

## Supporting Information

# Design of Pt-based pseudo-binary intermetallic catalysts for Dry Reforming of propane using CO<sub>2</sub>

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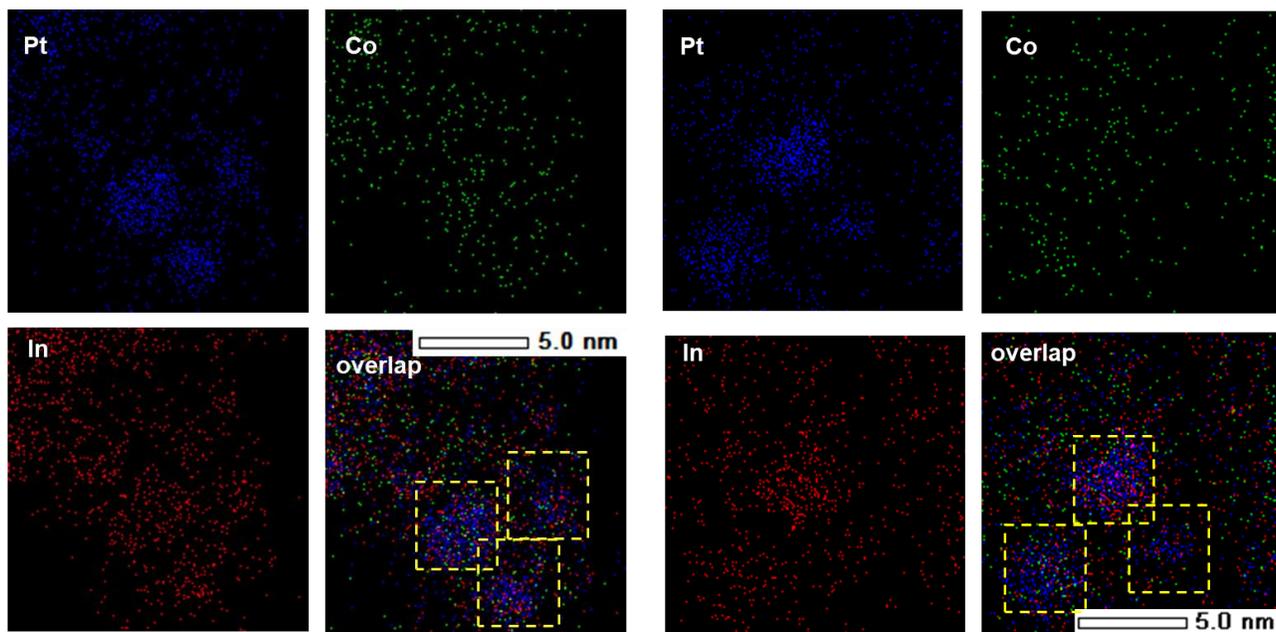
