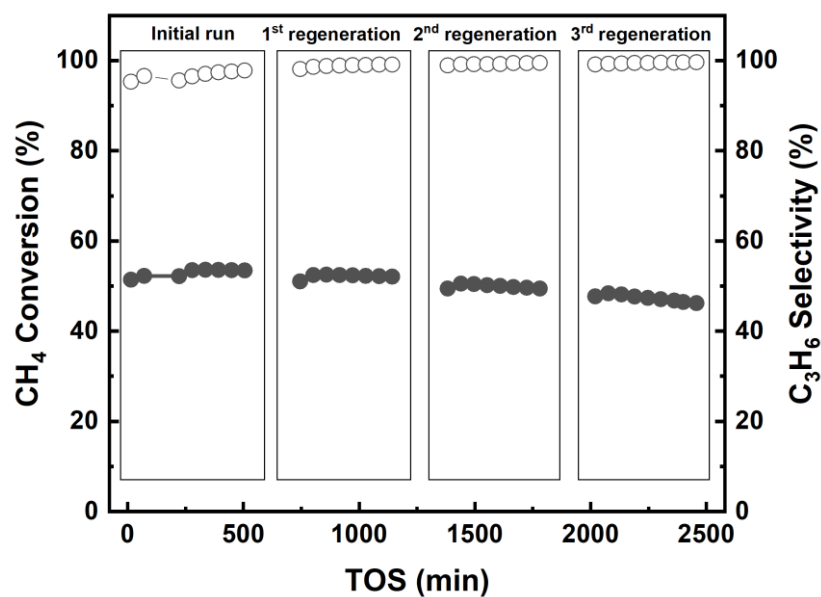
Supplementary Fig. 8 | Structural characterization of Pt@Sn-MFI₆. **a**, XRD patterns. **b**, DR UV-Vis spectrum. **c-d**, HAADF-STEM images. **e**, EDS-Mapping.



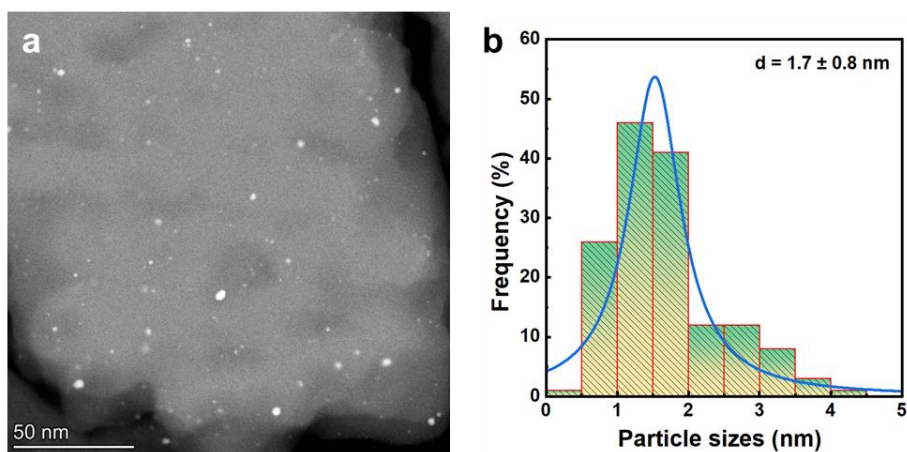
Supplementary Fig. 9 | Stability evaluation of the Pt@Sn-MFI catalyst for the dehydrogenation of pure propane. Reaction conditions: $T = 550\text{ }^{\circ}\text{C}$, pure C_3H_8 , $\text{GHSV} = 9600\text{ mL g}_{\text{cat}}^{-1}\text{h}^{-1}$.



