Supplementary Information

Promoted propane dehydrogenation reaction over Co confined within core-shell silicalite-1 zeolite crystals

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Supplementary tables and figures

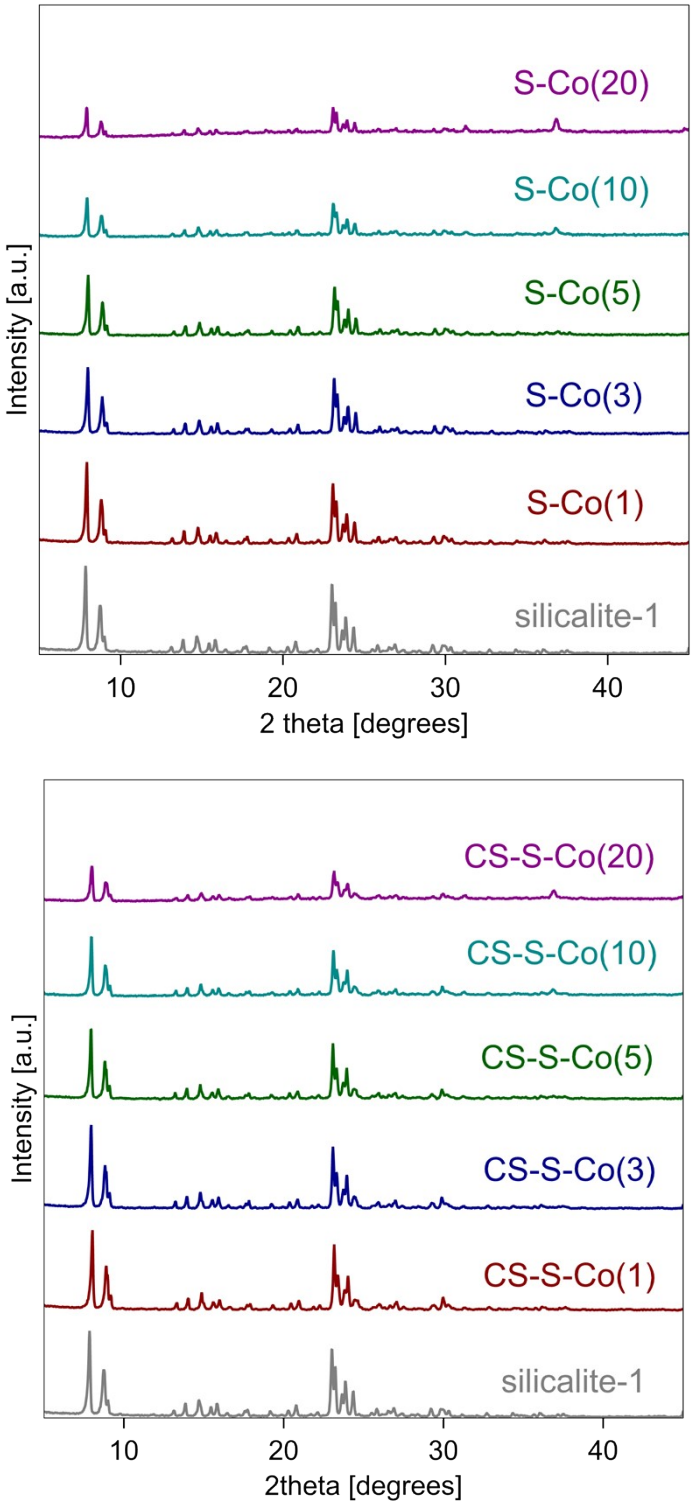


Fig. S1 XRD patterns of (a) S-Co (*x*) and (b) CS-S-Co (*x*).

