Supplementary Information

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1. General Information and Experimental Section

General Information: Unless otherwise noted, all commercially available reagents were used without further purification. The contents of Co in the catalysts were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES), using Iris advantage Thermo Jarrel Ash device. Fourier transform infrared (FT-IR) spectrum were recorded with a Bruker VERTEX 70FTIR spectrometer. The liquid nuclear magnetic resonance spectra (NMR) were recorded on a Bruker AvanceTM III 400 MHz in deuterated chloroform unless otherwise noted. Powder X-ray diffraction (PXRD) measurements were conducted by a STADIP automated transmission diffractometer (STOE) equipped with an incident beam curved germanium monochromator selecting CuKa1 radiation and a 6° position sensitive detector (PSD) (step size: 0.014°, step time: 25.05 s). The XRD patterns were scanned in the 2h range of 10-80°. Nitrogen adsorption-desorption isotherms were measured at 77 K using an American Quantachrome iQ2 automated gas sorption analyzer. The samples were outgassed at 120 °C for 12 h before the measurements. Surface areas were calculated from the adsorption data using Langmuir and Brunauer-Emmett-Teller (BET) methods. The poresize-distribution curves were obtained from the adsorption branches using the Barrett, Joyner, and Halenda (BJH) method. X-ray photoelectron spectroscopy (XPS) measurements were carried out by a VG ESCALAB 210 instrument equipped with a dual Mg/Al anode X-ray source, a hemispherical capacitor analyzer, and a 5 keV Ar⁺ ion gun. All spectra were recorded by using AlKa (1361 eV) radiation. The electron binding energy was referenced to the C1s peak at 284.8 eV. The thermal properties of catalysts were evaluated using a METTLER TOLEDO simultaneous thermal analyzer over the temperature range from 30 to 800 °C under nitrogen atmosphere (20 mL/min) with a heating rate of 10 °C/min. Field emission scanning electron microscopy (SEM) observations were performed on a Hitachi S-4800 microscope operated at an accelerating voltage of 5.0 kV. High-resolution transmission electron microscope (HR-TEM) analysis was carried out on a Talos F200S operating at 200 kV. The abreaction-corrected HAADF-STEM images were obtained on a FEI-Titan Cubed Themis G2 300 equipped with a probe corrector, with a guaranteed resolution of 80 pm and accelerating voltage of 200 kV.

Experimental Section: All solvents and chemicals were obtained commercially and used as received.

p-3v-PPh₃ monomers (340.0 mg, 1.0 mmol) were fully complexed with $Co_2(CO)_8$ (34.1 mg, 0.1 mmol) in tetrahydrofuran (THF, 10.0 mL) under an argon atmosphere, which stirred for 2 h at room temperature. Then transfer the above solution to a hydrothermal reaction kettle, in which the above solution copolymerized at 100 °C for 24 h under an argon atmosphere in the presence of azobisisobutyronitrile (AIBN, 12.0 mg). After washing with THF (10.0 mL) three times and drying under vacuum at 60 °C for 6 h, brown powdered catalyst named $Co_2(CO)_8@PPh_3-1/10$ were obtained. The other Co@PPh₃ (1/X ratio means molar ratio of Co/3v-PPh₃) were prepared under the same conditions as $Co_2(CO)_8@PPh_3-1/10$.

 $Co_2(CO)_8/PPh_3$ -1/10 was made by impregnation method. First, p-3v-PPh₃ (340.0 mg) and AIBN (12.0 mg) were dissolved in 10 mL of THF, the solution was transferred into a kettle which was heated to 100 °C for 24 h under an argon atmosphere. The resulting solid was washed by THF (10.0 mL) three times and dried under vacuum at 60 °C for 6 h; a white solid was obtained which named PPh₃. $Co_2(CO)_8$ (34.1 mg,0.1 mmol) was dissolved in 8 mL of THF under an argon

atmosphere, followed by the addition of 340 mg PPh₃. After stirring at room temperature for 24 h, the brown $Co_2(CO)_8/PPh_3$ catalyst was obtained after filtering, washing with THF and drying under vacuum.

