Dual anchoring strategy to construct ultra-low metal loading Co/BEA catalyst for propane dehydrogenation

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Supporting Information

Catalyst characterization.

X-ray diffraction (XRD) patterns of Alβ, DeAlβ, xCo/β-SC and xCo/β-IM samples were recorded on a Rigaku D/MAXRB XRD instrument (Japan) using Cu Kα radiation. H_2-Temperature Programmed Reduction (H_2-TPR) experiments were performed using BSD-C200 Automatic Chemisorption Analyzer. 0.05g catalyst was heated in a 100% Ar (30 mL/min) at a ramp rate of 10 °C/min to 700 °C, and the H_2 signal was tracked using a thermal conductivity detector (TCD).

Transmission electron microscopy (TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) images, along with energy dispersive X-ray spectroscopy mapping, were obtained using a JEOL JEM-F200 instrument operating at 300 kV. iDPC imaging were performed on a were collected on a Thermofisher Spectra 300 at 300 kV. In order to limit the damage of the electron beam, a fast image recording scheme is adopted, using the electron beam current of 1-2 pm.

X-ray photoelectron spectra (XPS) of catalyst samples were carried out on a PHI 5000 Versa Probe II spectrometer equipped with an Al Kα X-ray source (1486.6 eV).

The UV-Vis spectra were recorded on a TU-1901 spectrophotometer, and BaSO4 was

used as the standard for solid samples.

Pyridine adsorption FT-IR was recorded using Bruker VERTEX 70 spectrometer. Specific procedures were as follows: (1) The supporting wafer (10-12 mg/cm^2) of sample was pre-treated in the i*n-situ* IR cell equipped with CaF_2 window at 400 °C for 1 h under high vacuum, then cooled down to 150 °C and recorded background spectra between 4000 and 1200 cm^{-1} with 4 cm^{-1} spectral resolution and 32 scans. (2) The activated wafer was exposed to pyridine vapor at 150 °C for 0.5 h to obtain saturation adsorption and then the FTIR spectra were scanned after degassed at 150 °C for 1 h.

Temperature programmed surface reaction (TPSR) measurements of sample are analyzed using an on-line gas chromatograph, equipped with Flame Ionization Detector (FID) and Thermal Conductivity Detector (TCD). Before measurement, the fresh sample (200 mg, 60-100 mesh) is pretreated in pure N2 (20 ml·min^{-1}) at 873 K for 1 h. After cooling down, the measured sample is heated from 373 to 923 K with a step of 3 K min-1 in 66 mL min-1 of 12% propane flow. The FID and TCD signals of CH_4, C_2H_6, C_3H_6 and H_2 are tracked every 3 min

C_3H_8 FT-IR spectra were recorded using a BRUKER VERTEX 70 spectrometer equipped with a high-temperature reaction chamber. *In-situ* FT-IR spectra with the C_3H_8 consisted of the following steps: (1) The catalyst was pretreated in pure N_2 at 600 °C for 30 min, then collected the target temperature background data. (2) 5% C_3H_8/N_2 was introduced into the cell. (3) The cell was heated to the desired temperature at a ramp rate of 10°C/min, and FT-IR spectra were acquired at specific temperatures.

Raman spectroscopy is performed by Thermo Fischer DXR Raman Spectrometer with 532 nm laser to analyze the generated coke deposition.

Thermogravimetric-differential thermal analysis (TG-DTA). TG-DTA was measured on a STA449F3 Jupiter instrument. The variation in the weight of spent sample (20 mg) was monitored by increasing the temperature in air (50 mL·min^{-1}) from R.T. to 800 °C with a heating rate of 10°C·min^{-1}.