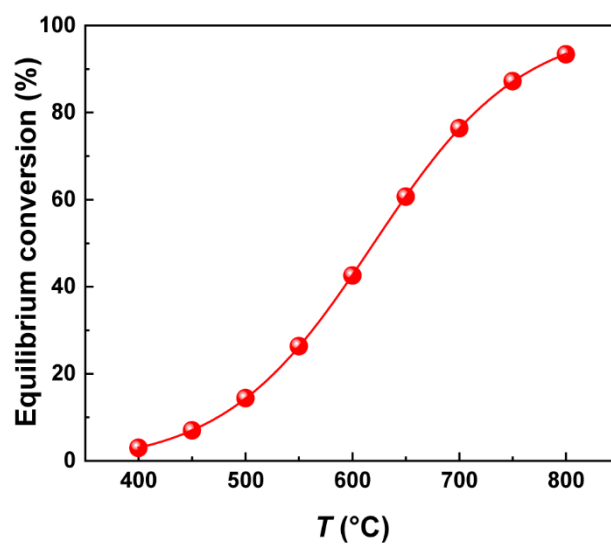
Supplementary Fig. 10 | Pt dispersion of spent Pt@Sn-MFI catalyst under pure propane flow. a, HAADF-STEM image. b, Corresponding cluster size distribution.



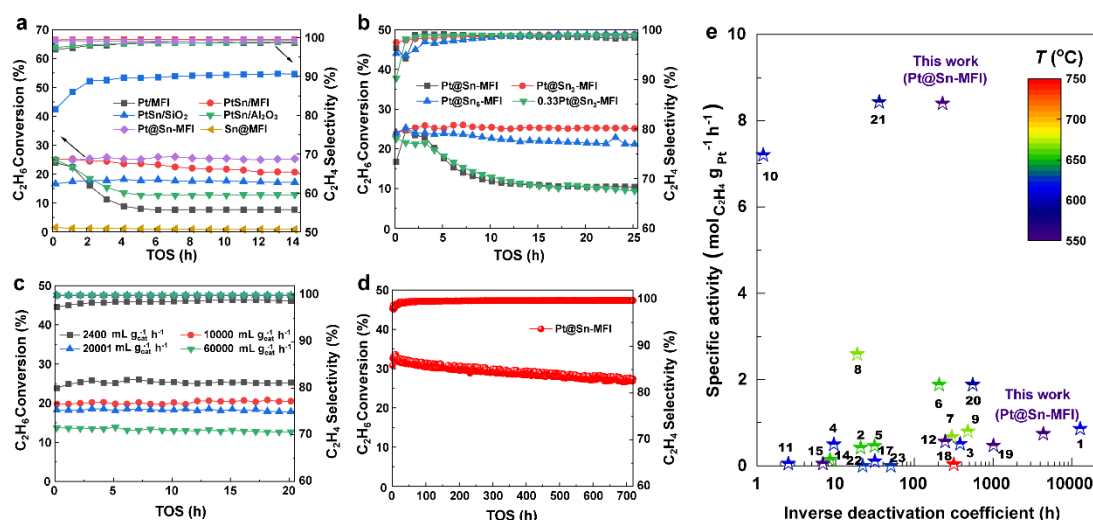
Supplementary Fig. 11 | Dehydrogenation-oxidative regeneration test over the Pt@Sn-MFI catalyst. Reaction conditions were as follows: 1 bar, 550 °C, GHSV = 15000 mL g_{cat}⁻¹ h⁻¹. Regeneration conditions were as follows: 500 °C in air atmosphere for 30 min and subsequent 550 °C in H₂ for 1 h.