As a typical hydroformylation recipe, the as-prepared $Co_2(CO)_8@PPh_3-1/10$ catalysts (50 mg), 1-octene (56 mg, 0.5 mmol), and THF (3.0 mL) were added into a stainless-steel autoclave (100 mL) with a magnetic stir bar. After the autoclave was sealed and purged with CO for three times, the pressure of syngas (H₂/CO = 1:1) was adjusted to 4 MPa and the autoclave was put into a preheated reactor, stirring at 170 °C for 12 h. After the reaction, the autoclave was cooled to room temperature and the pressure was carefully released. Subsequently, the reaction mixture was diluted with THF (6.0 mL), and the catalyst was removed from the system by centrifugation and analyzed by gas chromatography (Shimadzu GC-2014C equipped with a HP-5 capillary column with 5 wt% phenyl groups and the FID detector). Finally, the yield and regioselectivity were obtained by GC analysis using biphenyl as the internal standard.

For recycling, a mixture of $Co_2(CO)_8$ @PPh₃-1/10 catalyst (50 mg), 1-octene (0.5 mmol), and THF (3.0mL) were added into a stainless-steel autoclave (100 ml) with a magnetic stir bar. After the autoclave was sealed and purged with CO for three times, the pressure of syngas (CO/H₂ = 1:1) was adjusted to 4.0 MPa. Then the reaction mixture was stirred at 170 °C for 12 h or 1 h. The autoclave was cooled to room temperature and the pressure was carefully released. The reaction mixture (~ 0.2 mL) was taken out from the glass tube for analysis by gas chromatography. The catalyst was separated by centrifugation, washed with THF (10.0 mL × 3), dried under vacuum at 60 °C for 6 h and used directly for the next run.

For Hot Filtration, a mixture of $Co_2(CO)_8$ @PPh₃-1/10 catalyst (50 mg), 1-octene (0.5 mmol), and THF (3.0mL) were added into a stainless-steel autoclave (100 ml) with a magnetic stir bar. After the autoclave was sealed and purged with CO for three times, the pressure of syngas (CO/H₂ = 1:1) was adjusted to 4.0 MPa. Then the reaction mixture was stirred at 170 °C for 1 h. The autoclave was cooled to room temperature and the pressure was carefully released. The reaction mixture (~ 0.2 mL) was taken out from the glass tube for analysis by gas chromatography. After sealing and purging with CO for 3 times, the pressure of syngas (CO/H₂ = 1:1) was adjusted to 4.0 MPa. Next, the reaction mixture was stirred at 170 °C for another 11 h. The autoclave was cooled to room temperature and the pressure was carefully released. Subsequently, the reaction mixture was diluted with THF (6 mL), and the catalyst was removed from the system by centrifugation and analyzed by gas chromatography. The Co contents of the used catalyst and filtrate after each run were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

2. Optimization of the reaction conditions

Condition		ondition	Catalytic P	erformance		
Entry	Catalyst	Pressure	Temperature	Fresh	The third	Reference
		(Mpa)	(°C)	Calatlyst	cycle	
				$C_{00} = 0.02 \ 0.04$	$C_{00} = 60.0\%$	Catal. Today
1	fibrous Co ₃ O ₄	5.5	150	Coll. 93.076		2018, <i>309</i> , 147-
			Sel.	Sel. 93.0%	Sel. 55.0%	152.
				Com 00.90/		FPT 2023 ,
2	FeCu-Co ₃ O ₄	7	150	Con. 99.8%	-	107721-
				Sel. 67.9%	Sel. 67.9%	
				C 00.00/		Fuel 2024 , 365,
3	Co ₃ O ₄ -g-C ₃ N ₄	7	150	Con. 99.9%	-	131192-
				Sel. 77.8%		131200.
4	C - 7. D	4	100	Con. 99.9%	Con. 99.9%	J. Catal. 2022,
4	Cozrp	4	190	Sel. 94.5%	Sel. 94.5%	408, 245-260
~		4	170	Con. 99.0%	Con. 99.0%	
2	$Co_2(CO)_8$ (CO) PPh ₃	4	170	Sel. 94.0%	Sel. 93.5%	I his work

Table S1. Catalysts used in reductive hydroformylation

Table S2. Screening of Temperature for the Reductive Hydroformylation of 1-octene^{[a], [c]}

			Sel. (%) ^[b]				
Entry T	т (°С)	Con. (%) ^[0]	Octane	lso-octene	Nonanal (L/B)	Nonanol (L/B)	
1	110	-	-	-	-	-	
2	130	21	26	4	70 (53/47)	-	
3	140	98	4	1	91 (61/39)	4 (51/49)	
4	150	97	4	5	80 (55/45)	11 (65/35)	
5	160	99	5	2	3 (62/38)	90 (56/44)	
6	170	>99	4	<1	2 (54/46)	94 (63/37)	
8	180	>99	6	3	23 (61/39)	68 (56/44)	

[a] Reaction conditions: 1-octene (0.5 mmol), CO/H₂ = 2/2 MPa, $Co_2(CO)_8$ @PPh₃-1/10 (50 mg), THF (3 mL), 12 h.

