Selective hydrogenolysis of furfuryl alcohol towards 1,5-pentanediol over Co/CeO_2 catalyst

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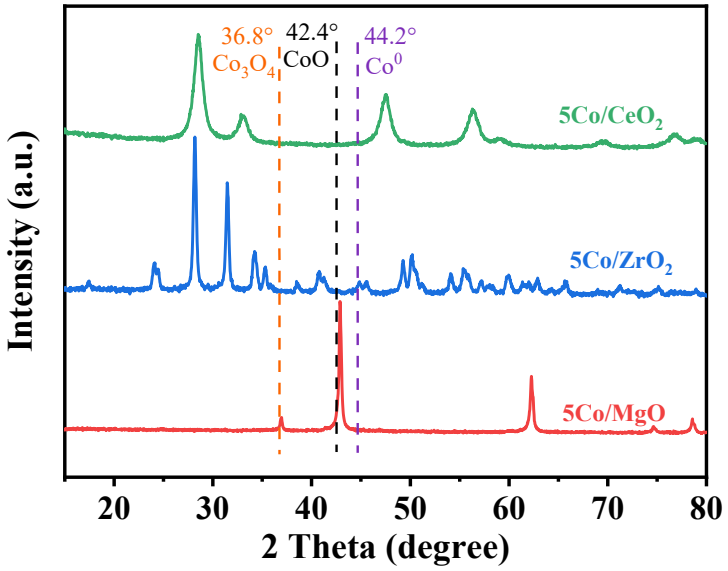

Figure S1 XRD patterns of the 5Co/Support catalysts.

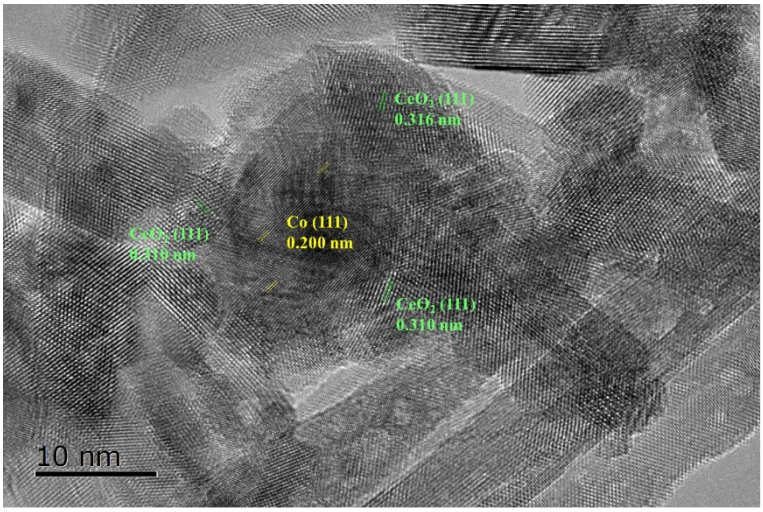

Figure S2 High-resolution TEM image of the 5Co/CeO_2 catalyst.

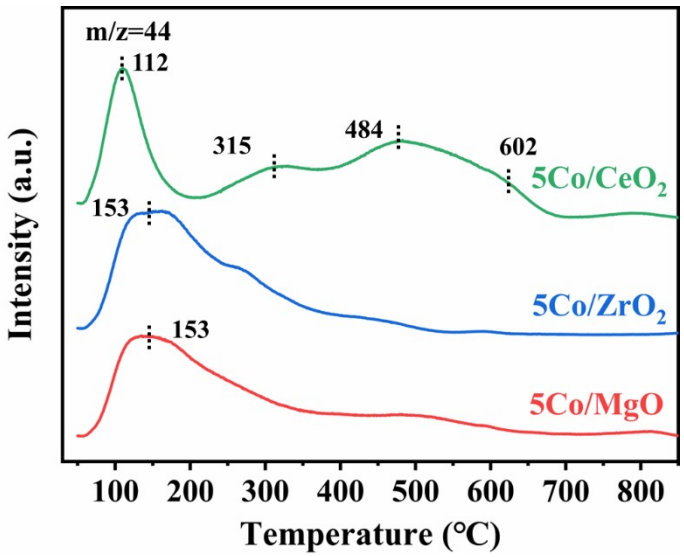

Figure S3 CO_2-TPD profiles of the 5Co/Support catalysts.