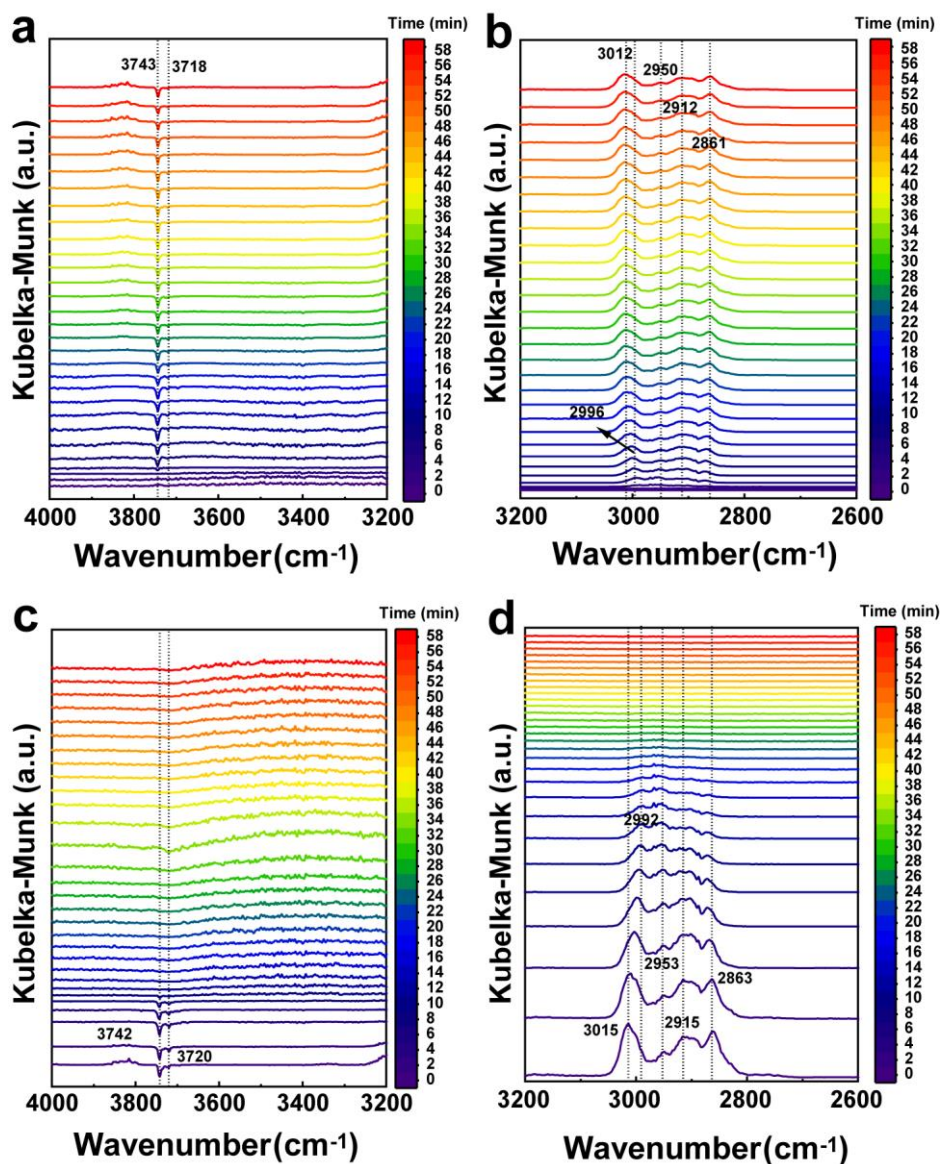
Supplementary Fig. 12 | Pt dispersion of spent Pt@Sn-MFI after three regeneration cycles. a, HAADF-STEM image. b, Corresponding cluster size distribution.



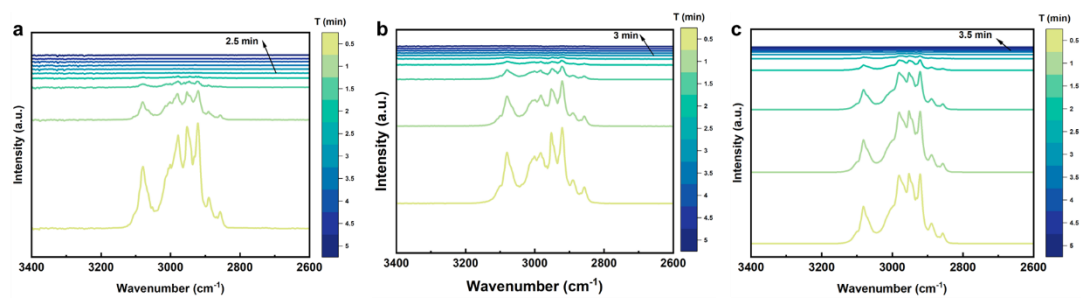
Supplementary Fig. 13 | Equilibrium propane conversion as a reaction temperature function calculated using Aspen Plus software. The partial pressure of propane is fixed at 0.10. Equilibrium conversion improves with increasing reaction temperature.



Supplementary Fig. 14 | Catalytic performance for EDH. **a**, Various catalysts. **b**, Different ratio of Pt with Sn. **c**, Different GHSV over Pt@Sn-MFI. **d**, Long-term stability test for PDH conversion over Pt@Sn-MFI over Pt@Sn-MFI. **e**, Compared with the catalytic performance of the state of art catalysts. The catalytic EDH performance was evaluated using a quartz fixed-bed reactor at atmosphere pressure, equipped with an online gas chromatograph. Reaction conditions of a, b, and d: catalyst mixed with 0.5 g of SiC, ambient pressure, GHSV=2400 mL g_{cat}⁻¹h⁻¹, 550 °C.