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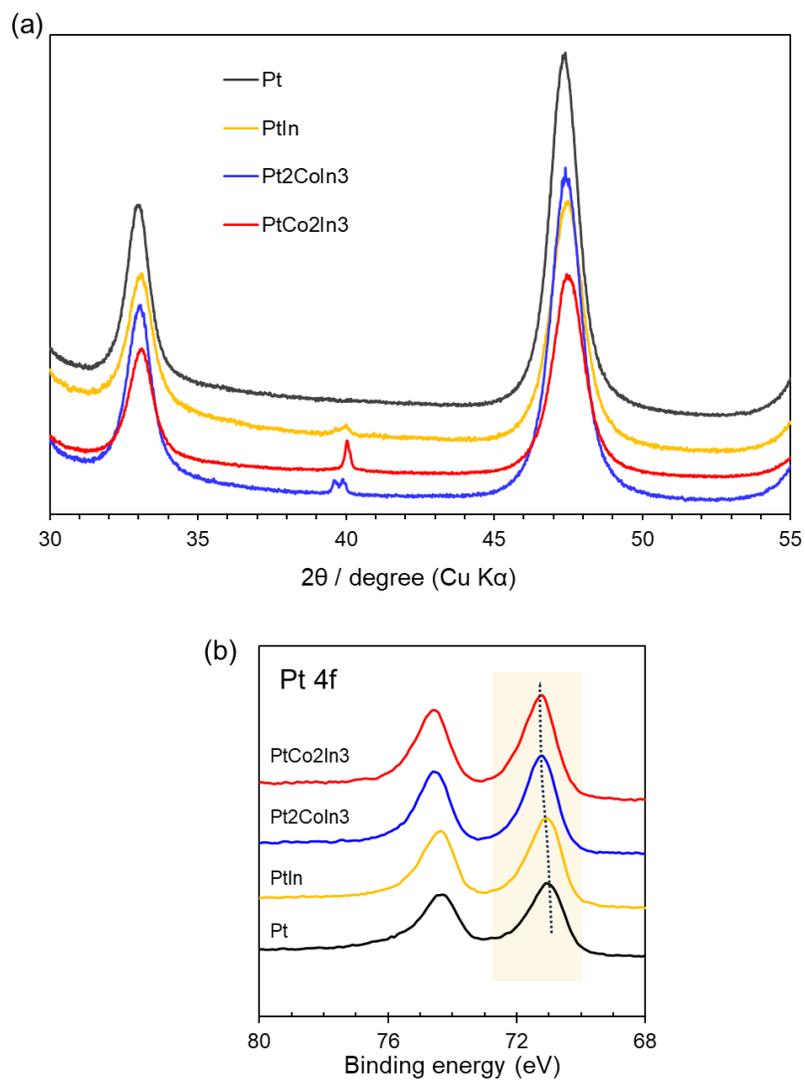
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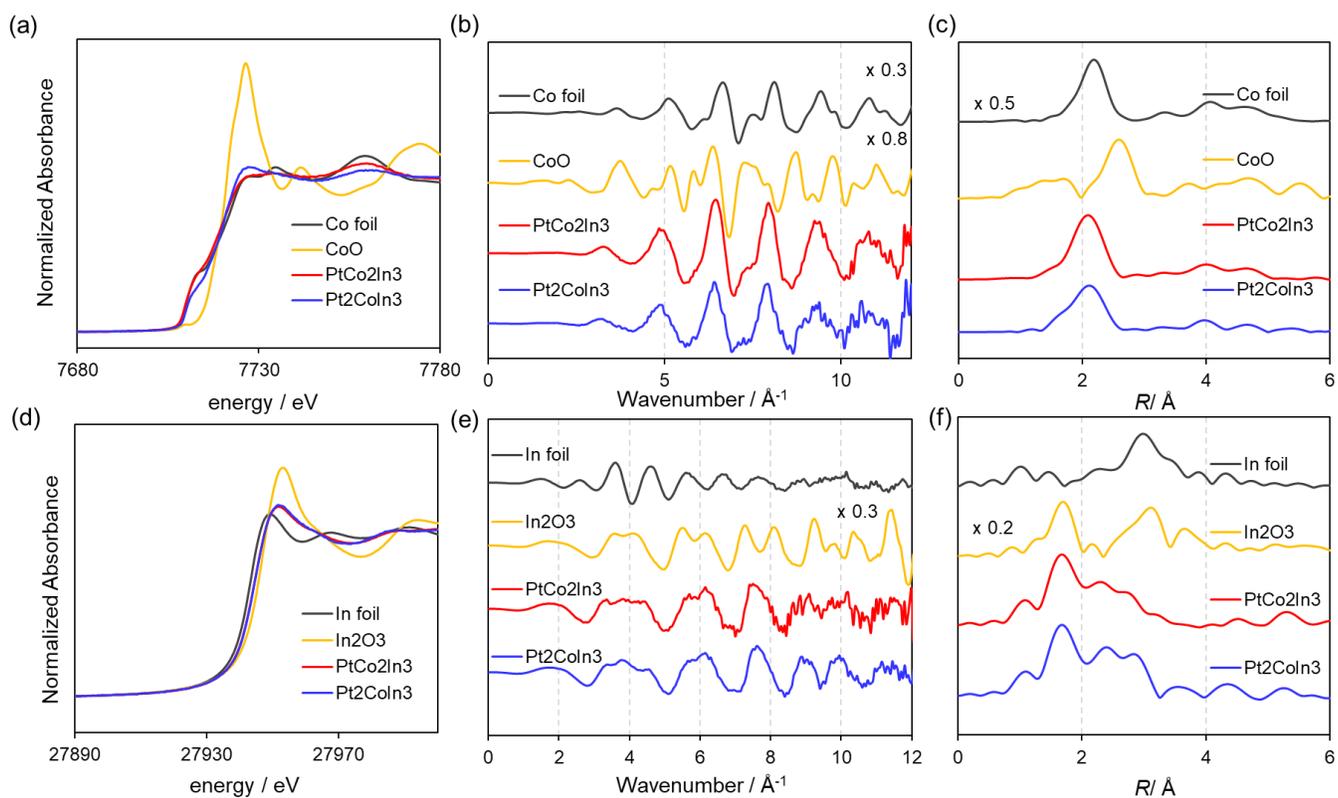