[b] Determined by GC analysis using biphenyl as the internal standard for GC yield.

[c] The value for the branched isomers is based on the mixture of all iso-isomers.

Entry		Con. (%) ^[b]	Sel. (%) ^[b]				
Entry			Octane	Iso-octene	Nonanal (L/B)	Nonanol (L/B)	
1	1/1	97	8	3	1 (56/44)	88 (58/42)	
2	2/2	>99	4	<1	1 (54/46)	94 (63/37)	
3	1/3	>99	5	<1	2 (61/39)	92 (59/41)	
4	3/1	>99	9	<1	1 (60/40)	88 (51/49)	
5	3/3	>99	4	<1	1 (48/52)	94 (53/47)	

Table S3. Screening of the pressure and the ratio of CO/H_2 for the Reductive Hydroformylation of 1-octene^{[a], [c]}

[a] Reaction conditions: 1-octene (0.5 mmol), $Co_2(CO)_8$ @PPh₃-1/10 (50 mg), THF (3 mL), 170 °C for 12 h.

[b] Determined by GC analysis using biphenyl as the internal standard for GC yield.9).

[c] The value for the branched isomers is based on the mixture of all iso-isomers.

Table S4. S	Screening o	of Solvent for	the Reductive	Hydroformy	lation of 1	-octene ^{[a], [c]}

Entry	Solvent	Solvent Con. (%) [b] ⁻	Sel. (%) ^[b]				
Entry			Octane	Iso-octene	Nonanal (L+B)	Nonanol (L+B)	
1	Toluene	90	10	5	26	51	
2	Anisole	75	6	4	69	21	
3	THF	>99	4	<1	1	94	
4	ACN	83	9	7	57	27	
5	NMP	8	45	55	-	-	

[a] Reaction conditions: 1-octene (0.5 mmol), $CO/H_2 = 2/2$ MPa, $Co_2(CO)_8$ @PPh₃-1/10 (50 mg), 170 °C for 12 h.

[b] Determined by GC analysis using biphenyl as the internal standard for GC yield.

[c] The value for the branched isomers is based on the mixture of all iso-isomers.

Entry	Time (b)	Con(%) [b]	Sel. (%) ^[b]				
Entry	Time (II)	COII. (//) [D]	Octane	lso-octene	Nonanal (L/B)	Nonanol (L/B)	
1	1	59	7	15	70 (63/37)	8 (60/40)	
2	2	88	5	12	66 (54/46)	17 (63/37)	
3	3	96	4	10	54 (49/51)	32 (59/41)	
4	6	98	4	6	45 (44/56)	45 (53/48)	
5	9	99	4	1	7 (43/57)	88 (51/49)	
6	12	>99	4	<1	1 (54/46)	94 (63/37)	

Table S5. Screening of Time for the Reductive Hydroformylation of 1-octene^{[a], [c]}

7	24	>99	4	<1	1 (50/50)	94 (66/34)
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[a] Reaction conditions: 1-octene (0.5 mmol), CO/H₂ = 2/2 MPa, Co₂(CO)₈@PPh₃-1/10 (50 mg), THF (3 mL), 170 °C.

[b] Determined by GC analysis using biphenyl as the internal standard for GC yield.

[c] The value for the branched isomers is based on the mixture of all iso-isomers.

Sel. (%) [b] Con. (%) [b] Entry Catalysts lso-Octane Nonanal (L/B) Nonanol (L/B) octene Co₂(CO)₈@PPh₃-1 91 (61/39) 96 4 1 4 (51/49) 1/10 2 Co₂(CO)₈/PPh₃-1/10 89 11 2 36 (44/56) 51 (52/48) Co(acac)₂@PPh₃-3 9 9 5 29 (38/62) 57 (66/34) 1/10 4 CoCl₂@PPh₃-1/10 n. r. Co(NO₃)₂@PPh₃-5 n. r. -1/10 Co2(CO)8@PPh3-1/5 8 84 (45/55) 96 1 7 (64/36) Co₂(CO)₈@PPh₃-6 89 10 4 74 (48/52) 12 (55/45) 1/15

Table S6. Catalyst Screening for the Hydroformylation of 1-octene [a], [c]

[a] Reaction conditions: 1-octene (0.5 mmol), CO/H₂ = 3/3 MPa, Catalyst (50 mg), THF (3 mL), 140 $^{\circ}$ C for 12 h.