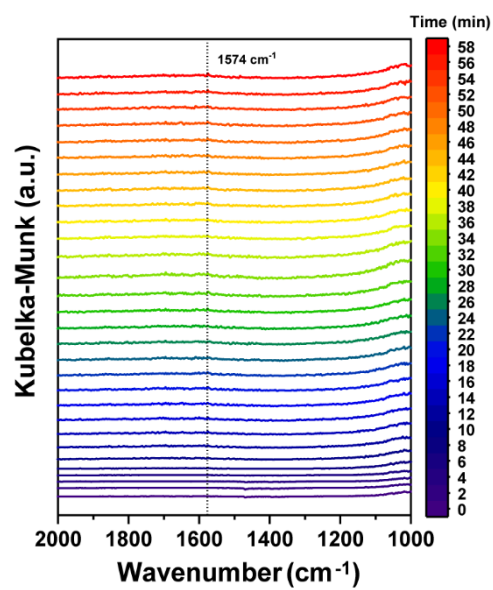


Supplementary Fig. 15 | *In-situ* time-resolved DRIFTS spectra of Pt@Sn-MFI. **a** and **b**, *In-situ* DRIFTS spectra with C₃H₈ flows. **c** and **d**, *In-situ* DRIFTS spectra with He flows.

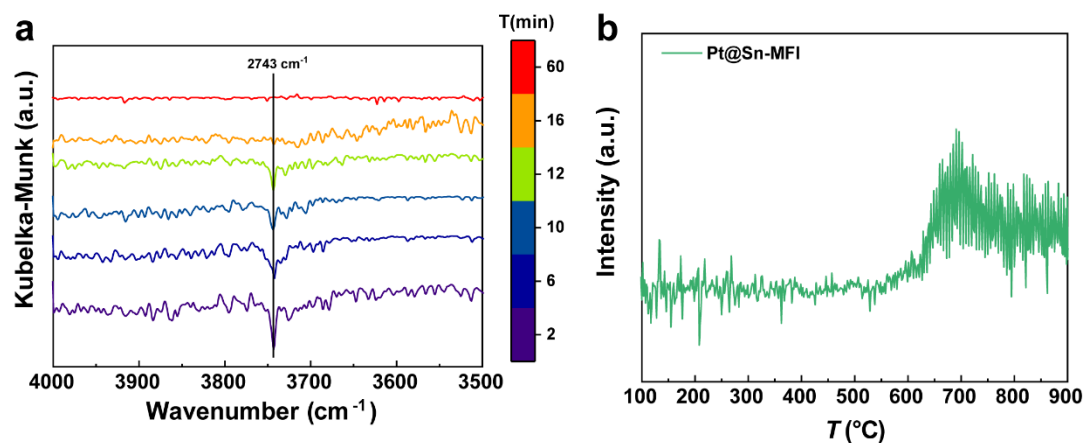


Supplementary Fig. 16 | *In-situ* DRIFTS experiment to monitor C₃H₆ desorption.

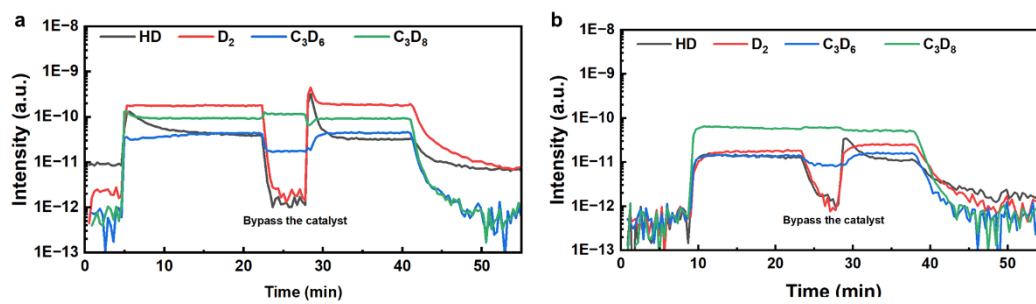
a, Pt@Sn-MFI. b, PtSn/MFI. c, Pt@MFI.