Supplementary Figures and Tables

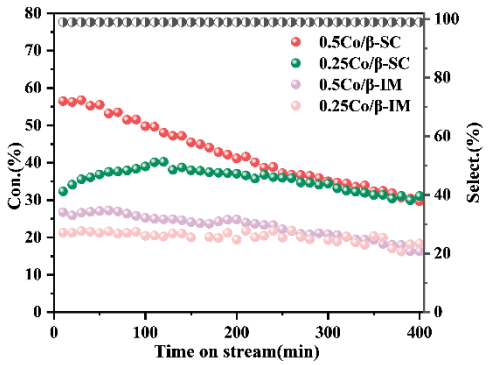

Figure. S1. xCo/β-IM catalytic activity, reaction condition:600℃, m_{cat}:0.2g, 12% C_3H_8 in Ar.

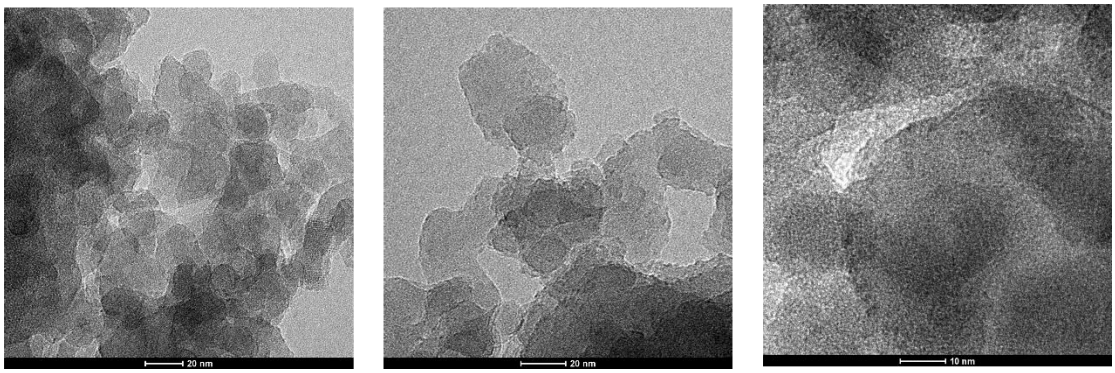

Figure. S2.TEM images of 0.25Co/β-SC

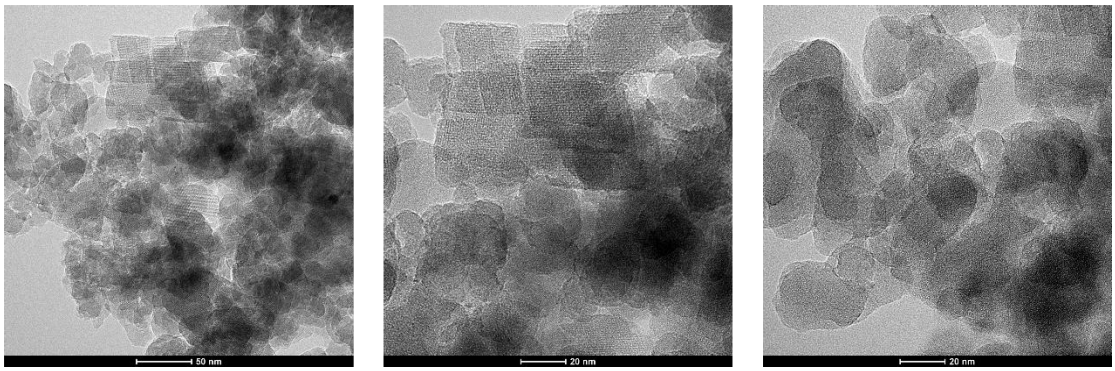

Figure. S3 TEM images of 0.5Co/β-SC