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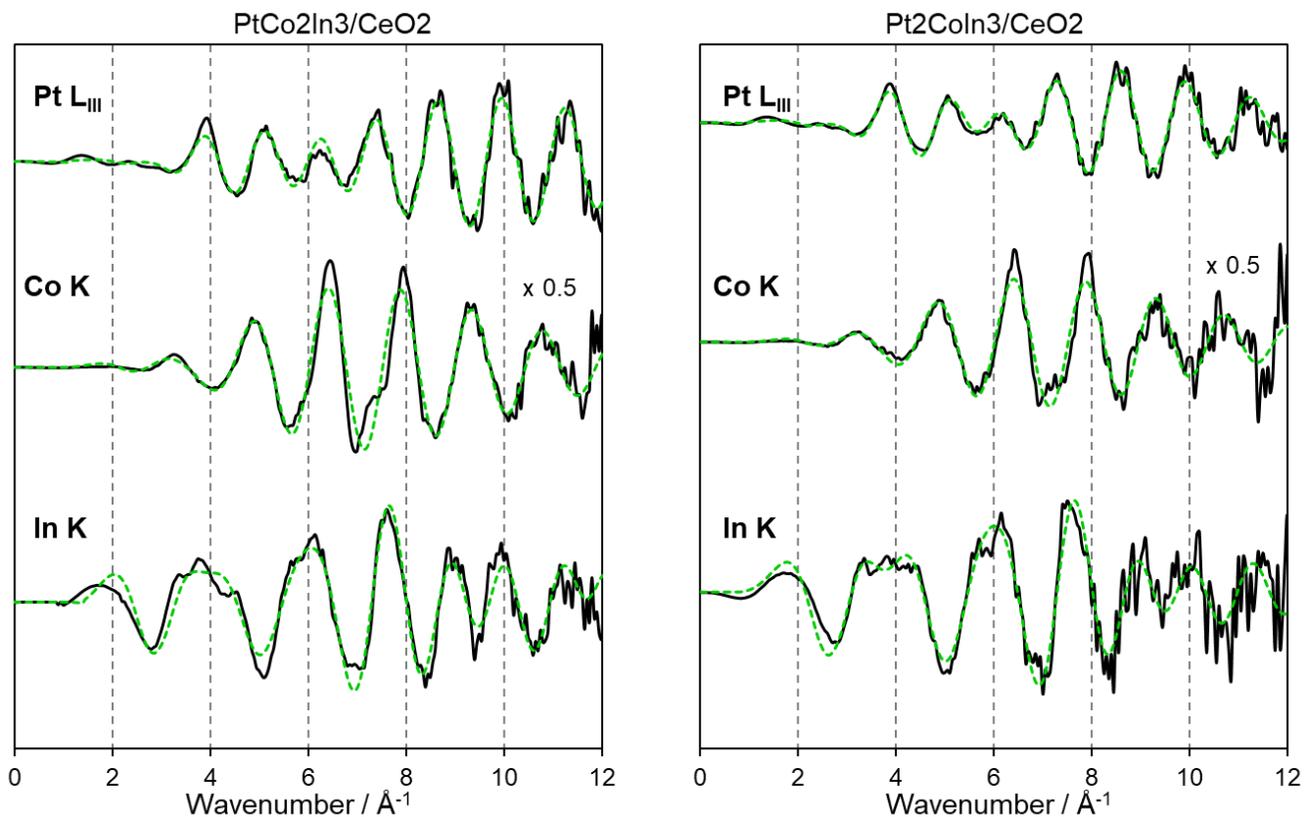
**Figure S1:** Elemental maps of Pt, Co, In, and overlap of these three metals on PtCo<sub>2</sub>In<sub>3</sub>/CeO<sub>2</sub> acquired using EDX analysis.



