Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic Supplementary Information

Framework-confined Sn in Si-Beta stabilizing ultra-small Pt nanoclusters as direct propane dehydrogenation catalysts with high selectivity and stability

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Experimental section

1 Preparation of Zn-Si-Beta catalyst.

Zn-Si-Beta catalyst was prepared by dealumination of H-Beta and then the introduction of Zn species via dry impregnation. In a typical process, commercial H-Beta zeolite was stirred in a 13 M nitric acid aqueous solution (20 mL $g_{zeolite}^{-1}$) at 100 ^{o}C for 10 h to obtain a dealuminated Beta (Si-Beta). The mixture was centrifuged and washed with deionized water for several times to remove residual nitric acid, then dried for 12 h in a vacuum oven (200 ^{o}C, -0.1 MPa) to remove physisorpted water. Afterwards, 1.0 g of Si-Beta was finely ground with a certain amount of $Zn(NO_3)_2 \cdot 6H_2O$ and calcined at 550 °C for 6 h. The as-prepared samples were labeled as Zn-Si-Beta. For comparison, Zn-H-Beta was synthesized with the similar procedure of Zn-Si-Beta sample.

2 Preparation of Pt/Zn-Si-Beta catalyst.

The Pt/Zn-Si-Beta catalyst was prepared by introducing the platinum precursor onto the Zn-Si-Beta using the wet impregnation method. Typically, 1 g Zn-Si-Beta was stirred in 20 mL deionized water for 2 h. Then, calculated H_2PtCl_6 solution (0.01 M) was added dropwise into the above solution, and then, the mixture was subsequently stirred at 25 °C for 6 h. After that, the solvent was slowly evaporated at 80 °C under stirring until the solvent was all evaporated, and the remaining solid was further dried at 100 °C for 12 h. Finally, the Pt/Zn-Si-Beta was obtained after calcination at 550 ^{o}C for 6.0 h with 3 ^{o}C min^{-1} heating rate. For reference, Pt/Zn-H-Beta was also prepared by the similar procedure.

Figures:

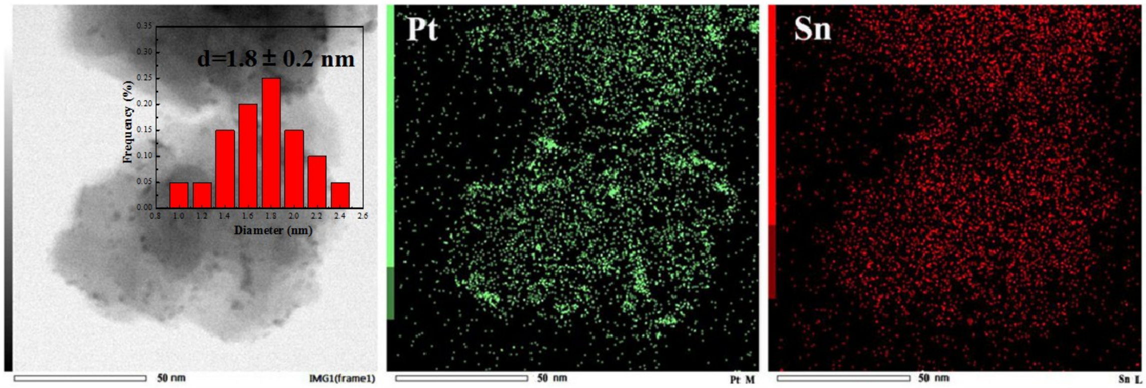

Fig. S1 TEM and EDS elemental mapping images of the 1.5Pt/2.5Sn-Si-Beta.

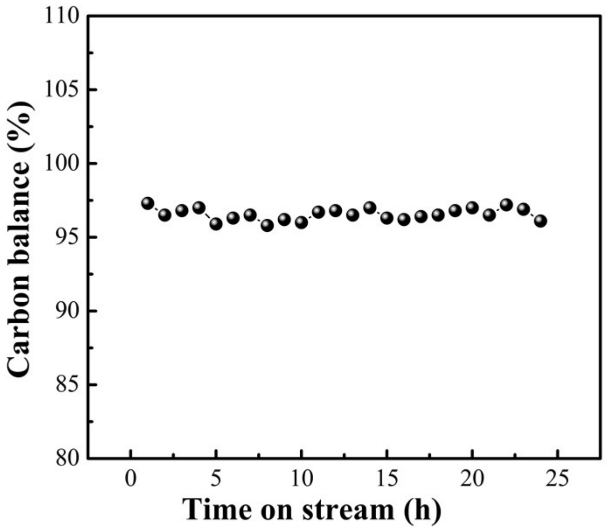

Fig. S2 Carbon balance value of 0.3Pt/0.5Sn-Si-Beta as a function of reaction time.