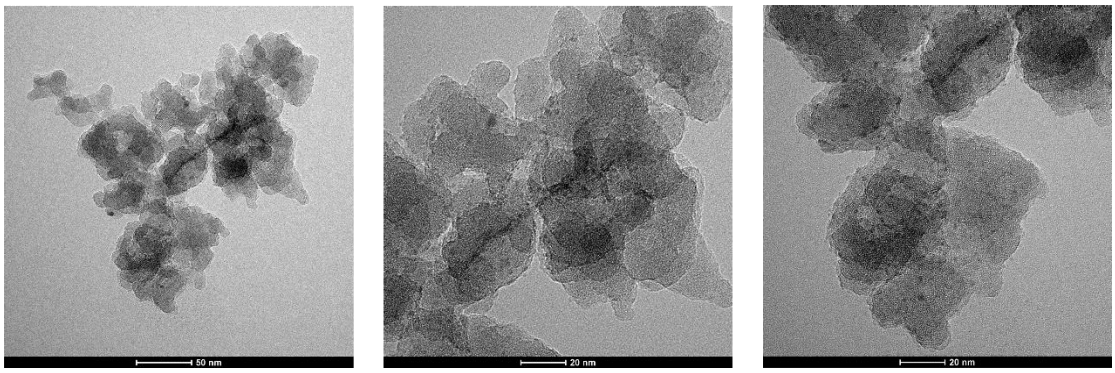

Figure. S4 TEM images of 1.0Co/β-SC

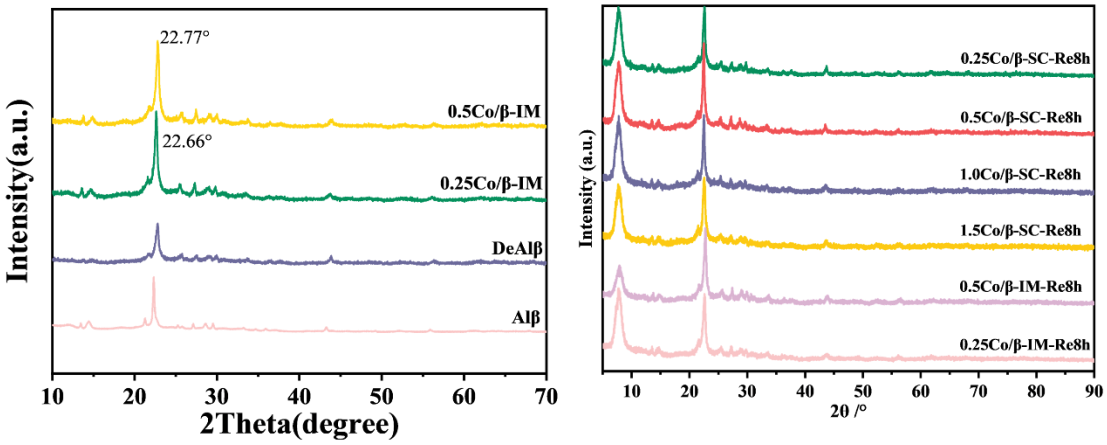

Figure. S5. XRD of xCo/β-IM (a) and spent catalysts (b)

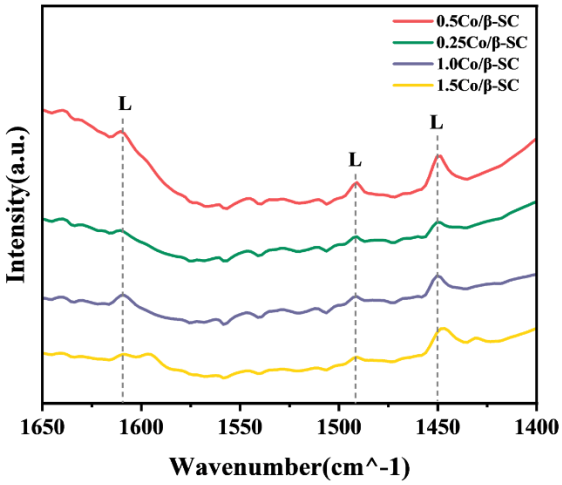

Figure. S6. FT-IR spectra of pyridine adsorption on the different catalysts, desorption at 150 °C