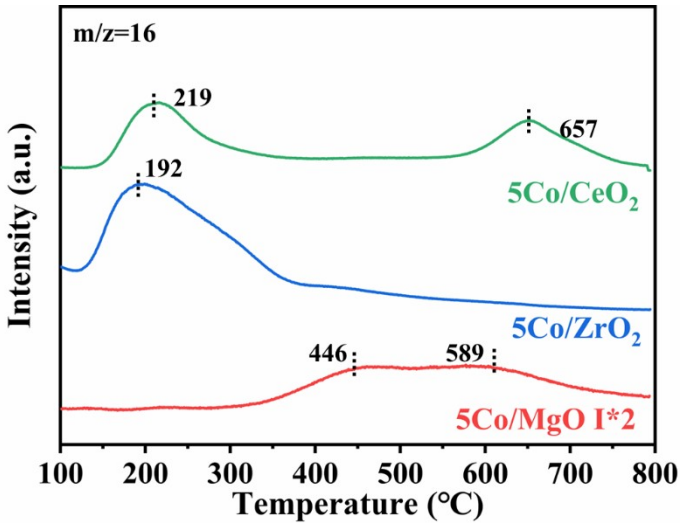

Figure S4 NH_3-TPD profiles of the 5Co/Support catalysts.

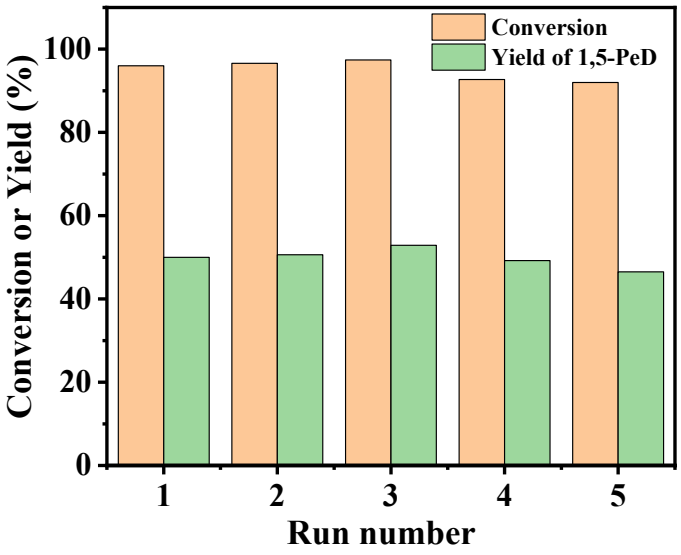

Figure S5 Recyclability of the 5Co/CeO_2 catalyst in the hydrogenolysis of FFA. Reaction conditions: 0.12 g of FFA in 5 g of ethanol, 50 mg of catalyst, 170 °C, 4 MPa H_2, 1 h, 800 rpm.

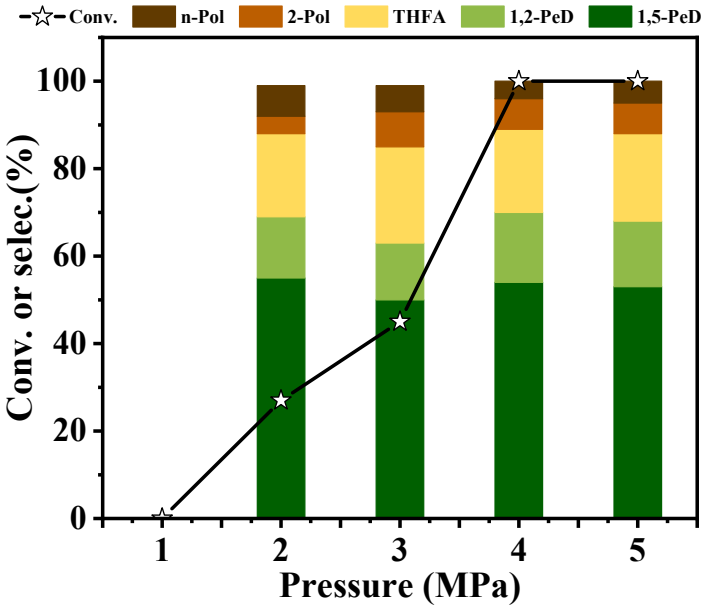

Figure S6 The effect of pressure on the catalytic performance of 5Co/CeO_2 catalyst. Reaction conditions: 0.1 g of FFA in 5 g of ethanol, 50 mg of catalyst, 1 h, 170 °C, 800 rpm.