**Figure S2:** (a) XRD patterns of Pt/CeO<sub>2</sub>, PtIn/CeO<sub>2</sub>, Pt<sub>2</sub>CoIn<sub>3</sub>/CeO<sub>2</sub>, and PtCo<sub>2</sub>In<sub>3</sub>/CeO<sub>2</sub> catalysts, (b) Pt 4f XPS spectra of Pt/CeO<sub>2</sub>, PtIn/CeO<sub>2</sub>, Pt<sub>2</sub>CoIn<sub>3</sub>/CeO<sub>2</sub> and PtCo<sub>2</sub>In<sub>3</sub>/CeO<sub>2</sub> catalysts.



**Figure S3:** XANES spectra of PtCo<sub>2</sub>In<sub>3</sub>/CeO<sub>2</sub> and Pt<sub>2</sub>CoIn<sub>3</sub>/CeO<sub>2</sub> catalysts and reference compounds (a) Co K and (d) In K-edge. EXAFS oscillations of (b) Co K- and (e) In K-edge. Fourier transforms of EXAFS spectra (c) Co K- and (f) In K

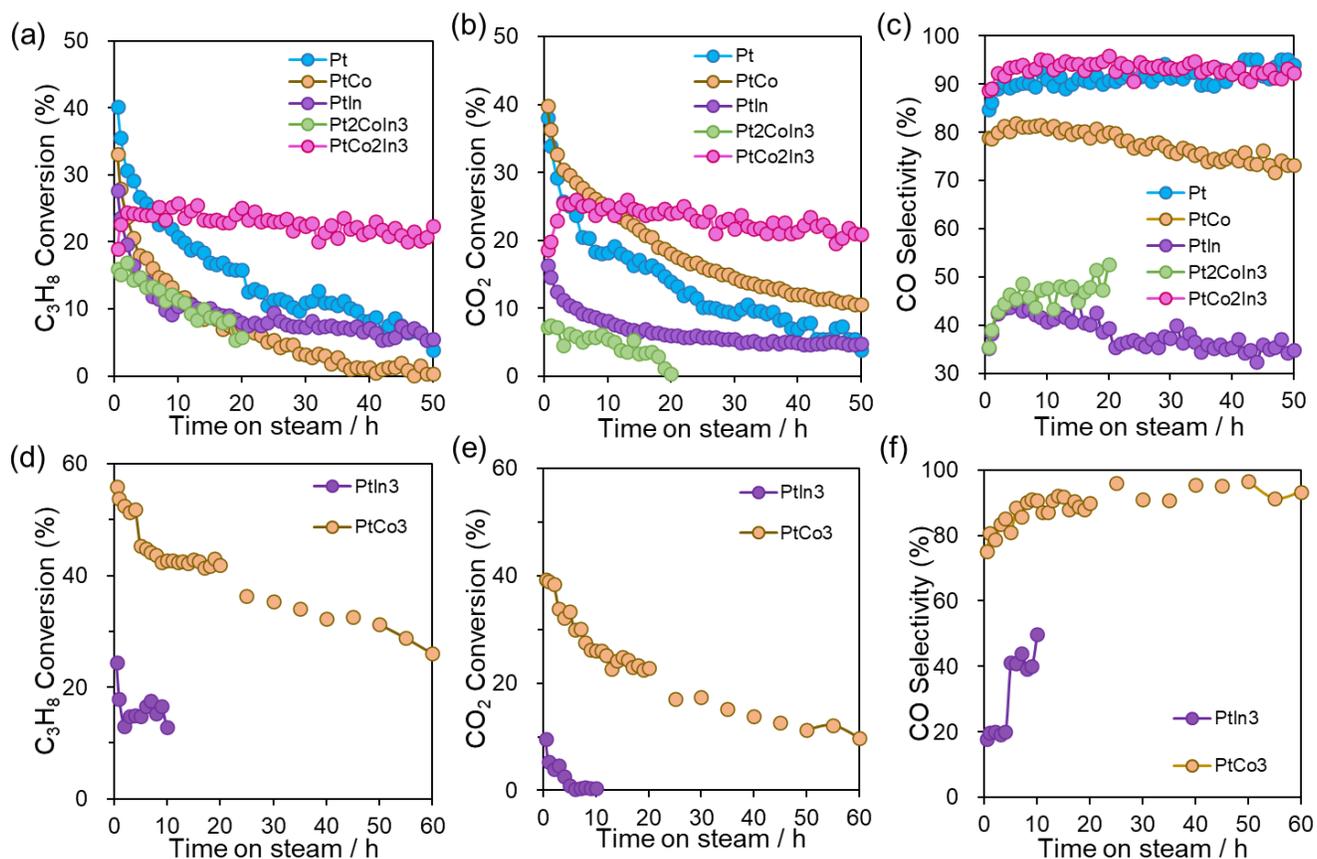


**Figure S4:** Curve-fitting analysis for of PtCo<sub>2</sub>In<sub>3</sub>/CeO<sub>2</sub> and Pt<sub>2</sub>CoIn<sub>3</sub>/CeO<sub>2</sub> catalysts. Curve-fitting for the Pt L<sub>III</sub>-, Co K-, and In K-edge  $k^3$ -weighted EXAFS oscillations of Pt<sub>2</sub>CoIn<sub>3</sub>/CeO<sub>2</sub> and Pt<sub>2</sub>CoIn<sub>3</sub>/CeO<sub>2</sub>. The  $k^3$ -weighted EXAFS oscillation was Fourier-transformed in the  $k$  range of 3–12 Å<sup>-1</sup> for all edges. Curve-fitting was performed using the back Fourier-transforms of the coordination peaks ranging between 1.0–3.0 Å, 1.0–3.0 Å, and 1.0–3.5 Å, for Pt L<sub>III</sub>-, Co K-, and In K-edge, respectively.