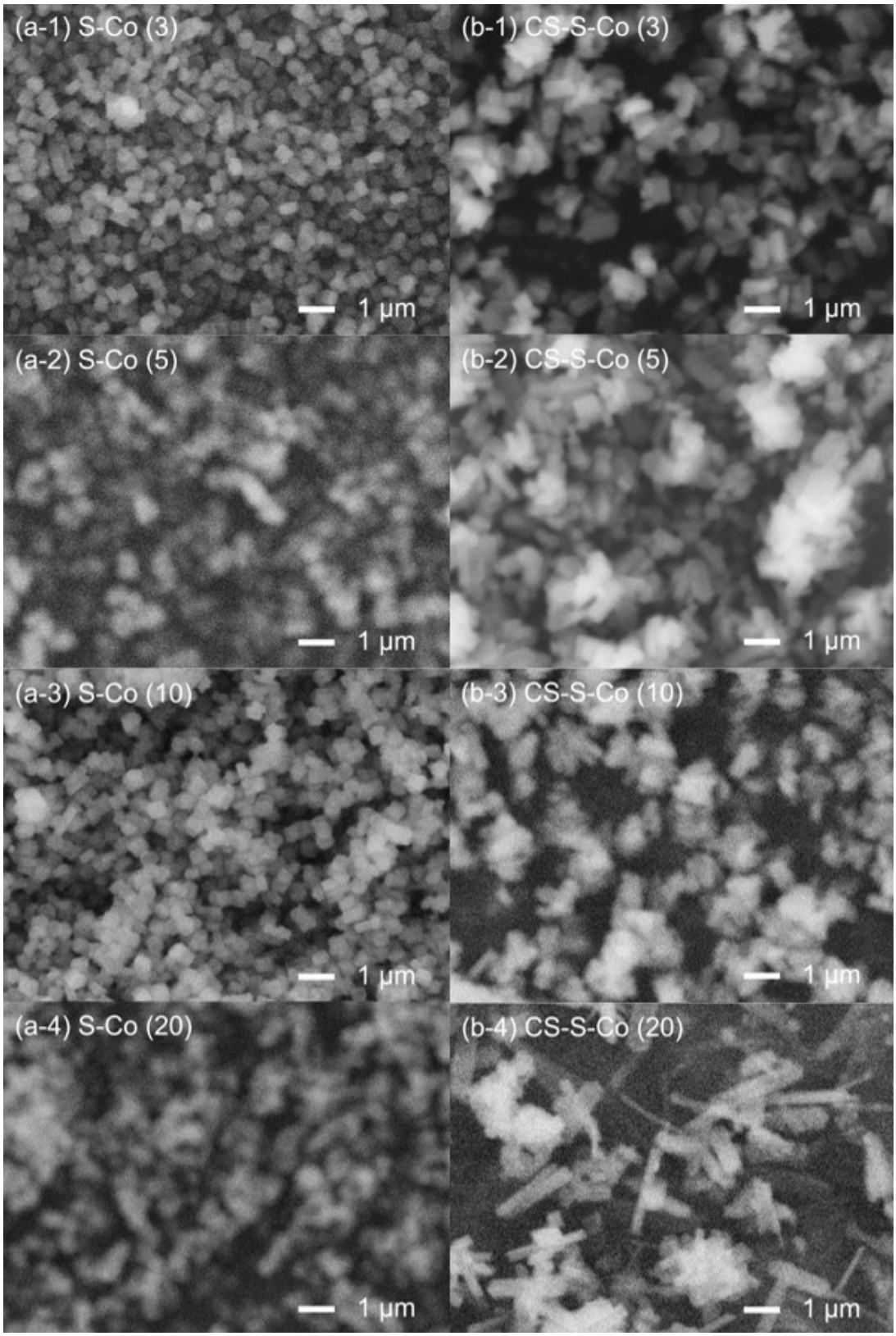


Fig. S2 SEM images of (a) S-Co (*x*) and (b) CS-S-Co (*x*).