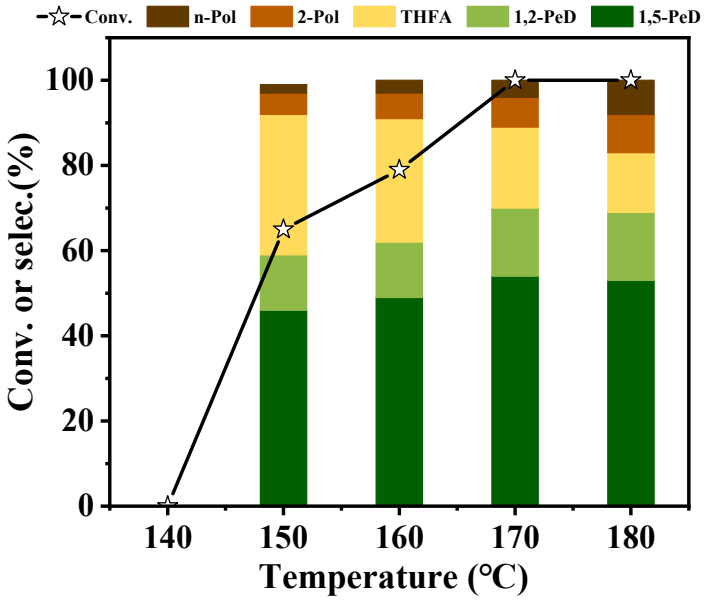

Figure S7 The effect of temperature on the catalytic performance of 5Co/CeO_2 catalyst. Reaction conditions: 0.1 g of FFA in 5 g of ethanol, 50 mg of catalyst, 1 h, 4 MPa H_2, 800 rpm.

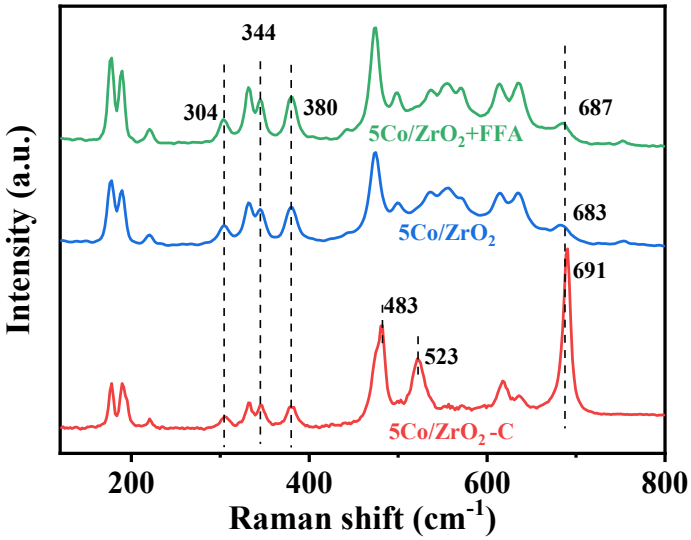

Figure S8 Raman spectra of $5Co/ZrO_2$ before and after adsorption of FFA.

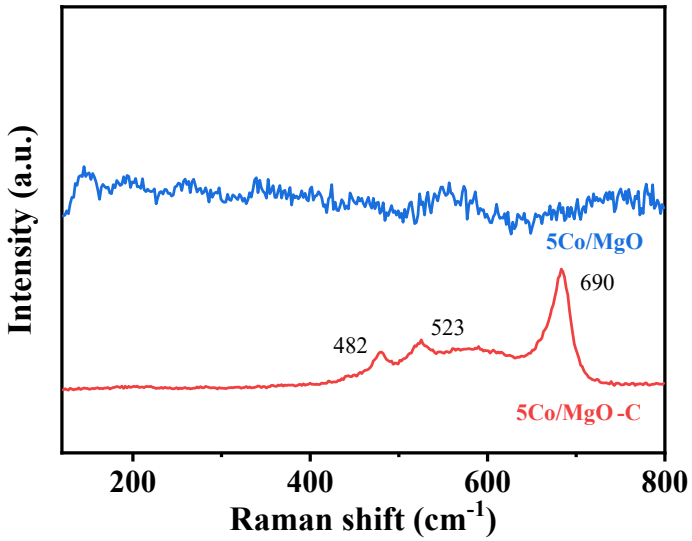

Figure S9 Raman spectra of 5Co/MgO before and after reduction treatment.