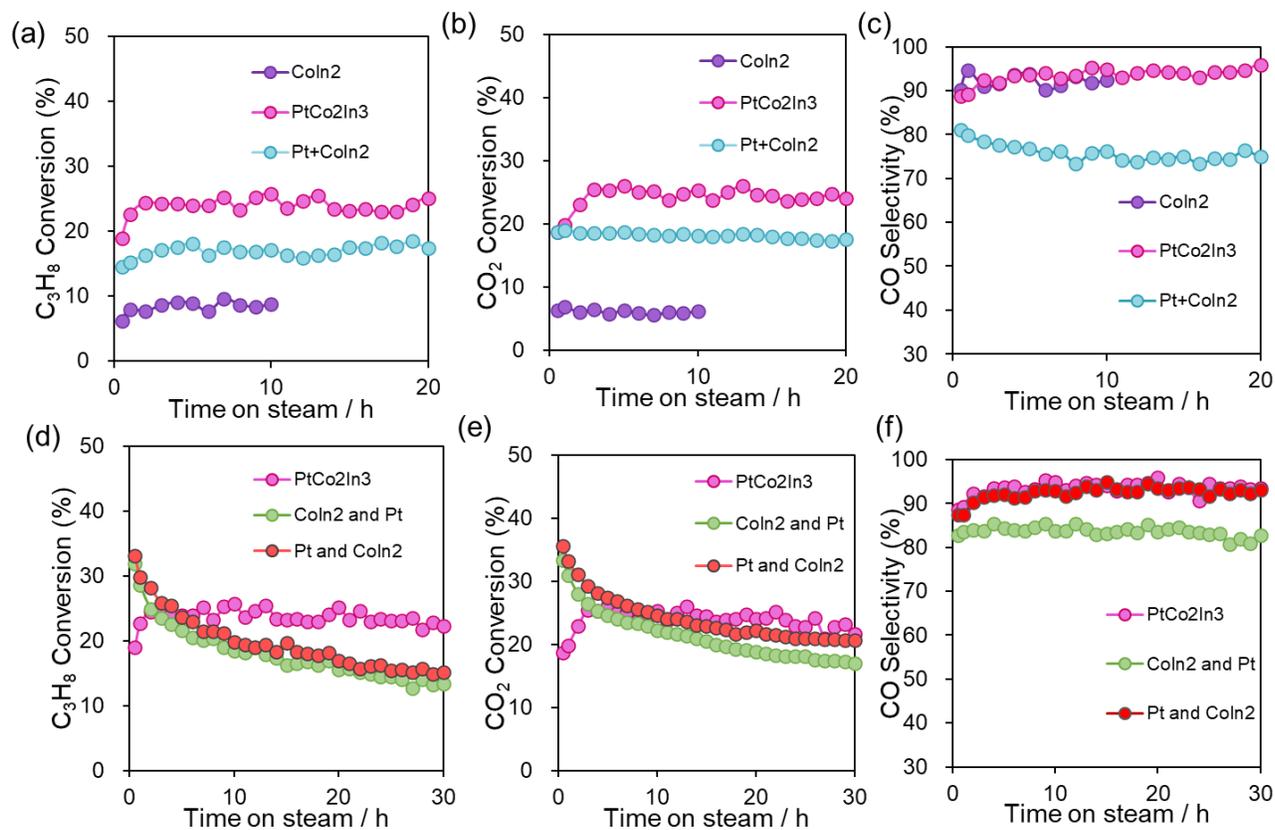
**Table S1.** Results of EXAFS curve-fitting for Pt<sub>2</sub>CoIn<sub>3</sub>/CeO<sub>2</sub> and PtCo<sub>2</sub>In<sub>3</sub>/CeO<sub>2</sub> and the reference foils

Sample	Edge	Shell	$S_0^{2a}$	CN <sup>b</sup>	$r$ (Å) <sup>c</sup>	$\Delta E_0$ (eV)	$\sigma^2$ (Å <sup>2</sup> ) <sup>d</sup>	R-factor <sup>e</sup>	
Pt foil	Pt L <sub>III</sub>	Pt–Pt	0.89	12 (fix)	$2.76 \pm 0.04$	$7.6 \pm 0.7$	0.005	0.003	
Co foil	Co K	Co–Co	0.80	12 (fix)	$2.49 \pm 0.00$	$7.5 \pm 0.1$	0.007	0.000	
In foil	In K	In–In	0.90	4 (fix)	$3.11 \pm 0.00$	$-2.9 \pm 0.8$	0.026	0.019	
		In–In		8 (fix)	$3.23 \pm 0.00$				
Pt <sub>2</sub> CoIn <sub>3</sub> / CeO <sub>2</sub>	Pt L <sub>III</sub>	Pt–Co	0.89	$0.9 \pm 0.7$	$2.57 \pm 0.01$	$3.6 \pm 1.6$	0.010	0.007	
		Pt–In		$4.3 \pm 0.7$	$2.69 \pm 0.00$		0.008		
	Co K	Co–Co	0.80	$5.5 \pm 3.9$	$2.49 \pm 0.04$	$-3.6 \pm 5.8$	0.011	0.019	
		Co–In		$0.3 \pm 1.3$	$2.62 \pm 0.05$		0.003		
			In–O		$2.4 \pm 1.1$	$2.15 \pm 0.02$		0.012	
	In K	In–Pt		0.90	$4.5 \pm 3.1$	$2.70 \pm 0.02$	$2.4 \pm 3.1$	0.014	0.029
In–Co				$0.7 \pm 3.0$	$2.78 \pm 0.05$		0.021		
	Pt L <sub>III</sub>	Pt–In	0.89	$3.2 \pm 0.5$	$2.72 \pm 0.01$	$4.8 \pm 1.2$	0.008	0.017	
PtCo <sub>2</sub> In <sub>3</sub> / CeO <sub>2</sub>	Co K	Co–Co	0.80	$5.3 \pm 0.7$	$2.48 \pm 0.01$	$-2.4 \pm 1.9$	0.008	0.010	
		Co–In		$1.8 \pm 1.7$	$2.69 \pm 0.11$		0.034		
			In–O		$2.1 \pm 0.6$	$2.15 \pm 0.02$		0.010	
	In K	In–Pt		0.90	$3.6 \pm 1.9$	$2.73 \pm 0.01$	$3.6 \pm 3.0$	0.012	0.023
In–Co				$1.3 \pm 1.2$	$2.79 \pm 0.03$		0.009		