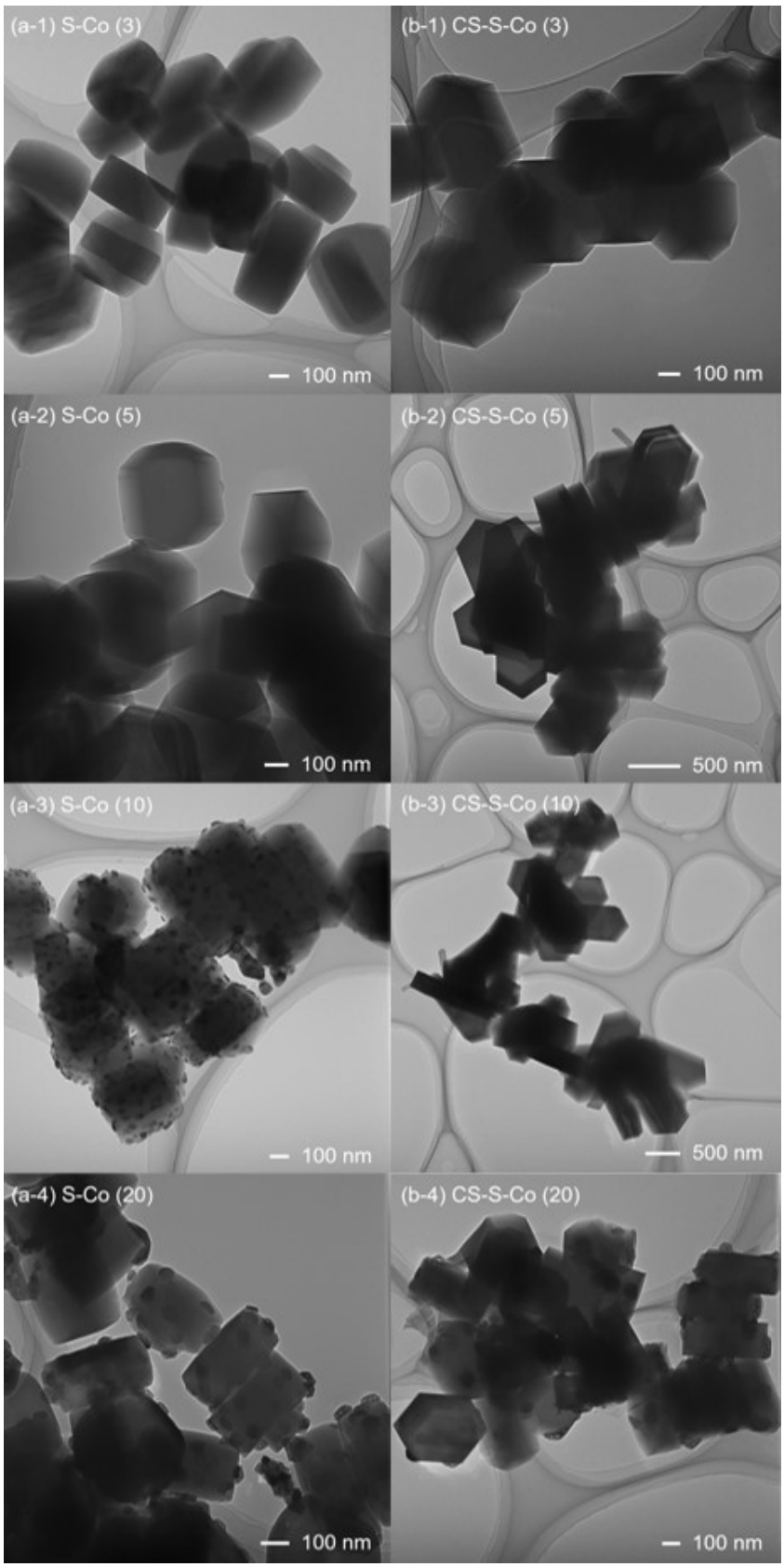


Fig. S3 TEM images of (a) S-Co (*x*) and (b) CS-S-Co (*x*).

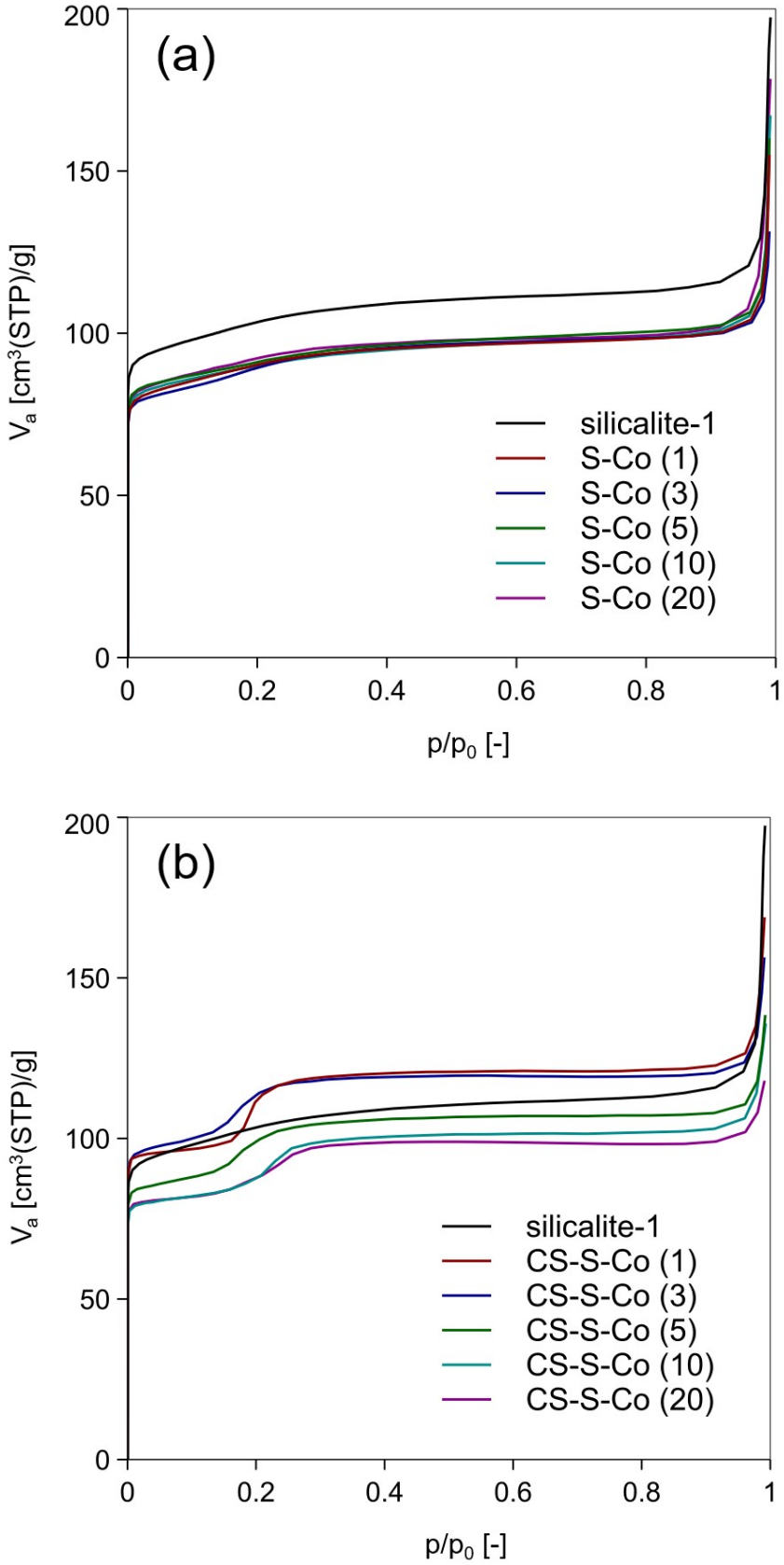


Fig. S4 N_2-adsorption isotherms of (a) S-Co (*x*) and (b) CS-S-Co (*x*).