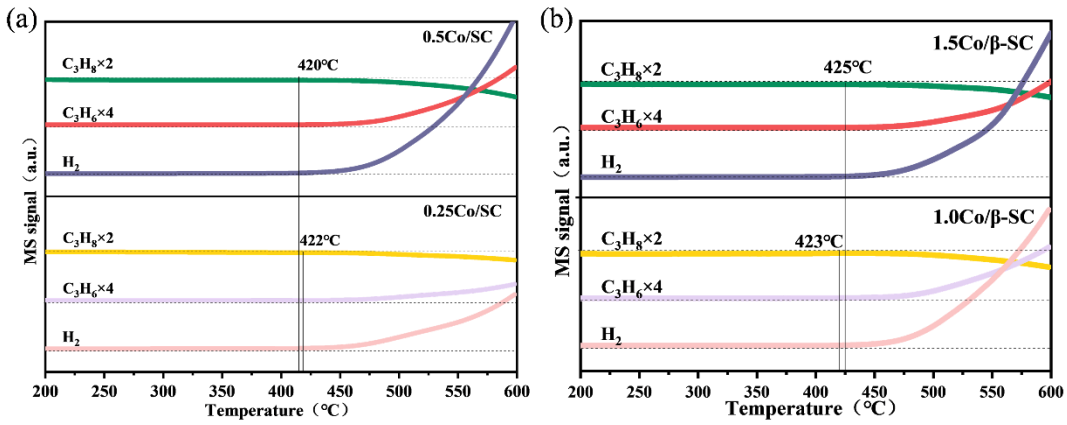

Figure. S7. Propane TPSR and MASS signal of production of 0.25/0.5Co/β-SC(a), 1.0/1.5Co/β-SC(b)

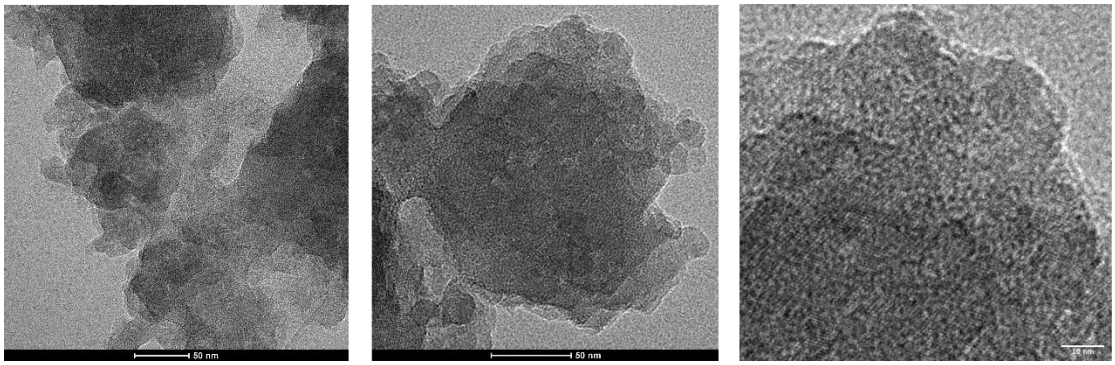

Figure. S8. TEM images of spent 0.25Co/β-SC after 110h PDH

Table S1. Summary of PDH performance data for reported Co containing catalysts.