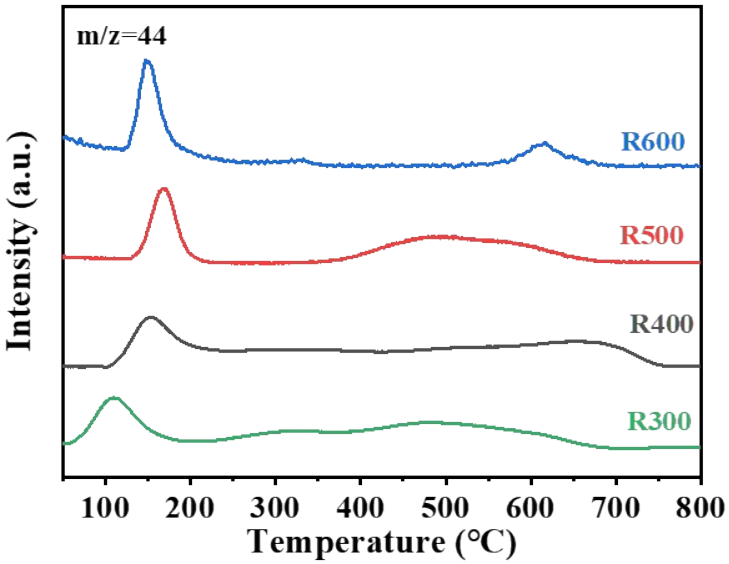

Figure S10 CO_2-TPD profiles of the $5Co/CeO_2$ catalysts treated at different reduction temperatures.

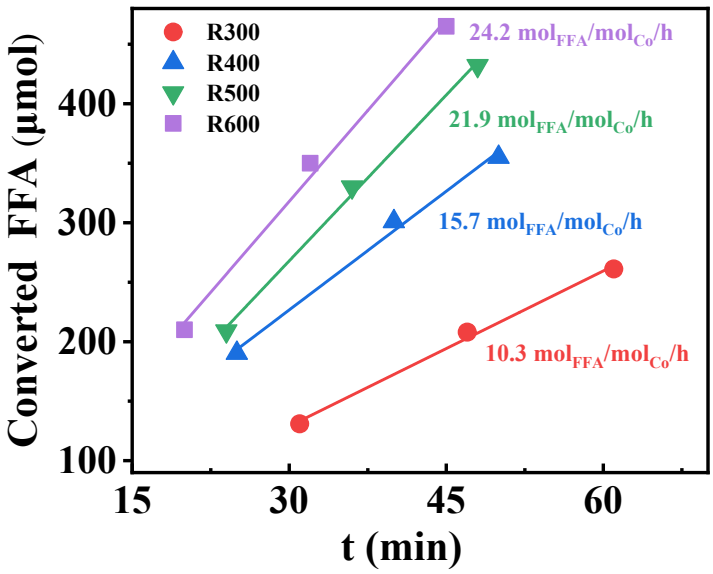

Figure S11 The reaction rate of FFA hydrogenolysis over the 5Co/CeO_2-C catalyst treated at different reduction temperatures. Reaction conditions: 0.12 g of FFA in 5 g of ethanol, 30 mg of catalyst, 150 °C, 4 MPa H_2, 800 rpm.

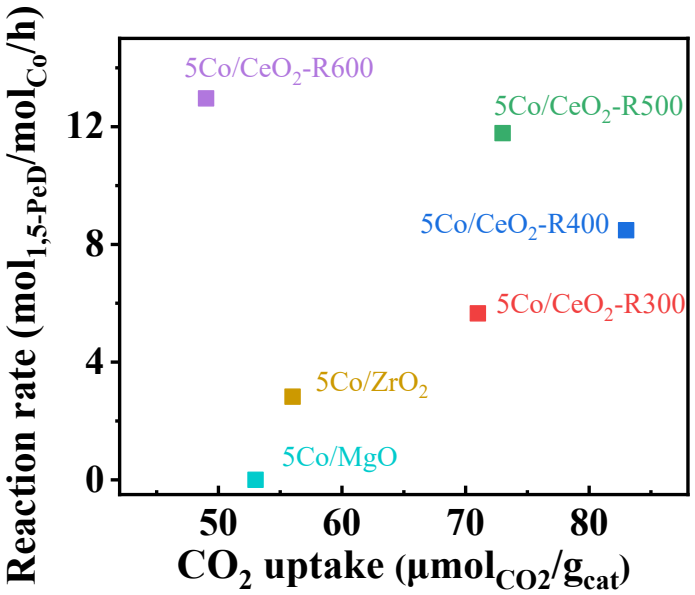

Figure S12 The change of reaction rate with the CO_2 uptakes. No obvious correlation could be found.

Table S1 Physicochemical properties of the 5Co/Support catalysts.