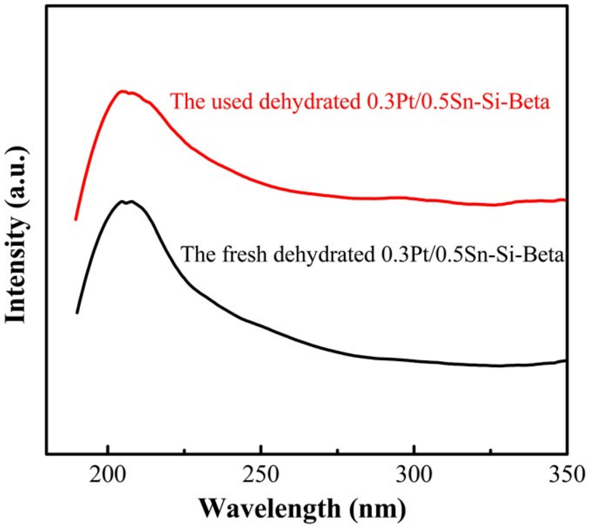

Fig. S3 Diffuse reflectance UV-vis spectra of the dehydrated fresh 0.3Pt/0.5Sn-Si-Beta and the used 0.3Pt/0.5Sn-Si-Beta after 12 h on stream at 550 ^{o}C.

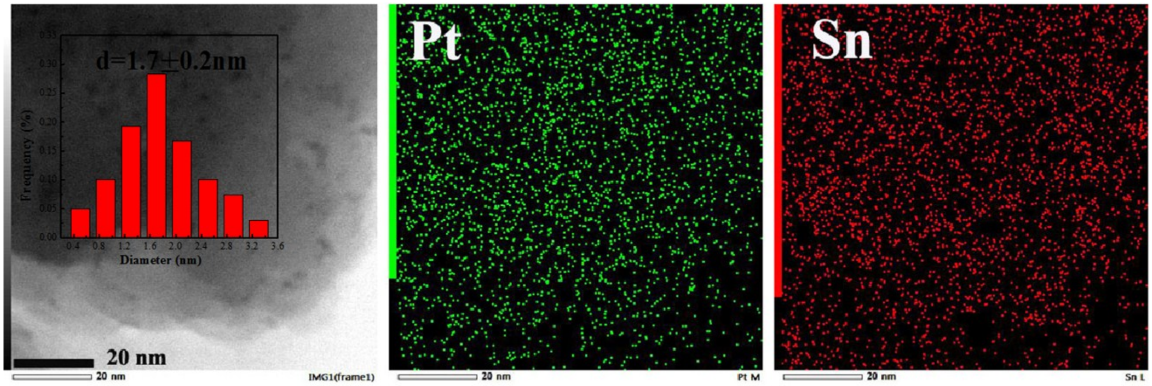

Fig. S4 TEM and EDS elemental mapping images of the used 0.3Pt/0.5Sn-Si-Beta after 12 h on stream at 550 ^{o}C,, as well as the corresponding histograms of Pt particle size distribution (*inset)*.

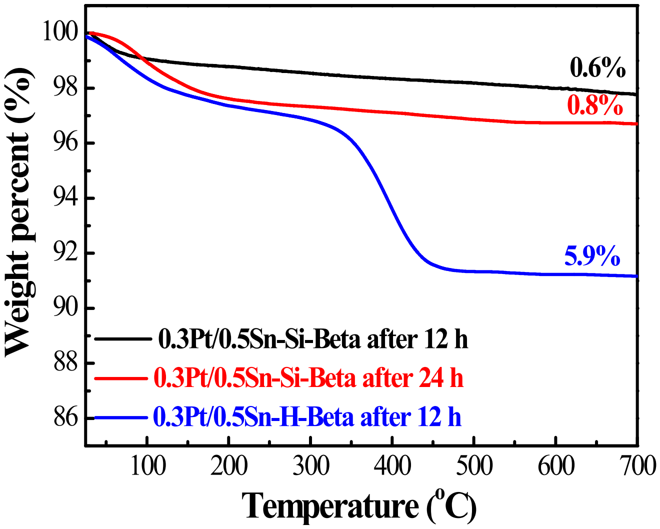

Fig. S5 TG results of the used 0.3Pt/0.5Sn-Si-Beta and 0.3Pt/0.5Sn-H-Beta after PDH at 550 °C for different time on stream.