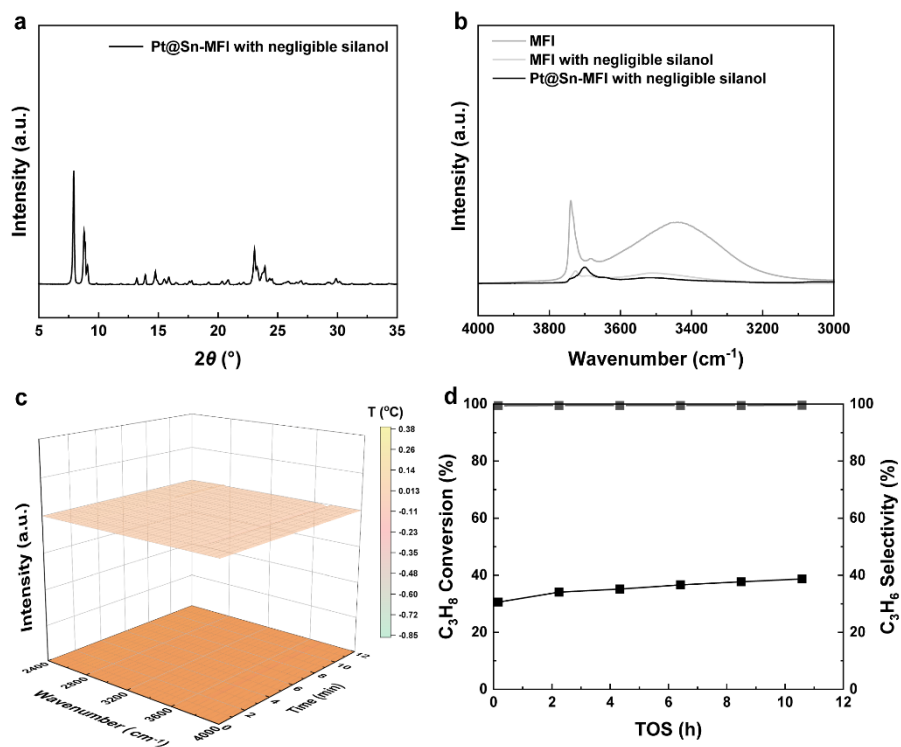
Supplementary Fig. 17 | *In-situ* time-resolved DRIFTS spectra of Pt@Sn-MFI under the He flow.



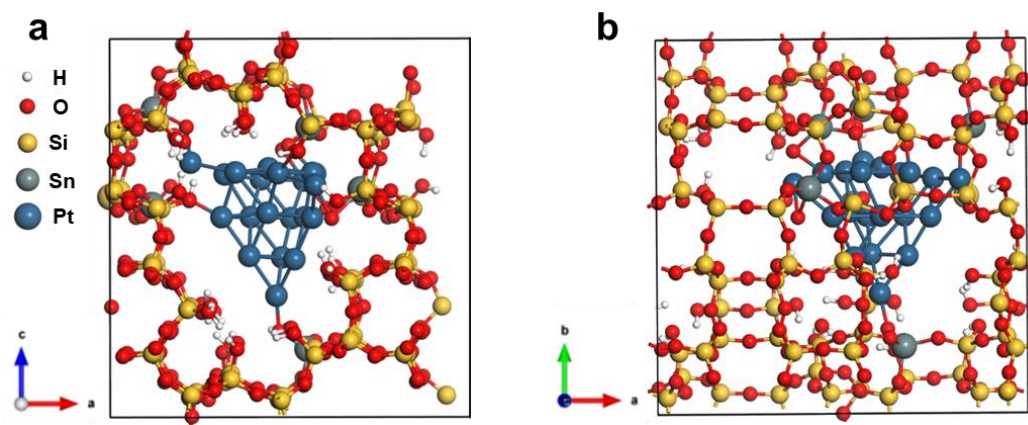
Supplementary Figure 18 | H spillover exists on Pt@Sn-MFI. **a**, *In-situ* DRIFTS spectra of Pt@Sn-MFI pre-treated H_2 under the He flow. **b**, H_2 -TPD/MS curve of Pt@Sn-MFI. $\text{m/s}=2$.