Catalyst	Co content[a] (wt%)	S_{BET} (m^2/g)	CO_2 uptake ($\mu mol_{CO2}/g_{cat}$)	NH_3 uptake ($\mu mol_{NH3}/g_{cat}$)
$5Co/ZrO_2$	5.1	30	56	23
5Co/MgO	5.0	66	53	8
$5Co/CeO_2$-R300	5.1	105	71	26
$5Co/CeO_2$-R400	-	97	83	-
$5Co/CeO_2$-R500	-	82	73	-
$5Co/CeO_2$-R600	-	67	49	-
$5Co/CeO_2$-used	5.1	-	-	-

[a] Determined by ICP analysis.

Table S2 Semi-quantitative analysis results by XPS.

Catalysts	Co		O		
	Co^0/Co (%)	Co^{2+}/Co (%)	O1/O (%)	O2/O (%)	O3/O (%)
5Co/CeO_2	41	59	72	16	12
5Co/ZrO_2	37	63	79	11	10
5Co/MgO	0	100	87	8	5

Table S3 Summary of the H_2-TPR results.

Catalyst	Peak 1		Peak 2		Peak 3		Peak 4		Toal (μmol/g)
	T (℃)	H_2 (μmol/g)	T (℃)	H_2 (μmol/g)	T (℃)	H_2 (μmol/g)	T (℃)	H_2 (μmol/g)	
$5Co/CeO_2$	188	296	277	326	372	355	445	462	1439
5Co/MgO	263	83	395	48	-	-	-	-	131
$5Co/ZrO_2$	216	65	295	70	331	386	424	634	1226

Note: The theoretical hydrogen consumptions for the reduction of Co_3O_4 to CoO and the reduction of CoO to Co were 283 μmol/g and 849 μmol/g, respectively. The total theoretical hydrogen consumption is 1132 μmol/g.

Table S4 Catalytic performance of the $5Co/CeO_2$ catalyst for the THFA hydrogenolysis.

Entry	Conversion (%)	Selectivity (%)	
		1,2-PeD	1,5-PeD
1	0	0	0

Reaction conditions: 0.1 g of THFA in 5 g of ethanol, 50 mg of catalyst, 4 MPa H_2 and 150 °C for 4 h.

Table S5 The reaction kinetic data for FFA hydrogenolysis over $5Co/CeO_2$ catalyst under different reaction conditions. [a]

T (℃)	C[b] (%)	P (MPa)	t (min)	Conv. (%)	Sel. (%)				
					1,2-PeD	1,5-PeD	THFA	n-Pol	2-Pol
170	2	4	30	2	-	38	62	-	-
			40	9	15	42	43	-	-
			50	17	17	46	29	5	3
		3	53	6	17	47	36	-	-
			63	11	20	49	31	-	-
			70	16	15	51	25	5	4
		2	52	1	-	36	64	-	-
			70	9	18	45	30	4	3
			90	16	20	49	24	4	3
		1	120	6	24	45	31	-	-
			140	9	20	47	23	6	4
			155	14	20	49	20	6	5
170	1	4	24	5	13	41	39	4	3
			32	13	15	45	32	4	4
			40	18	16	50	25	5	4
	3		38	2	-	36	64	-	-
			50	12	13	43	36	4	4
			61	21	15	51	23	6	5
160	2	4	47	12	13	38	43	3	3
			60	17	15	43	35	4	3
			74	26	14	46	34	3	3
150			75	2	-	31	69	-	-
			100	11	11	37	49	2	1
			120	16	12	40	45	2	1

[a] Reaction conditions: FFA in 5 g of ethanol, 20 mg of catalyst.

[b] Concentration of FFA.

Table S6 The concentration of surface oxygen vacancies of $5Co/CeO_2$ catalysts treated at different reduction temperatures.

Catalyst	$\Delta\omega$ (cm^{-1})	δ	Ov concentration (nm^{-2})
$5Co/CeO_2$-R300	10	0.0576	1.92
$5Co/CeO_2$-R400	14	0.0806	2.91
$5Co/CeO_2$-R500	17	0.0979	4.18
$5Co/CeO_2$-R600	19	0.1094	5.72

ω: The Raman shift corresponding to Ce-O symmetrical stretching F_{2g} mode in CeO_2 of the reference sample ($5Co/CeO_2$-C).

$\Delta\omega$: The change in the Raman shift relative to the reference sample.

δ: The molar fraction of oxygen vacancies in $CeO_{2-\delta}$. $\delta = 2.66*(\Delta\omega/\omega)$

O_v concentration = $\delta*N_A/(M*S)$, M is the molecular weight of CeO_2, 172.9 g/mol; S is the specific surface area of $5Co/CeO_2$-Rx (Table S1).