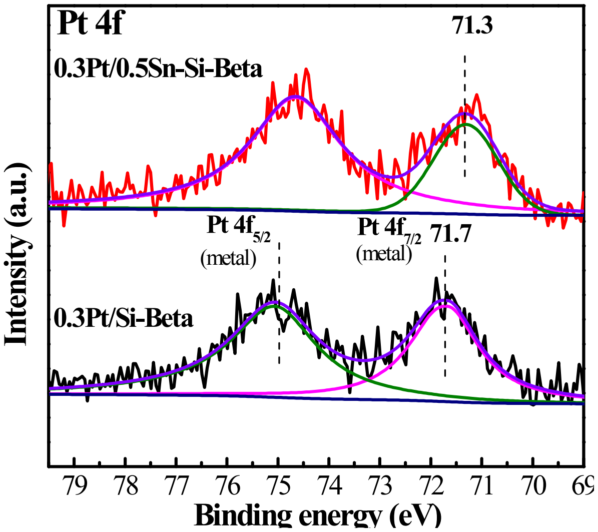

Fig. S6 Pt 4f XPS spectra of 0.3Pt/Si-Beta and 0.3Pt/0.5Sn-Si-Beta catalysts.

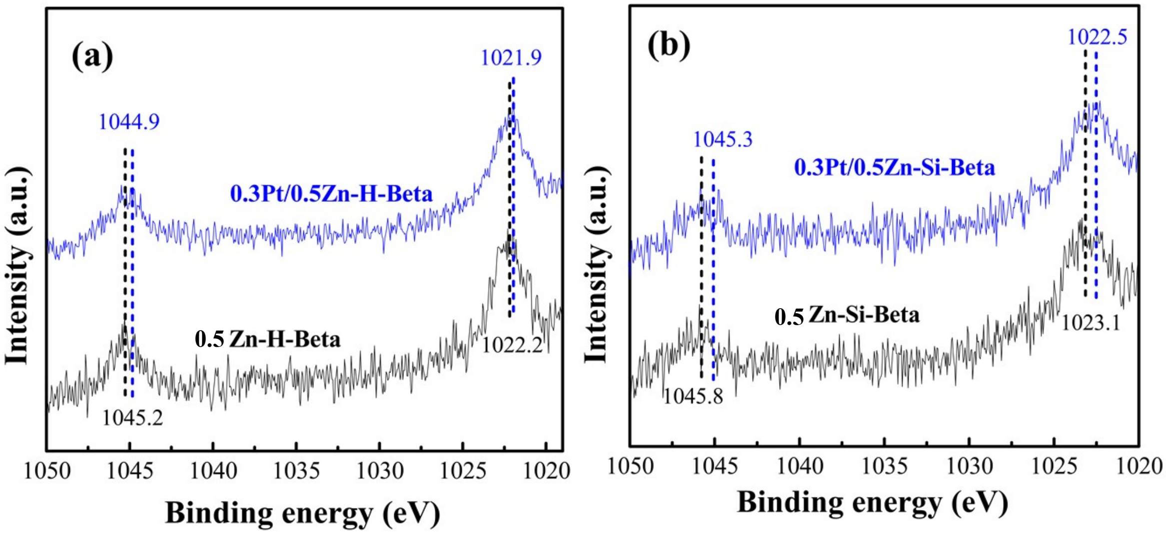

Fig. S7 Zn 2p XPS spectra for (a) 0.5Zn-H-Beta and 0.3Pt/0.5Zn-H-Beta and (b) 0.5Zn-Si-Beta and 0.3Pt/0.5Zn-Si-Beta.

Tables:

Table S1. Metal loading amounts measured by ICP-OES for the prepared catalysts.

Samples	Pt loading (wt%)	Sn loading (wt%)
0.1Pt/0.5Sn-Si-Beta	0.08	0.44
0.2Pt/0.5Sn-Si-Beta	0.19	0.47
0.3Pt/0.5Sn-Si-Beta	0.28	0.42
0.4Pt/0.5Sn-Si-Beta	0.38	0.44
0.5Pt/0.5Sn-Si-Beta	0.47	0.46
0.6Pt/0.5Sn-Si-Beta	0.55	0.42
0.3Pt/0Sn-Si-Beta	0.27	0
0.3Pt/0.1Sn-Si-Beta	0.28	0.07
0.3Pt/0.3Sn-Si-Beta	0.29	0.26
0.3Pt/0.5Sn-Si-Beta	0.26	0.47
0.3Pt/0.7Sn-Si-Beta	0.28	0.63
0.3Pt/1Sn-Si-Beta	0.29	0.8
0.3Pt/1.3Sn-Si-Beta	0.28	1.21
0.3Pt/1.5Sn-Si-Beta	0.26	1.3

Table S2. Catalytic properties of propane dehydrogenation over Pt-based catalysts in this work and in the literature.