Supplementary Figure 19 | Mass spectra tracing the dehydrogenation process of C_3D_8 . **a**, Pt@Sn-MFI. **b**, Defect-free Pt@Sn-MFI with negligible hydroxyl groups.



Supplementary Figure 20 | Structure characterization and catalytic performance of Pt@Sn-MFI with negligible silanol. a, PXRD pattern. **b**, *In-situ* DRIFTS spectra with He flow. **c**, *In-situ* DRIFTS spectra of Pt@Sn-MFI pre-treated with H₂ under the D₂ flow. **d**, Catalytic performance for PDH.



Supplementary Figure 21 | Stable structure of Sn doped into MFI framework bonding with Pt. a, View from the x-axis. b, view from the z-axis.

Supplementary Table 1 | Pt L3-edge EXAFS fitting parameters for Pt@Sn-MFI using one fitting path of Pt-Pt.^[a]

Sample	Path	R (Å)	CN	E ₀ (eV)	100* δ^2	R-factor
Pt@Sn-MFI	Pt-Pt	2.76 (0.01)	7.5 (1.0)	6 (1)	0.4 (0.1)	0.014

[a] R, distance between absorber and backscatter atoms; CN, coordination number; δ^2 , Debye-Waller factor to account for thermal and structural disorder; ΔE_0 , inner potential correction; R-factor indicates the goodness of the fit.

Supplementary Table 2 | Catalytic activity over Pt-based state-of-the-art catalysts for PDH.

#	Catalysts	T (°C)	Mass flow rate ($\text{L g}_{\text{cat}}^{-1}\text{h}^{-1}$)	Mass flow rate ($\text{L C}_3\text{H}_8 \text{g}_{\text{cat}}^{-1}\text{h}^{-1}$)	Reaction time (h)	Catalytic performance						Ref.
						Cov. C_3H_8 (%)	Sel. C_3H_6 (%)	Rate ($\text{mol g}_{\text{metal}}^{-1}\text{h}^{-1}$)	Yield ($\text{mol C}_3\text{H}_6 \text{g}_{\text{metal}}^{-1}\text{h}^{-1}$)	k_f ($\text{mol C}_3\text{H}_6 \text{g}_{\text{metal}}^{-1}\text{h}^{-1} \text{bar}^{-1}$)	Inverse deactivation coefficient, $1/k_d$ (h)	
1	Pt/Sn-Beta	500	2	0.1	410	48.0- 38.0	85.0- 99.5	1.27- 1.01	1.08-1.00	177.7	1001.2	1
2	Pt/Sn-Beta	500	12	0.6	5	27.5- 25.0	95.5- 97.5	2.25- 2.04	2.15-2.0	72.4	38.7	2
3	PtZn@S-1	550	8.0	2	216.7	47.4- 40.4	93.2- 99.2	5.38- 4.59	5.02-4.55	-	761.1	3
4	0.1Pt-2Zn/Si- Beta	550	22	2.2	150	65.0- 38.0	98.0- 99.5	35.45- 20.73	34.74- 20.62	-	135.3	4
5	GaPt/SiO ₂	550	5.56	1.12	19.7	40.7- 38.5	63.5- 70.1	0.42- 0.40	0.27-0.28	5.2	100	5

6	Pt/Sn-Beta (DG)	550	26.1	10.4	123	15.3- 13.3	~99.0	5.44- 4.72	5.38-4.68	17.9	752.6	6
7	PtSn/ZSM-5	570	39.3(H ₂)	3.93	12	46.0- 33.5	92.0- 99.5	23.1- 16.8	21.2-16.7	525.1	22.8	7
8	Pt/Sn-Beta	570	13.1(H ₂)	1.31	48	50.0- 42.0	92.0- 99.0	5.34- 4.49	4.91-4.44	144.8	148.7	8
9	PtSn/MFI-80 (IWI)	570	1.95	1.95	8	56.8- 39.3	13.5- 14.5	0.85- 0.59	0.12-0.09	-	9.9	9
10	Pt ₁ Sn ₁ /S-1	580	12.0 (H ₂)	2.4	24	37.9- 36.6	98.3- 98.8	3.72- 3.59	3.65-3.55	38.7	431.5	10
11	PtLa/mz-deGa	580	6.1	6.1	480	40.0- 16.0	98.5- 98.0	0.98- 0.39	0.97-0.38	-	383.2	11
12	PtSn/SiO ₂	580	16.3	2.61	8	66.2- 62.0	99.0- 99.5	7.07- 6.68	7.00-6.64	-	100.9(49.6)	12
13	Pt- Sn/MgAl ₂ O ₄	580	12(H ₂)	1.2	90	45.5- 38.9	99.1- 99.7	5.72- 4.89	5.67-4.88	129.5	332.1	13
14	PtSn/2Mg-	580	6.54	4.58	6	43.0-	95.0-	5.43-	4.79-3.94	-	23.3	14