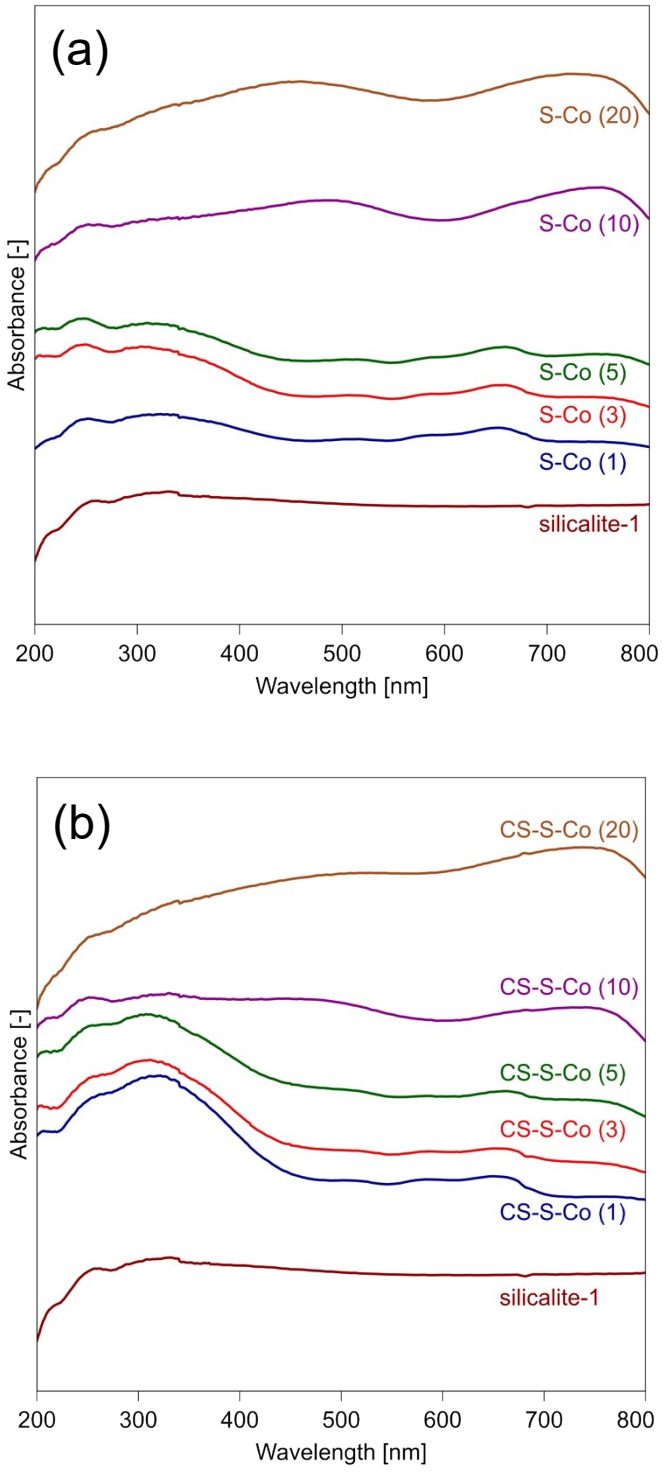
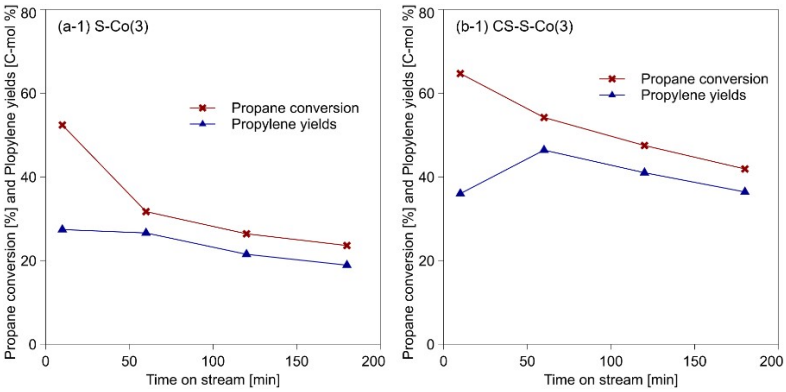


Fig. S5 UV-vis spectra of (a) S-Co (*x*) and CS-S-Co (*x*).