No.	Catalysts [a]	T [^{o}C]	WHSV [h^{-1}]	Feed composition	Conversion [b] [%]	Selectivity [%]	Specific activity of C_3H_6 formation [s^{-1}][c]	k_d [d] [h^{-1}]	[h] [e]	Ref
1	0.6wt%Pt-5wt% $Ga/MgAl_2O_4$	605	3.9	C_3H_8=73, H_2=27	31-30	97-98	0.176	0.024	41.7	[1]
2	0.9wt%Pt/Mg(Ga)(Al)O	600	2.6	C_3H_8=20, H_2=25, He=55	16-11.4	99.2	0.0113	0.20	5	[2]
3	0.7wt%Pt/Mg(In)(Al)O	600	2.6	C_3H_8=20, H_2=25, He=55	20.4-16.3	98	0.183	0.14	2	[3]
4	0.35wt%Pt-1.26wt%Sn/Al_2O_3	519	3.5	C_3H_8=30, N_2=70	31-20	95-98	0.109	0.29	3.4	[4]
5	0.36wt%Pt-0.68wt%Sn/Al_2O_3-sheet	590	9.4	C_3H_8=16, H_2=20, N_2=64	48.7-44.6	98.7	1.58	0.007	143	[5]
6	0.1Pt10Cu/Al_2O_3	520	4	C_3H_8/H_2=1/1, N_2=50	13.1-12.4	87-89	0.56	0.0005	2000	[6]
7	PtNa/Zn(1.0%)-ZSM-5	590	3	H_2/C_3H_8=0.25	40.6-37.9	93-97	-	0.073	13.7	[7]
8	0.5 wt% Pt-Sn-Na/Al-SBA-15	590	3	C_3H_8=75, H_2=25	27.5-12.6	~94	0.143	0.024	40	[8]
9	0.5wt%Pt-0.6wt%Sn/TS-1	590	3	$C_3H_8/H_2/N_2$=1/1/4	53.5-47.7	92.5-93.0	0.4	0.033	30.3	[9]
10	0.5wt%Pt-2.0wt%Sn-1.0wt%Na/SUZ-4	590	3	H_2/C_3H_8=3/1	24-22	90-91	0.160	0.011	88	[10]
11	0.5 wt % Pt/Zn-Beta	555	2.6	C_3H_8=100	40-29	55-90	0.141	0.04	12	[11]
12	0.5wt%Pt-Na/ Sn-ZSM-5	590	3	C_3H_8=75, H_2=25	41.7- 39.1	95.3-98	0.220	0.012	83.3	[12]
13	0.3Pt/0.5Sn-H-Beta	550	1	N_2/C_3H_8=19/1	14.3-7.4	99.4-99.9	0.06	0.058	17.2	This work
14	0.3Pt/0.5Sn-Si-Beta	550	1	N_2/C_3H_8=19/1	27.5-25.2	99.1-99.9	0.13	0.007	142.8	This work

[a] Catalysts described in this work and in the literature.

[b] First value is obtained at the start of the cycle, second at the end.

[c] Specific activity is defined as the moles of C_3H_6 formation per mole of Pt atom per second.

[d] k_d, deactivation rate constant calculated from $\ln [(1-X_{final})/X_{final}]=k_d * t + \ln [(1-X_{intial})/X_{intial}]$.

[e] Time required for rates to decrease by e^{-1}, $\tau=1/k_d$.

Table S3. Physicochemical parameters of 0.3Pt/Si-Beta, 0.3Pt/0.5Sn-Si-Beta and 0.3Pt/0.5Sn-H-Beta catalysts.

Samples	cluster size [a] (nm)	cluster size [b] (nm)	Dispersion of Pt [c] (%)	Loading [d] (wt%)		Loading [e] (wt%)	
				Pt	Sn	Pt	Sn
0.3Pt/0.5Sn-Si-Beta	-	1.6	75	0.28	0.46	0.26	0.45
0.3Pt/0.5Sn-H-Beta	3.5	6.5	30	0.27	0.48	0.20	0.41
0.3Pt/Si-Beta	2.6	6.9	41	0.27	-	0.18	-

[a] Evaluated using the TEM images for fresh catalysts.

[b] Evaluated using the TEM images for spent catalysts.

[c] Determined by H_2-O_2 titration measurements for fresh catalysts.

[d] Measured by ICP-OES for fresh catalysts.

[e] Measured by ICP-OES for spent catalysts.

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