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Electronic Supplementary Information

Improvement of nano-particulate $Ce_xZr_{1-x}O_2$ composite oxides supported cobalt oxide catalysts for CO preferential oxidation in H_2-rich gases

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Fig. S1 Gas chromatograph for reaction mixture as reaction being performed at 250 °C

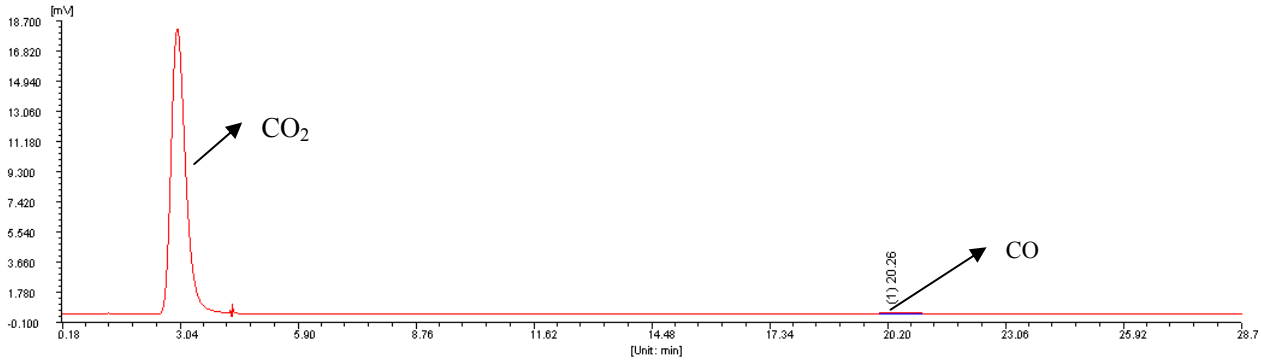

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Fig. S2 Gas chromatograph for reaction mixture as reaction being performed at 300 °C

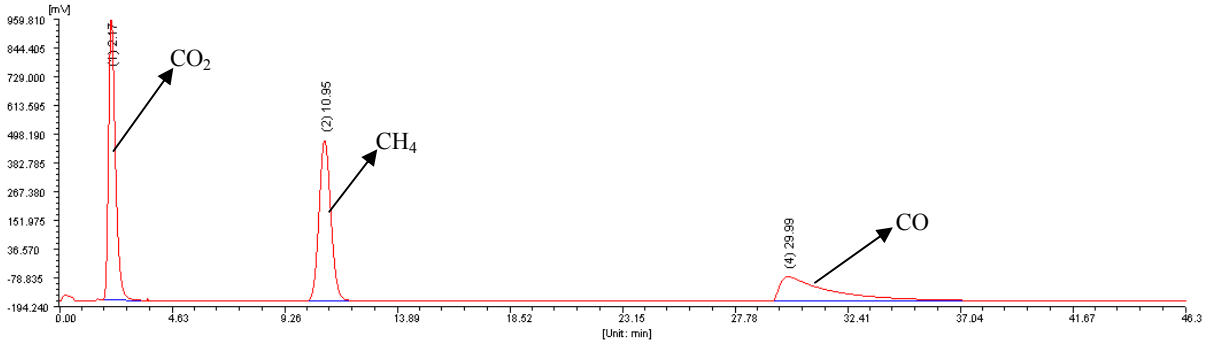

Table S1

The average crystallite size and lattice parameters of Co_3O_4/RM-$Ce_xZr_{1-x}O_2$ catalysts with various Ce/(Ce+Zr) atomic ratios from X-ray diffraction patterns.

Atomic ratio (*x*) of Ce/(Ce+Zr)	Lattice type	Lattice parameters (Å)	Average crystallite size (nm)
1[a]	Cubic *Fm*3*m*	a=5.4225	6.6
1	Cubic *Fm*3*m*	a=5.4177	7.3
0.95	Cubic *Fm*3*m*	a=5.4057	5.1
0.85	Cubic *Fm*3*m*	a=5.3961	5.1
0.80	Cubic *Fm*3*m*	a=5.3795	4.3
0.75	Cubic *Fm*3*m*	a=5.3584	4.7
0.25	Tetragonal *P*42/*nmc*	a=3.6654 c=5.1879	5.2

[a] Pure CeO_2, without Co_3O_4 loading.