[b] Determined by GC analysis using biphenyl as the internal standard for GC yield.

[c] The value for the branched isomers is based on the mixture of all iso-isomers.

Entra		D (MPa) Con. (%) ^[b]		Sel. (%) ^[b]				
Entry	H ₂ /CO (MPa)		Octane	Iso-octene	Nonanal (L/B)	Nonanol (L/B)		
1	1/1	91	7	8	82 (34/66)	3 (35/65)		
2	2/2	95	5	4	83 (62/38)	8 (41/59)		
3	1/3	93	5	6	87 (53/47)	7 (58/42)		
4	3/1	96	9	-	81 (55/45)	10 (43/57)		
5	3/3	96	4	1	91 (61/39)	4 (51/49)		
6	1/5	95	4	1	91 (58/42)	4 (46/54)		

Table S7. Screening of the Pressure and the Ratio of CO/H₂ for the Hydroformylation of 1-octene^{[a], [c]}

[a] Reaction conditions: 1-octene (0.5 mmol), Co2(CO)8@PPh3-1/10 (50 mg), THF (3 mL), 140 °C for 12 h.

[b] Determined by GC analysis using biphenyl as the internal standard for GC yield.

[c] The value for the branched isomers is based on the mixture of all iso-isomers.

Entry	Solvent	lvont Con (%) [b]	Sel. (%) ^[b]				
Entry	Solvent	Con. (%) [b]	Octane	lso-octene	Nonanal	Nonanol	
1	Toluene	81	12	7	53	28	
2	Anisole	69	9	4	81	6	
3	THF	96	4	1	91	4	
4	CH₃CN	75	10	5	62	23	
5	NMP	n. r.	-	-	-	-	

Table S8. Screening of Solvent for the Hydroformylation of 1-octene^{[a], [c]}

[a] Reaction conditions: 1-octene (0.5 mmol), $CO/H_2 = 3/3$ MPa, $Co_2(CO)_8$ @PPh₃-1/10 (50 mg), 140 °C for 12 h.

[b] Determined by GC analysis using biphenyl as the internal standard for GC yield.

[c] The value for the branched isomers is based on the mixture of all iso-isomers.

				Sel.	(%) ^[b]	
Entry	nime (n)	Con. (%) [b]	Alkanes	lso- olefins	Aldehydes	Alcohols
1	3	17	22	28	50 (62/38)	-
2	6	72	5	12	80 (56/44)	3 (48/52)
3	9	84	4	11	81 (51/49)	4 (38/62)
4	12	96	4	1	91 (61/39)	4 (51/49)
5	24	>99	4	<1	75 (54/55)	20 (57/43)

Table S9. Screening of Time for the Hydroformylation of 1-octene^{[a], [c]}

[a] Reaction conditions: 1-octene (0.5 mmol), CO/H₂ = 3/3 MPa, Catalyst (50 mg), THF (3 mL), 140 $^{\circ}$ C.

[b] Determined by GC analysis using biphenyl as the internal standard for GC yield.

[c] The value for the branched isomers is based on the mixture of all iso-isomers.

3. Characterization Result of Catalyst



Figure S1. Stability tests of the 1-octene reductive hydroformylation reaction over $Co_2(CO)_8$ @PPh₃-1/10 catalyst. (a) at full conversion of 1-octene; (b) at relatively low conversions (59%-61%) of 1-octene.

Table S10. Co Contents in the Fresh and Recycled Catalysts, and in the Filtration after Each Cycle.

Entry	Co contents in the catalysts (wt.%)	Co contents in the filtration (wt.%)
The fresh Co ₂ (CO) ₈ @PPh ₃ -1/10	3.27	-
The 1st recycled $Co_2(CO)_8$ @PPh ₃ - 1/10	3.23	1.24
The 2nd recycled Co ₂ (CO) ₈ @PPh ₃ -1/10	3.19	1.21
The 3rd recycled $Co_2(CO)_8$ @PPh ₃ -1/10	3.16	0.93
The 4th recycled $Co_2(CO)_8$ @PPh ₃ - 1/10	3.15	0.13

[a] Co contents were determined by ICP-AES.



Figure S2. XPS wide-scan spectra of Co₂(CO)₈@PPh₃-1/10.



Figure S3. P 2p XPS spectra of fresh $Co_2(CO)_8$ @PPh₃-1/10 and used $Co_2(CO)_8$ @PPh₃-1/10.