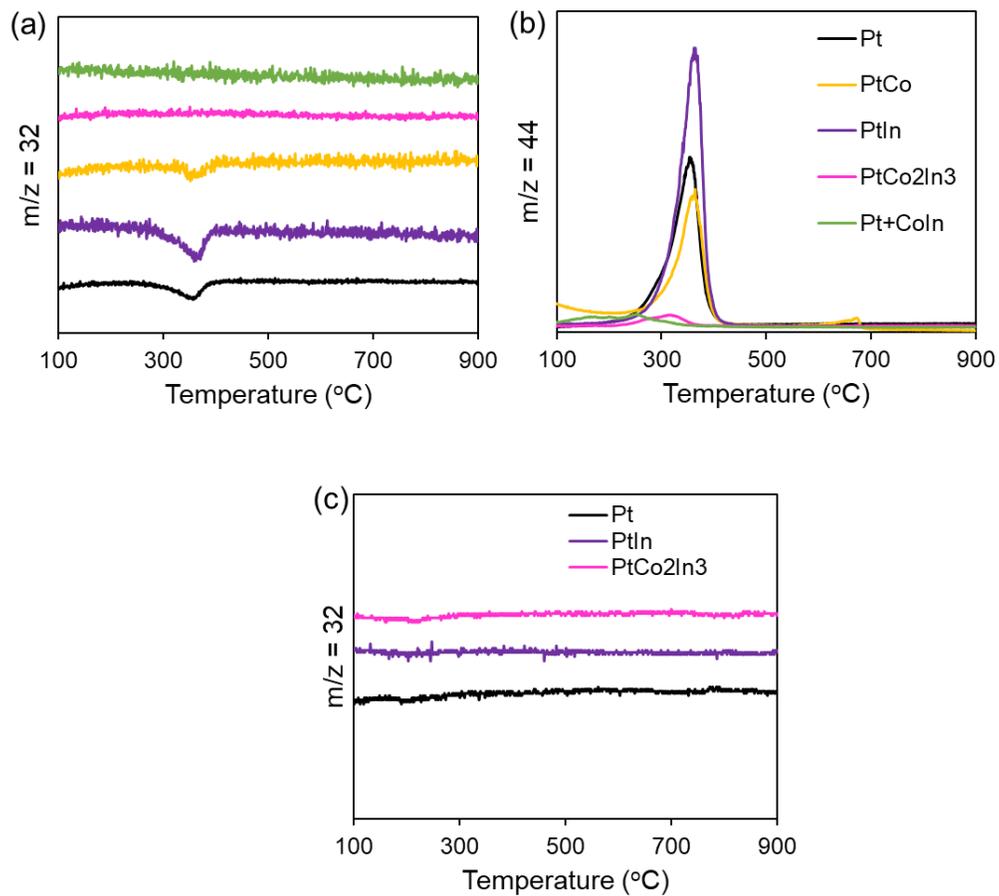
<sup>a</sup> Amplitude factor. <sup>b</sup> Coordination number. <sup>c</sup> Distance between absorber and backscatterer atoms. <sup>d</sup> Correction term in the absorption edge. <sup>e</sup> Debye–Waller factor.