(a-1) S-Co(3)
Propane conversion
Propylene yields
Propane conversion [%] and Plopylene yields [C-mol %]
Time on stream [min]
0
20
40
60
80
0
50
100
150
200
(b-1) CS-S-Co(3)
Propane conversion
Propylene yields
Propane conversion [%] and Plopylene yields [C-mol %]
Time on stream [min]

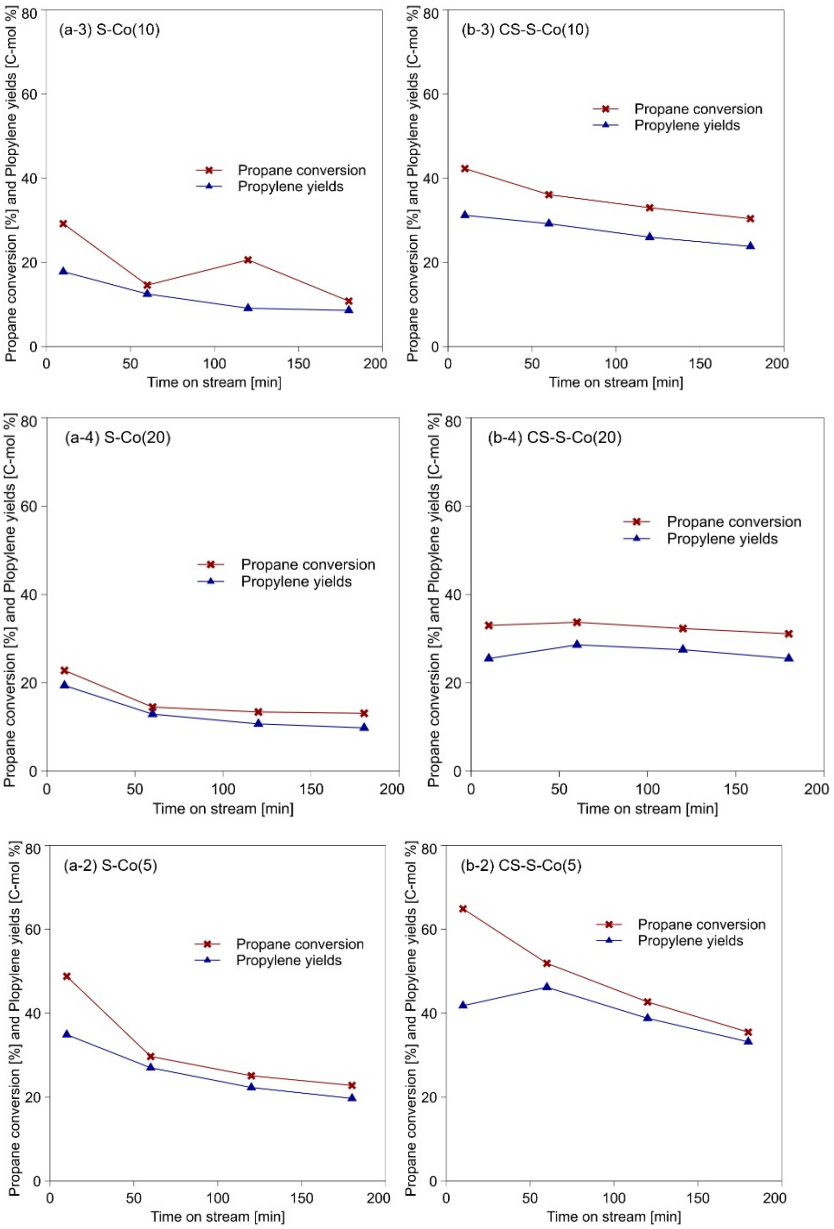

(a-3) S-Co(10)
(b-3) CS-S-Co(10)
(a-4) S-Co(20)
(b-4) CS-S-Co(20)
(a-2) S-Co(5)
(b-2) CS-S-Co(5)
Propane conversion
Propylene yields
Propane conversion [%] and Plopylene yields [C-mol %]
Time on stream [min]
0
20
40
60
80
0
50
100
150
200

Fig. S6 Results of PDH reaction over (a) S-Co (*x*) and (b) CS-S-Co (*x*).