Samples	Co loading [wt%]	M cat [g]	T[°C]	C_3H_8 Feed [$L\cdot h^{-1}$]	C_3H_8 concentration	Con[%]	Sel[%]	TOF[h^{-1}]	C_3H_6 formation rate mol_{C3H6} [$g_{Co}^{-1}\cdot h^{-1}$]	Specific activity [μmol(C_3H_8)g_{Co}^{-1} $^1S^{-1}$)]	k_f [mol_{C3H6}/g_{Co}^{-1} $^1h^{-1}bar^{-1}$]	Ref.
0.25Co/β-IM	0.19	0.2	600	0.475	12.00%	20.4	99.0	670.80	667.44	3163.53	588.69	This work
0.5Co/β-IM	0.379	0.2			12.00%	27.2		448.38	446.14	2114.59	324.91	
0.25Co/β-SC	0.145	0.2			12.00%	40.1		1727.79	1719.15	8148.40	1056.78	
0.5CO/β-SC	0.356	0.2			12.00%	56.7		995.05	990.08	4692.77	638.74	
1.0Co/β-SC	0.789	0.2			12.00%	52.2		413.34	411.27	1949.35	254.34	
1.5Co/β-SC	1.431	0.2			12.00%	52.0		227.03	225.89	1070.68	139.51	
0.25Co/β-SC	0.145	0.2	550	0.12	10.00%	42.6	99.5	463.51	461.19	2185.96	371.27	
Co-m-Al_2O_3	1.00	0.5	600	0.600	58.80%	34.0	95.0	107.24	101.88	505.75	15.65	1
Co/γ-Al_2O_3	1.10	0.5	600	0.600	58.80%	49.0	85.0	140.50	119.43	662.61	23.79	1
5Si-5Co-Al_2O_3	5.00	0.15	590	1.620	20.00%	25.3	91.0	143.69	130.76	677.68	66.22	2
Co-SBA15	2.00	0.4	600	0.300	14.29%	37.0	96.0	36.48	35.02	172.06	19.29	3
Co/γ- Al_2O_3-NS	5.00	0.3	600	0.164	9.09%	32.0	82.0	9.18	7.53	43.29	8.00	4
Co/γ- Al_2O_3-NF	5.00	0.3	600	0.164	9.09%	30.0	70.0	8.61	6.02	40.58	7.76	4
Co/γ- Al_2O_3-NP	5.00	0.3	600	0.164	9.09%	26.0	67.0	7.46	5.00	35.17	7.31	4
Co-Al	11.10	0.2	600	0.060	5.00%	34.0	81.0	2.42	1.96	11.40	3.69	5
Co-mSiO_2	2.00	0.5	600	0.180	10.00%	36.0	71.0	17.04	12.10	80.36	12.85	6
Co-Zr/SiO_2	1.50	0.5	550	0.036	3.00%	9.5	97.0	1.20	1.16	5.65	7.90	7
Co- Al_2O_3-HAT	5.00	0.15	590	0.240	20.00%	24.8	97.0	20.87	20.24	98.41	9.73	8
Co/γ- Al_2O_3	5.00	3	560	0.715	99.30%	25.0	80.0	3.13	2.51	14.78	0.32	9
CoO_x@MFI	1.00	0.2	600	0.120	10.00%	58.0	93.0	91.51	85.10	431.55	96.25	10
CoO/AlO	3.00	0.3	600	0.480	40.00%	40.0	95.0	56.10	53.29	264.55	11.30	11
Co-MFI	1.00	0.2	580	0.036	5.00%	38.0	96.0	17.99	17.27	84.82	26.51	12
Co@MFI	6.00	0.3	600	0.180	20.00%	60.0	95.0	15.78	14.99	74.40	7.03	13
Co@MFI-B50	3.00	0.1	600	0.600	100.00%	35.0	92.0	184.06	169.34	868.06	17.53	14
Co-m-Al_2O_3	1.00	0.5	600	0.592	58.00%	43.0	95.0	133.78	127.09	630.92	20.38	1
Zn_1Co_1/NC	1.00	0.1	600	0.090	5.00%	20.0	95.0	47.33	44.95	223.21	100.74	15
Co@Mo-S-1	1.40	0.3	600	0.750	25.00%	40.0	95.0	187.82	178.43	885.77	57.55	16
5Co1.6Fe/Al $_2O_3$	6.60	0.1	590	0.300	20.00%	22.0	95.0	26.29	24.98	124.01	13.25	17
Co–Zr/SiO_2	7.50	0.5	550	0.036	3.00%	9.0	97.0	0.23	0.22	1.07	1.57	7

Table S2. Summary of PDH performance data for reported noble& non- noble metals containing catalysts.