	SBA-15					38.1	97.84	4.50				
15	PtSn/TS-1	590	0.17(H ₂)	0.03	7	53.5- 47.5	92.3- 93.5	0.12- 0.11	0.11-0.10	2.5	29.1	15
16	PtSn/Al ₂ O ₃	590	32.7	3.27	25	48.7- 44.6	98.1- 99.1	29.73- 27.22	29.16- 26.98	704.9	151.7	16
17	PtNa/Sn-ZSM- 5	590	2.2(H ₂)	1.7	9	41.7- 39.1	95.6- 98.4	5.68- 5.33	5.43-5.24	348.1	83.3	17
18	PtSnNa (1.0%)/AlSBA- 15	590	2.2(H ₂)	1.7	7	27.5- 17.4	94.2- 94.6	4.26- 2.70	4.01-2.55	10.8	11.9	18
19	PtSn@MFI	600	3.9	0.93	20	65.0- 38.0	91.0- 95.0	5.93- 3.47	5.39-3.30	2814.6	18.0	19
20	K-PtSn@MFI	600	3.9	0.93	67	69.0- 48.0	89.5- 98.5	6.29- 4.38	5.63-4.31	-	76.1	19
21	K-PtSn@ MFI-600H ₂ -1h	600	64.5	15.0	16.5	41.0- 16.0	92.5- 98.0	60.0- 23.4	55.5-22.9	521.4	12.7	20
22	K-PtSn@	600	64.5	15.0	16.5	44.0- 44.0	98.0- 98.0	64.4- 64.4	63.1-39.2	666.0	22.7	20

	MFI-600H ₂ -3h					27.5	99.0	40.2				
23	Pt/Sn-ZSM-5	600	3.9	0.90	24	70.0-45.0	92.5-99.5	7.83-5.06	7.24-5.04	-	23.0	21
24	PtSn/SBA-15	600	60(H ₂)	8.4	8	40.0-24.0	92.0-92.0	18.31-10.99	16.85-10.11	229.8	10.7	22
25	PtGa@MFI	600	12(H ₂)	3	20	22.0-15.0	98.5-97.5	5.74-3.91	5.65-3.82	30.6	42.6	23
26	0.6PtSn/1.5In-Al	600	/(H ₂)	/	53.3	55.0-42.0	97.5-96.5	/	/	-	101.8	24
27	PtSn/θ-Al ₂ O ₃ (ethanol)	600	22.5(H ₂)	13.5	5	29.4-23.7	88.4-87.7	17.8-14.7	15.6-12.9	49.1	19.4	25
28	Pt@Sn-MFI	600	85.7	17.1	12.1	55.0-33.9	99.0-98.7	96.34-59.30	95.37-58.61	-	13.9	This work
29	Pt@Sn-MFI	550	9.6	0.96	120.5	59.2-55.7	98.5-99.4	5.80-5.46	5.72-5.43	1064.5	844.2	

Supplementary Table 3 | Catalytic activity over the state-of-the-art catalysts for EDH.