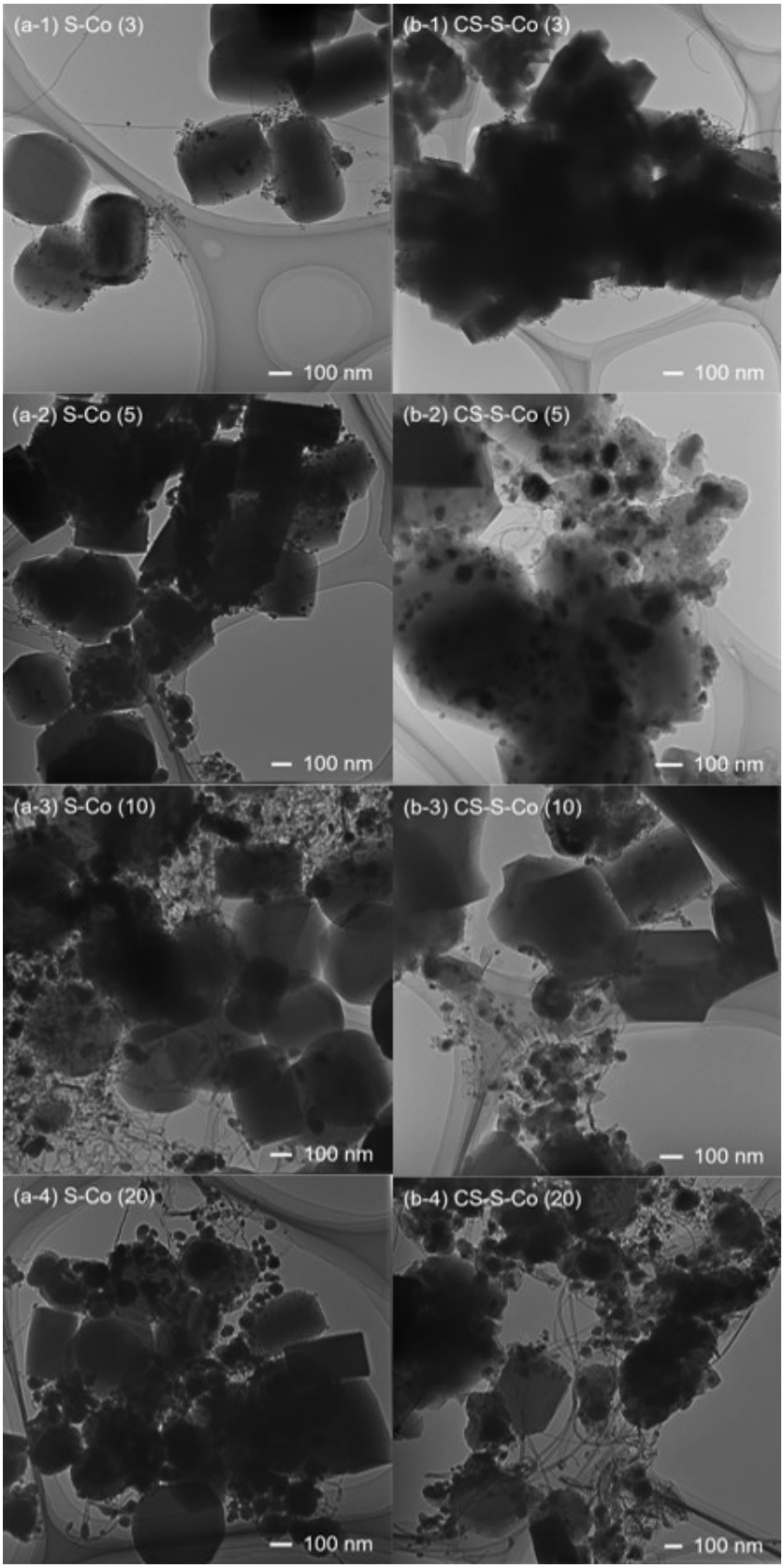


Fig. S7 TEM images of spent (a) S-Co (*x*) and (b) CS-S-Co (*x*).

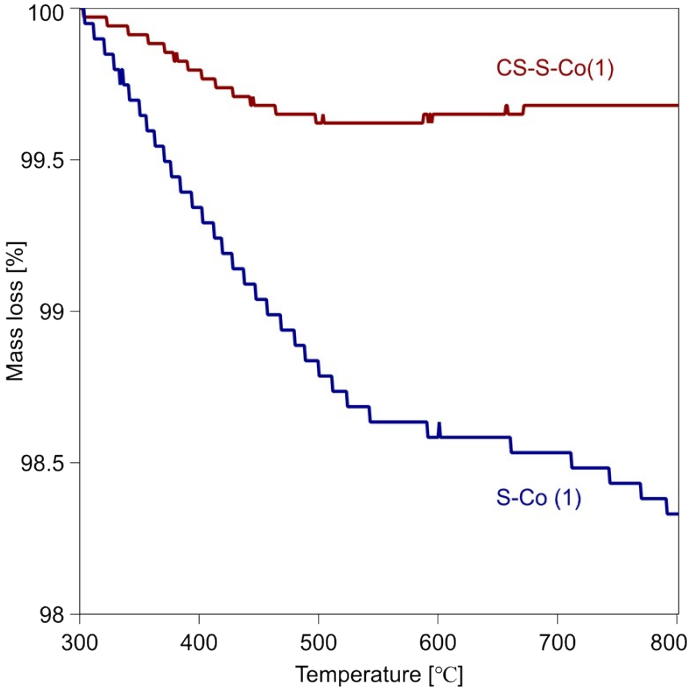


Fig. S8 Curves of S-Co (1) and CS-S-Co (1) by TGA.

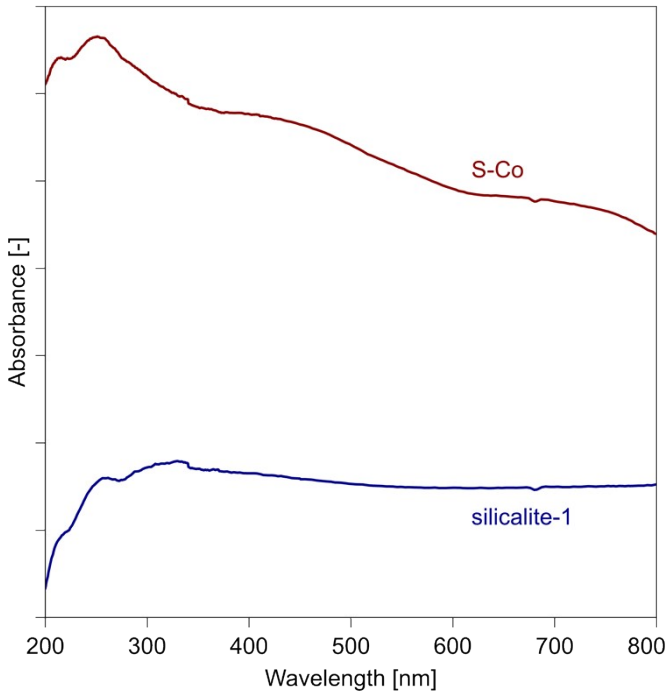


Fig. S9 UV-vis spectra of silicalite-1 and one-pot S-Co.