Samples	M loading [wt%]	M cat [g]	T[°C]	C_3H_8 Feed [L·h^{-1}]	C_3H_8 concentration	Con[%]	Sel[%]	TOF[h^{-1}]	C_3H_6 formation rate mol$_{C3H6}$ [g$_{Co}^{-1}$·h^{-1}]	Specific activity [μmol(C_3H_8)g$_M^{-1}$S^{-1})]	k_f [mol$_{C3H6}$/g$_M^{-1}$h^{-1}bar^{-1}]	Ref.
PtLa/mz-deGa	1.00	0.05	580	0.280	100.00%	40.0	98.0	1952.19	1913.15	2779.76	84.90	18
PtSn/2Mg-SBA-15	1.00	0.2	580	0.840	70.00%	35.7	95.0	1305.82	1240.53	1859.38	49.55	19
PtGa-R	0.50	0.2	600	0.600	10.00%	40.0	95.0	2090.14	1985.64	2976.19	460.52	20
PtZnAl$_{0.2}$/SBA-15	0.50	0.2	590	0.253	16.67%	55.9	99.0	1233.14	1220.81	1755.89	177.97	21
Pt–Sn/CeO_2	1.00	0.1	580	0.120	3.85%	39.5	84.5	412.80	348.82	587.80	232.88	22
Pt–Sn/Al_2O_3	1.00	0.1	580	0.120	3.85%	32.6	71.4	340.69	243.26	485.12	208.10	22
Pt/Zn-Al_2O_3	0.85	0.1	600	0.252	14.00%	46.0	97.0	1187.69	1152.06	1691.18	186.83	23
Pt- Zn_3O_x@RUB-15	0.50	1	600	0.594	33.00%	40.0	96.0	413.85	397.29	589.29	29.79	24
Rh(0.5)Sn(3.0)	0.50%	0.1	600	0.400	33.30%	30.0	96.0	1102.39	1058.29	2975.89	160.98	25
NiV_2O_x/Al_2O_3	3.00	0.5	500	0.216	16.67%	16.5	95.1	6.23	5.92	29.46	4.65	26
0.5NiSiBeta	0.50	0.3	600	0.075	6.25%	35.0	84.0	45.85	38.52	217.01	55.70	27
Ni_1/Al_2O_3	1.00	0.5	580	0.240	20.00%	29.4	93.0	36.97	34.39	175.00	15.92	28
0.2Ni0.06Zn-S-1	0.20	0.32	600	0.300	23.26%	20.0	90.0	245.62	221.06	1162.53	114.00	29
(1:1 Ni:Ga) @Ni3Ga/Al_2O_3	5.00	0.1	600	0.120	10.00%	13.0	94.0	8.17	7.68	38.69	12.34	30
(3Fe:P)/Al2O3	13.30	0.14	600	0.030	5.00%	12.0	82.4	0.48	0.40	2.40	1.64	31
(2Fe:P)/Al2O3	3.00	0.2	600	0.600	5.00%	35.0	92.0	0.34	0.28	1.68	1.15	31
(1Fe:P)/Al2O3	1.00	0.4	600	0.592	5.00%	43.0	95.0	0.17	0.14	0.84	0.57	31
20Fe/5S-Al	20.00	2	560	0.009	1.20%	20.0	80.0	0.01	0.01	0.05	0.10	32
Cr-MSU-x28	1.27	0.2	600	0.180	10.00%	30.0	90.0	49.35	44.42	263.64	45.87	33
Cr/HZSM-5(260)	5.00	0.2	580	0.060	5.00%	32.6	94.2	4.54	4.28	24.26	8.07	34
Mo-SH	5.00	0.5	600	0.120	10.00%	37.0	92.0	7.61	7.00	22.02	3.49	35
			550			20.0	86.0	4.11	3.54	11.90	2.74	35
12V/Al	12.00	0.25	600	0.420	28.00%	32.0	94.0	10.19	9.58	55.56	3.45	36
1VZr	1.00	0.4	550	0.420	14.00%	25.0	90.0	59.70	53.73	325.52	46.95	37
PV-0.7	10.00	1	610	0.360	20.00%	50.0	88.5	4.09	3.62	22.32	1.77	38
ZnO–S-1_3	1.20	0.05	550	0.960	40.00%	31.0	87.0	1447.70	1259.50	6150.79	338.15	39
			600			40.0	88.0	1868.00	1643.84	7936.51	339.14	39

ZnO@S-1	**4.00**	**0.15**	**600**	**0.362**	**67.00%**	**31.4**	**93.9**	**55.26**	**51.89**	**234.80**	**6.58**	**40**

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