#	Catalysts	T (°C)	Mass flow rate ($\text{L g}_{\text{cat}}^{-1} \text{h}^{-1}$)	Mass flow rate ($\text{L C}_2\text{H}_6 \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$)	Reaction time (h)	Catalytic performance					Ref.
						Cov. C_2H_6 (%)	Sel. C_2H_4 (%)	Rate ($\text{mol g}_{\text{metal}}^{-1} \text{h}^{-1}$)	Yield ($\text{mol C}_2\text{H}_4 \text{g}_{\text{metal}}^{-1} \text{h}^{-1}$)	Inverse deactivation coefficient, 1/kd (h)	
1	Fe-S1	600	2	0.6	200	26.3- 26.0	97.5- 97.5	0.88- 0.87	0.86-0.85	12874.4	26
2	0.89Fe/HZ5	650	6	0.3	21.67	52.0- 27.7	74-90	0.58- 0.31	0.42-0.28	20.8	27
3	0.088Pt/M-TS1	600	12	9.0	6	6.9-6.8	99-99	0.52-5.3	0.51-0.51	382.8	28
4	0.61Fe/HZ5	600	36	3.2	4.5	9.9- 15.0	65.0- 68.8	0.77-1.2	0.50-0.83	9.5	29
5	1.0Co/HZ5	650	9	0.27	6	42.8- 38.2	89.3- 95.0	0.52- 0.46	0.46-0.44	31.4	30
6	0.8Cr/S1	650	6	1.2	40	27.7- 24.0	99-99	1.90- 1.65	1.88-1.63	206.9	31
7	1.0In-CHA	660	6	0.6	20	25.9- 27.2	96.1- 96.9	0.70- 0.73	0.67-0.71	300.0	32
8	PtSn/Al ₂ O ₃	660	6	0.6	20	53.1- 28.2	79.6- 95.7	3.26- 1.73	2.59-1.66	18.9	32

9	1.0In-CHA	660	6	0.6	40	32.7-30.9	90.7-91.2	0.88-0.83	0.80-0.76	481.9	33
10	PtSn/Mg(Al)O	600	144	28.8	1.67	4.9-2.7	99.8-99.9	7.2-4.0	7.2-4.0	1.2	34
11	1P-Mo/ZSM5	600	5	0.5	4.33	44.0-12.5	25-74	0.19-0.05	0.05-0.04	2.5	35
12	Pt@HZ-5	550	2	1.8	40	18.0-15.2	86.1-88.4	0.94-0.79	0.56-0.70	246.7	36
13	PtIn/SiO ₂	600	/	/	/	15.0	99.0	0.67	0.66	/	37
14	Cr/SBA-15	650	9	0.45	6	41.0-25.5	91.5-96.3	0.15-0.09	0.14-0.09	8.5	38
15	PtSn-Mg(Ga)(Al)O	550	/	/	2	28.1-24.2	> 99	0.05	0.05	6.9	39
16	Pt ₃ Ir/Mg(Al)O	600	144	28.8	0.5	/	89.5-95.0	3.13-2.65	2.80-2.52	/	40
17	Ni 3Ga/Al ₂ O ₃	600	12	1.2	32	15.0-6.0	84.0-90.5	0.14-0.05	0.11-0.05	31.5	41
18	PtZn/SiO ₂	600	/	/	18	0.2-0.055	> 99	/	/	55.5	42
19	1Pt0.7Zn@S-1	550	2.4	0.72	30	16.3-15.9	98.5	0.48-0.47	0.47-0.46	1013.0	43
20	Co/S-1	590	5.3	5.3	9.7	13.2-13.0	85.9-92.4	2.20-2.16	1.88-2.00	552.11	44
21	PtSn/Al ₂ O ₃	590	5.3	5.3	9.7	12.1-9.5	96.6-97.8	8.73-6.86	8.43-6.70	35.8	44

22	PtSn-SA	625	3.24(H ₂)	0.648	10	29.5- 21.0	85.0- 95.0	0.00078- 0.00056	0.00066- 0.00053	22.0	45
23	PtSnZnGa-SA	625	3.24(H ₂)	0.648	10	30.0- 26.0	97.5- 99.1	0.0008- 0.00069	0.00078- 0.00068	50.3	45
24	La _{0.9} Mn _{0.8} Ni _{0.2} O ₃	750	30	15	30	42.8- 40.5	98.0	0.034- 0.029	0.033-0.028	316.9	46
25	Pt@Sn-MFI	550	2.4	0.12	720	30.8- 27.4	98.1- 99.8	0.76- 0.67	0.74-0.67	4365.3	This work
26	Pt@Sn-MFI	550	60	6	20	13.7- 12.7	99.9- 99.9	8.40- 7.79	8.40-7.79	229.1	

Supplementary References

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