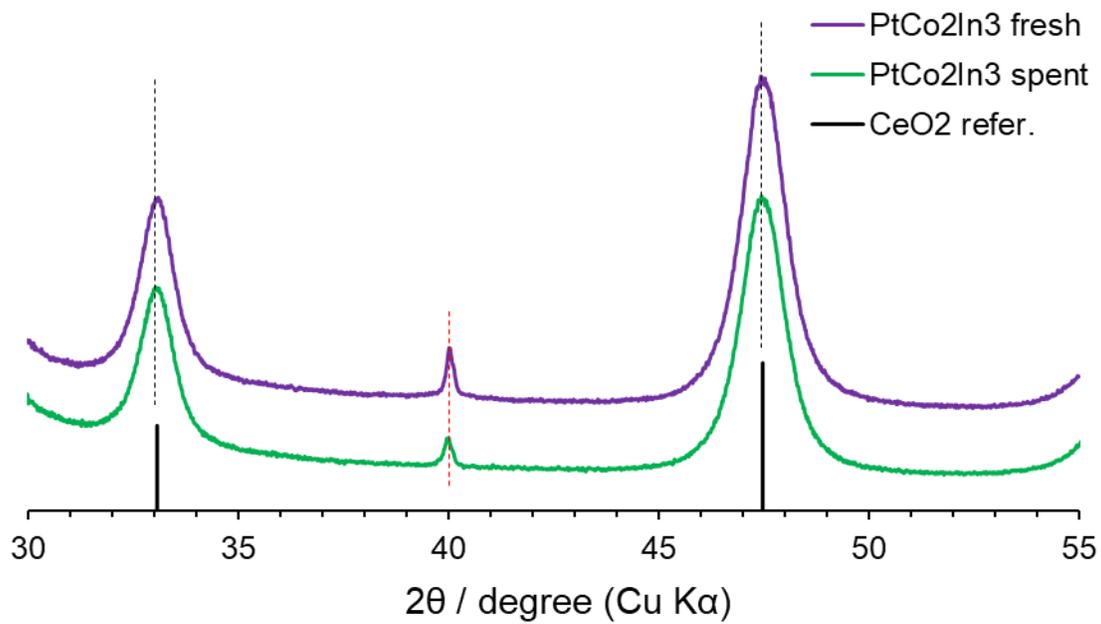
**Figure S5:** Catalytic performance of monometallic Pt/CeO<sub>2</sub>, PtCo/CeO<sub>2</sub>, PtIn/CeO<sub>2</sub>, PtCo<sub>2</sub>In<sub>3</sub>/CeO<sub>2</sub>, and Pt<sub>2</sub>CoIn<sub>3</sub>/CeO<sub>2</sub> in DRP. (a) C<sub>3</sub>H<sub>8</sub> conversion, (b) CO<sub>2</sub> conversion, (c) CO selectivity. Catalytic performance of comparison experiment for PtIn<sub>3</sub>/CeO<sub>2</sub> and PtCo<sub>3</sub>/CeO<sub>2</sub> (d) C<sub>3</sub>H<sub>8</sub> conversion, (e) CO<sub>2</sub> conversion, (f) CO selectivity.



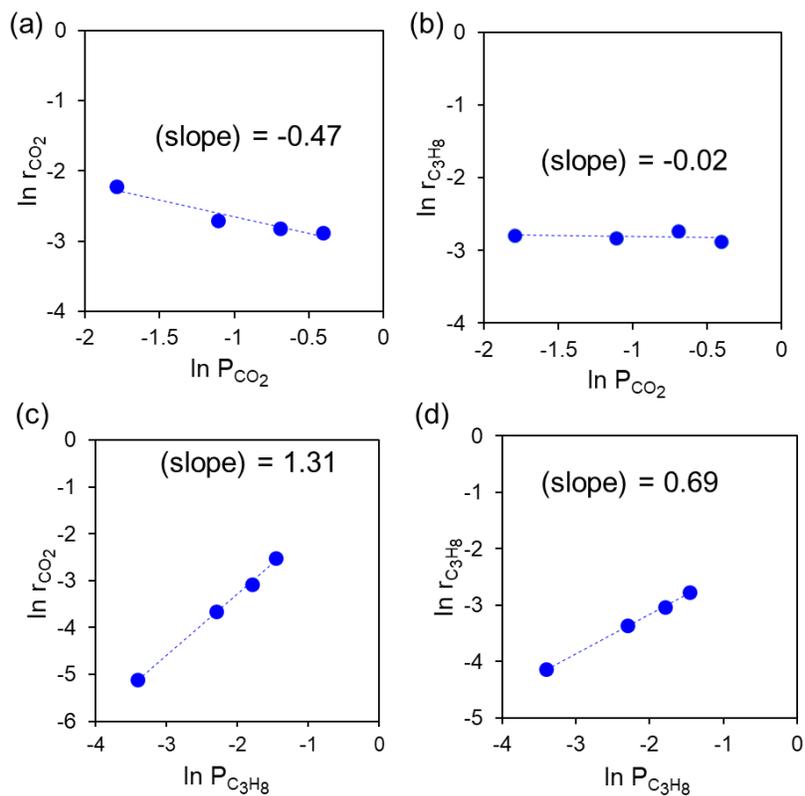
**Figure S6:** Catalytic performance of CoIn/CeO<sub>2</sub>, PtCo<sub>2</sub>In<sub>3</sub>/CeO<sub>2</sub>, and physical mixture catalysts (Pt/CeO<sub>2</sub>+CoIn/CeO<sub>2</sub>) in DRP. (a) C<sub>3</sub>H<sub>8</sub> conversion, (b) CO<sub>2</sub> conversion, (c) CO selectivity. Catalytic performance of tandem catalytic systems in DRP (Pt/CeO<sub>2</sub>+quartz wool+Co–In/CeO<sub>2</sub>, donated as Pt and CoIn<sub>2</sub>, and CoIn/CeO<sub>2</sub>+quartz wool+Pt/CeO<sub>2</sub> donated as CoIn<sub>2</sub> and Pt.), (d) C<sub>3</sub>H<sub>8</sub> conversion, (e) CO<sub>2</sub> conversion, (f) CO selectivity.