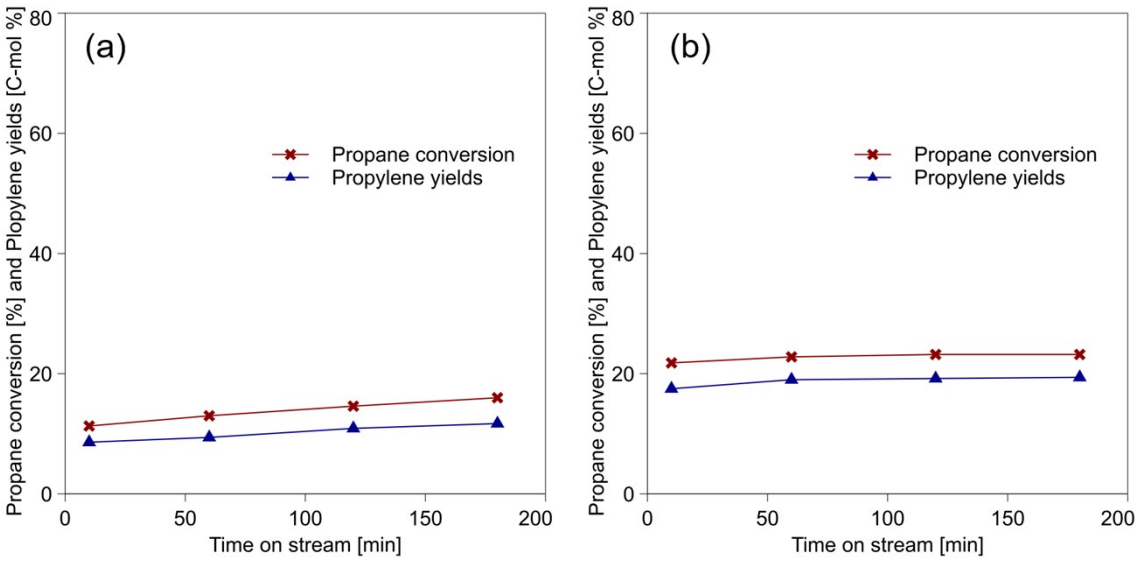


Fig. S10 Results of PDH reaction over (a) one-pot S-Co and (b) silicalite-1 coated one-pot S-Co.

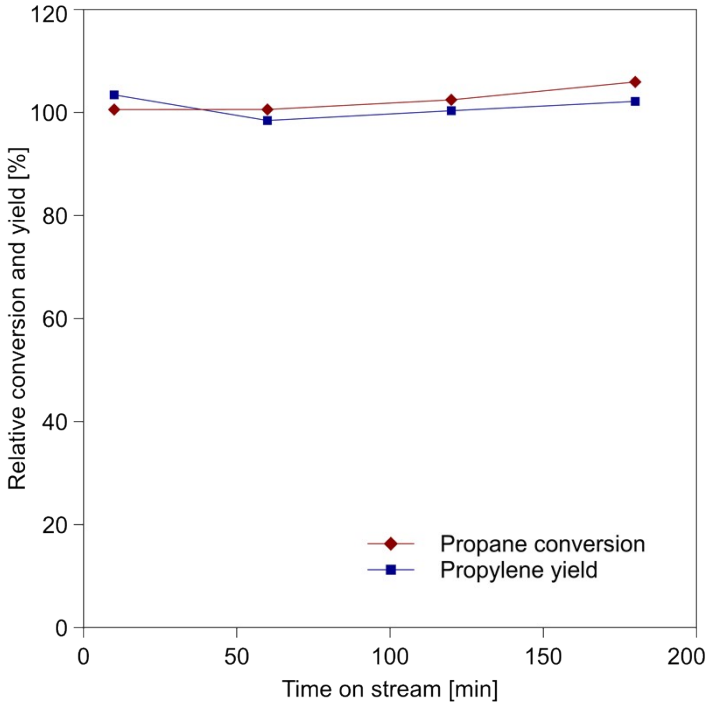


Fig. S11 Relative propane conversion and propylene yield over regenerated CS-S-Co (1).

Table S1 Chemical compositions of S-Co (x) and CS-S-Co(x) determined by EDX analysis.

x	Si/Co molar ratios [-]	
	S-Co (*x*)	CS-S-Co (*x*)
1	344.4	573.8
3	64.5	182.1
5	68.6	337.6
10	18.2	72.1
20	5.2	53.3

Table S2 Deactivation rate over each catalyst.