Figure S4. Morphology of used $Co_2(CO)_8$ @PPh₃-1/10. (a) TEM. (b) HRTEM, (c-f) EDS mapping.



Figure S5. HAADF-STEM image of used Co₂(CO)₈@PPh₃-1/10.



Figure S6. SEM images of fresh Co₂(CO)₈@PPh₃-1/10.



Figure S7. SEM images of used $Co_2(CO)_8$ @PPh₃-1/10.



Figure S8. N₂ adsorption–desorption analysis of fresh $Co_2(CO)_8$ @PPh₃-1/10.

Samples	Surface area (m² g⁻¹)	Pore volume (cm³ g ⁻¹)	Average pore Radius (nm)
Co ₂ (CO) ₈ @PPh ₃ -1/10	355.270	0.4066	4.578
Co ₂ (CO) ₈ /PPh ₃ -1/10	364.359	0.3760	4.128
Used Co ₂ (CO) ₈ @PPh ₃ - 1/10	411.581	0.4698	4.566
PPh ₃	345.615	0.4240	4.866



Figure S9. TG analysis of catalysts.

Table S11	. The information	of BET o	f Catalysts
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Figure S10. In situ DRIFTS spectra of $Co_2(CO)_8$ @PPh₃-1/10 by introducing 1 MPa syngas and ethylene at 130 and 170 °C.



Figure S11. In situ DRIFTS spectra of $Co_2(CO)_8$ @PPh₃-1/10 by introducing 1 MPa syngas and ethylene as the reaction gas at different temperature.

4. Representative GC Data and NMR data of the Products



C₅H₁₁







							2	
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	面积%
1	11.490	159550	33511	M	35.481	mg	4	23.918
2	11.890	268296	82681	M	49.778	mg	5	40.221
3	13.868	239212	75534	M	0.000	mg	6	35.861



峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	面积\$
1	12.423	649413	122921	M	120.487	ng	5	31.506
2	12.777	535858	162357	M	0.000			25.99
3	13.838	875996	271617	M	0.000	mg	6	42.498

C₈H₁₇ OH







峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	面积%	
1	3.082	579985	181086	M	0.000			22.765	
2	16.040	1028536	160994	M	0.000			40.371	
3	16.393	939204	283650	M	0.000			36.864	



峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	面积%
1	9.323	349529	80537	M	0.000			13.096
2	10.523	1288978	344540	M	0.000			48.295
3	13.832	1030480	327186	M	0.000	ng	6	38.609

C₆H₁₃ OH



l	峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	面积%
L	1	11.491	194801	40875	M	43.321	ng	4	28.750
L	2	11.891	229663	71937	M	42.610	ng	5	33.896
L	3	13.869	253093	80388	M	0.000	ng	6	37.354





峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	面积%	面积比
1	8. 781	408647	115401	M	0.000			21.072	0
2	9.422	593106	132458	M	0.000			30.584	0
3	13.830	937534	265536	M	0.000	ng	6	48.344	1.00000



峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	面积%
1	11.490	171411	35938	M	38.119	ng	4	28.585
2	11.890	203818	62223	M	37.815	mg	5	33.990
3	13.868	224416	70731	M	0.000	mg	6	37.425

()₇ OH



峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	面积\$
1	13.280	778857	138749	M	0.000	mg	6	33.087
2	13.603	631711	191956	M	0.000	mg	6	26.836
3	13.842	943382	296602	M	0.000	mg	6	40.077
							·	









峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	面积%	面积比
1	11.797	423257	75293	M	78.528	mg	5	21.103	0.434756
2	12.203	608875	189295	M	112.966	ng	5	30.357	0.625417
3	13.842	973550	300884	M	0.000	mg	6	48.540	1.00000



L	峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	面积%
L	1	12. 728	767074	133860	M	0.000			25.643
L	2	13.093	1184373	367869	M	0.000	3		39.593
L	3	13.839	1039955	325647	M	0.000	mg	6	34.765















峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	面积%	面积比
1	12.728	786904	134277	M	0.000			25.663	0
2	13.093	1236725	369132	M	0.000			40.333	0
3	13.839	1042655	325899	M	0.000	mg	6	34.004	1.00000

C₁₆H₃₃ OH --5.597 3.786 3.666 3.572 3.440 -6500 -6000 -5500 -5000 -4500 -4000 -3500 -3000 -2500 -2000 -1500 -1000 -500 -0 1.00-1 0.71---500 16 14 6 ppm 2 0 -2 -4 12 10 8 4