**Figure S7:** O<sub>2</sub>-TPO profiles of the spent catalysts after 50 h of DRP reaction at 550 °C: (a) O<sub>2</sub> signal (m/z = 32) and (b) CO<sub>2</sub> signal (m/z = 44). (c) O<sub>2</sub>-TPO profiles (m/z = 32) of the fresh catalysts.



**Figure S8:** XRD patterns of for the PtCo<sub>2</sub>In<sub>3</sub>/CeO<sub>2</sub> fresh catalyst and PtCo<sub>2</sub>In<sub>3</sub>/CeO<sub>2</sub> spent catalyst.



**Figure. S9.** Dependence of  $\text{C}_3\text{H}_8/\text{CO}_2$  partial pressure ( $P_{\text{C}_3\text{H}_8/\text{CO}_2}$ ) on the reaction rate of  $\text{C}_3\text{H}_8/\text{CO}_2$  conversion ( $r_{\text{C}_3\text{H}_8/\text{CO}_2}$ ) in  $\text{CO}_2$ -DRP over  $\text{PtCo}_2\text{In}_3/\text{CeO}_2$ . (a)  $P_{\text{CO}_2}$  on  $r_{\text{CO}_2}$ , (b)  $P_{\text{CO}_2}$  on  $r_{\text{C}_3\text{H}_8}$ , (c)  $P_{\text{C}_3\text{H}_8}$  on  $r_{\text{CO}_2}$ , and (d)  $P_{\text{C}_3\text{H}_8}$  on  $r_{\text{C}_3\text{H}_8}$ .

**Table S2.** Summary of the catalytic performance of Pt–Co–In/CeO<sub>2</sub> and other reported catalysts for CO<sub>2</sub>-DRP.

catalyst	temp (°C)	flow rate (ml/min)	catal. (g)	GHSV (ml g <sup>-1</sup> h <sup>-1</sup> )	gas composition	C <sub>3</sub> H <sub>8</sub> Conce. (%)	C <sub>3</sub> H <sub>8</sub> conv. (%)	CO <sub>2</sub> conv. (%)	CO sel. (%)	TOS (h)	r <sub>C<sub>3</sub>H<sub>8</sub></sub> (mmol g <sup>-1</sup> h <sup>-1</sup> )	ref
PtCo <sub>2</sub> In <sub>3</sub> /CeO <sub>2</sub>	550	30	0.1	18000	1:03:01	20.0	19-26	20-25	89-95	10	3826	This work
PtCo <sub>2</sub> In <sub>3</sub> /CeO <sub>2</sub>	550	30	0.1	18000	1:03:26	3.3	42-48	31-30	82-97	100	1165	This work
Ni <sub>3</sub> Pt <sub>1</sub>	550	20	0.1	12000	1:01:02	25	20-11.6	63-39	90-96	13	1422	1
Co <sub>3</sub> Pt <sub>1</sub>	550	20	0.1	12000	1:01:02	25	10-5.6	38-20	80-88	13	687	1
A-LaCoO <sub>3</sub> (R)	550	40	0.1	24000	10:10:20	25	19-15	35-30	50	70	3679	2
FeNi/Ce-Vo-D	550	10	1	600	2.4:4.8:2.8	24	50-38	--	84-95	3.5	224	3
20NiO-CeO <sub>2</sub>	580	300	10	1800	10:30:60	10	97	90	--	50	714	4
4Pt-2Ni-CeO <sub>2</sub>	600	100	0.05	120000	0.4: 1:98.6	0.4	100-82	95-94	96-99	65	1609	5
4Pt-CeO <sub>2</sub>	600	100	0.05	120000	0.4: 1:98.6	0.4	100-75	97-95	--	4	1471	5
2Ni-CeO <sub>2</sub>	600	100	0.05	120000	0.4: 1:98.6	0.4	100-45	93-60	--	4	883	5
5%V/TiOx	600	3	0.45	400	1:20:00	4.76	93	28	68	5	72	6
1%Ir/TiOx	600	3	0.45	400	1:20:00	4.76	72	20	75.2	5	56	6
40Ni <sub>0.75</sub> (Ce <sub>0.75</sub> Fe <sub>0.25</sub> ) <sub>0.25</sub> /Al <sub>2</sub> O <sub>3</sub>	600	75	0.1	45000	1:1.5:4.5	14.28	99-30	90-50	70	12	7880	7
Rh/TiO <sub>2</sub>	650	60	0.3	12000	12.5:37.5:50	12.5	60	58	--	2	3679	8
SrNiO <sub>3</sub> /Ni F-R	700	200	2	6000	10:30:60	10	87-85	69-66	96	50	2085	9
FeCe <sub>2</sub> O <sub>4</sub> /Al-F	700	200	1	12000	10:30:60	10	83.4-80	60-55	93.2	60	4091	10
NiO-CeO <sub>2</sub> /Al-F	700	200	1	12000	10:30:60	10	100-49	75-24	97.5	60	2403	10
NiO-CeO <sub>2</sub> /Al-F	750	200	1	12000	10:30:60	10	100	90	94	12	4905	10

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