Sample	$Conv._{start}$ [%]	$Conv._{end}$ [%]	k_d [min^{-1}]
S-Co (1)	27.3	17.0	0.00357
S-Co (3)	52.4	23.6	0.00748
S-Co (5)	48.8	22.8	0.00689
S-Co (10)	29.2	10.8	0.00721
S-Co (20)	22.8	13.1	0.00396
CS-S-Co (1)	52.3	40.7	0.00276
CS-S-Co (3)	64.7	41.9	0.00549
CS-S-Co (5)	64.9	35.5	0.00713
CS-S-Co (10)	42.3	30.4	0.00305
CS-S-Co (20)	33.0	31.1	0.00051

The first-order deactivation model was used to estimate the catalytic stability. k_d and τ were defined by the following equation. Here, lower k_d and higher τ values are indicative of higher stability.

$$k_d = \frac{\ln\left(\frac{1 - Conv._{end}}{Conv._{end}}\right) - \ln\left(\frac{1 - Conv._{start}}{Conv._{start}}\right)}{t}$$

$$\tau = \frac{1}{k_d}$$

Where, $Conv._{start}$ and $Conv._{end}$ indicates initial and final propane conversion, respectively. In this work, $Conv._{start}$ is the conversion at 10 min, and $Conv._{end}$ is the conversion at 180 min. t represents the reaction time, assigned 170 min.

However, since the assumption is that the reaction is of the first order, sometimes this equation is not applicable.

Table S3 The catalytic data for PDH reaction in current study and in published reports.

Catalyst	Reaction condition	C_3H_8 conversion	C_3H_6 yield	C3H6 selectivity	Reference
CS-S-Co (1)	Temp.=600 ℃ Catalyst weight=0.05 g F_{total}=10 cm^3/min, $F_{propane}$=1.0 cm^3/min	52.3 %	47.1 C-mol%	90.0 %	This work
Co-1.3-Zr/SiO_2	Temp.=550 ℃ Catalyst weight=0.5 g F_{total}=20 mL/min, $F_{propane}$=0.6 mL/min	9.5 %	9.2 %	96.9 %	[43]
Co-Al_2O_3-HT	Temp.=590 ℃ Catalyst weight=0.15 g F_{total}=20 mL/min, $F_{propane}$=0.6 mL/min	24.8 %	24.2 %	97.6 %	[44]
Co/Al_2O_3 (5 wt% Co_3O_4)	Temp.=560 ℃ Catalyst weight=3 g F_{total}=12 mL/min, $F_{propane}$=11.9 mL/min	25.7 wt%	21.3 wt%	83 %	[45]
Co/Al_2O_3-NS (Al_2O_3 nano-sheet)	Temp.=600 ℃ Catalyst weight=0.3 g F_{total}=30 mL/min, $F_{propane}$=2.7 mL/min	32.5 %	26.7 %	82.2 %	[46]

Table S4 Selectivity of propylene over S-Co (*x*) and CS-S-Co (*x*)

TOS [min]	Selectivity of propylene over S-Co (x)				
	x = 1	*x* = 3	*x* = 5	*x* = 10	*x* = 20
10 min	79.7	52.4	71.5	61.1	85.4
60 min	81.7	83.9	90.9	85.3	88.6
120 min	78.2	81.5	88.9	44.3	79.6
180 min	74.6	80.0	86.4	79.5	74.6

TOS [min]	Selectivity of propylene over CS-S-Co (x)				
	x = 1	*x* = 3	*x* = 5	*x* = 10	*x* = 20
10 min	90.1	55.7	64.5	73.9	77.3
60 min	90.1	85.6	89.0	81.0	85.0
120 min	90.1	86.3	90.9	78.9	85.1
180 min	88.2	86.8	93.5	78.1	82.1

Table S5 Distribution of Co particle size distribution in spent catalysts（unit : nm）

	S-Co (*x*)					CS-S-Co (*x*)				
No.	*x*=1	*x*=3	*x*=5	*x*=10	*x*=20	*x*=1	*x*=3	*x*=5	*x*=10	*x*=20
1	10	25	28	55	32	-	43	97	20	78
2	8	10	48	12	93	-	22	21	48	32
3	11	19	72	72	106	-	18	34	56	106
4	9	52	52	45	67	-	10	78	27	91
5	10	10	24	96	57	-	9	12	35	24
6	5	38	16	69	81	-	11	46	108	88
7	10	16	10	82	102	-	30	55	32	32
8	7	14	36	25	95	-	51	24	86	111
9	9	32	85	61	18	-	13	15	24	45
10	10	18	45	63	115	-	12	16	17	65
average	8.9	23.4	41.6	58	76.6	-	21.9	39.8	48.1	67.2

Table S6 Coke amount of spent catalyst by TGA.

Sample	W_{coke}/W_{cat} [%]
S-Co (1)	1.73
S-Co (3)	3.90
S-Co (5)	5.04
S-Co (10)	11.0
S-Co (20)	3.14
CS-S-Co (1)	0.32
CS-S-Co (3)	2.16
CS-S-Co (5)	3.57
CS-S-Co (10)	5.81
CS-S-Co (20)	9.91

We calculated W_{coke}/W_{cat} using the following equation.

$$W_{coke}/W_{cat} = \frac{W_{300} - W_{800}}{W_{800}} \times 100$$

Where, W_{300} and W_{800} means the mass of the sample at 300 °C and 800 °C.

W_{coke}/W_{cat} indicates the amount of produced coke during the reaction.