Table S2

H_2-TPR quantitative analysis results for the Co_3O_4/RM-$Ce_xZr_{1-x}O_2$ catalysts with various Ce/(Ce+Zr) atomic ratios

x	H_2 Uptake (μmol/g)	CeO_2 Content (μmol/g)	Reducible CeO_2 Content (μmol/g)[b]	Reducible CeO_2[c] (%)
1	1218	5709	1838	32.2
0.95	1294	5502	1992	36.2
0.85	1573	5070	2550	50.3
0.80	1635	4843	2673	55.2
0.75	1675	4610	2752	59.7
0.50	1687	3329	2776	83.4
0.25	1107	1815	1615	89.0
0	400	7984[a]	200	2.5[d]

[a] ZrO_2 content in ZrO_2 support and Co_3O_4/ZrO_2 catalyst; [b] Calculated by 2×[H_2 Uptake-299], where the value 299 μmol.g^{-1} is the H_2 uptake for the 1.8 wt% Co_3O_4 in the catalysts; [c] The reducible CeO_2 percentage in CeO_2 content of catalysts (except for the sample with the pure ZrO_2 as support), which is calculated by [Reducible CeO_2 Content]/[CeO_2 Content of Catalyst]×100%, [d] The reducible ZrO_2 percentage in ZrO_2 amount of support and Co_3O_4/ZrO_2 catalyst.

Fig. S3 Catalytic activity of the RM-$Ce_{0.85}Zr_{0.15}O_2$ with (1.8 wt.% of cobalt oxide loading) and without cobalt oxide. Operation conditions: GHSV=15,000 $ml.h^{-1}.g^{-1}$, 0.5-1.25 vol.% CO, 1.0 vol.% O_2, 50 vol.% H_2 and balance Ar.

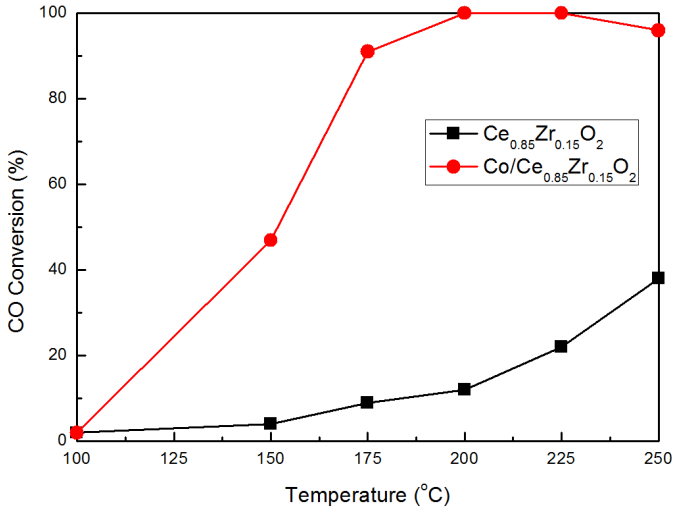

Table S3

The analysis results for the XRD of $Co_3O_4/Ce_{0.85}Zr_{0.15}O_2$ catalysts with a loading range in 2-27 wt%

Catalysts	Co_3O_4		CZ	
	Lattice type	Average crystallite size (nm)	Lattice type	Crystallite size (nm)
CZ	-	-	Fm3m	5.5
2% Co_3O_4/CZ(450-450)	-	-	Fm3m	5.4
4% Co_3O_4/CZ(450-450)	-	-	Fm3m	5.8
8% Co_3O_4/CZ(450-450)	Fd3m	13.1	Fm3m	5.7
14% Co_3O_4/CZ(450-450)	Fd3m	14.2	Fm3m	5.8
16% Co_3O_4/CZ(450-450)	Fd3m	14.9	Fm3m	5.8
20% Co_3O_4/CZ(450-450)	Fd3m	15.0	Fm3m	6.1
27% Co_3O_4/CZ(450-450)	Fd3m	16.4	Fm3m	6.0

Table S4

H_2-TPR quantitative analysis results for the $Co_3O_4/Ce_{0.85}Zr_{0.15}O_2$ catalysts with a loading range in 2-27 wt%.

Catalysts	H_2 uptake (μmol g^{-1})	α (°C)	β (°C)	γ (°C)	γ′ (°C)	δ (°C)	H_2 uptake for Co_3O_4 (μmol g^{-1})	H_2 uptake for CeO_2 (μmol g^{-1})
2%Co_3O_4/CZ(450-450)	1268	100	261	-	350	496	332	936
4%Co_3O_4/CZ(450-450)	1370	98	266	-	350	499	664	706
8%Co_3O_4/CZ(450-450)	1961	98	275	342	357	501	1328	633
14%Co_3O_4/CZ(450-450)	2921	99	285	342	364	503	2324	597
16%Co_3O_4/CZ(450-450)	3038	98	285	337	355	506	2656	427
20%Co_3O_4/CZ(450-450)	3589	102	289	334	359	522	3320	269
27%Co_3O_4/CZ(450-450)	4709	104	296	340	367	528	4481	228

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Fig. S4 **H_2 TPR profile of the bare $Ce_{0.85}Zr_{0.15}O_2$ support without cobalt loading**