Supporting information

Redox behavior of potassium doped and transition metal co-doped $Ce_{0.75}Zr_{0.25}O_2$ for thermochemical H_2O/CO_2 splitting

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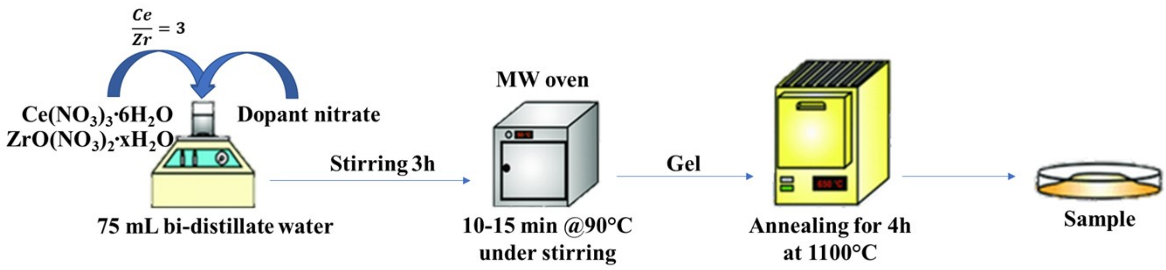

Figure S1. Co-precipitation synthesis steps of the doped ceria materials.

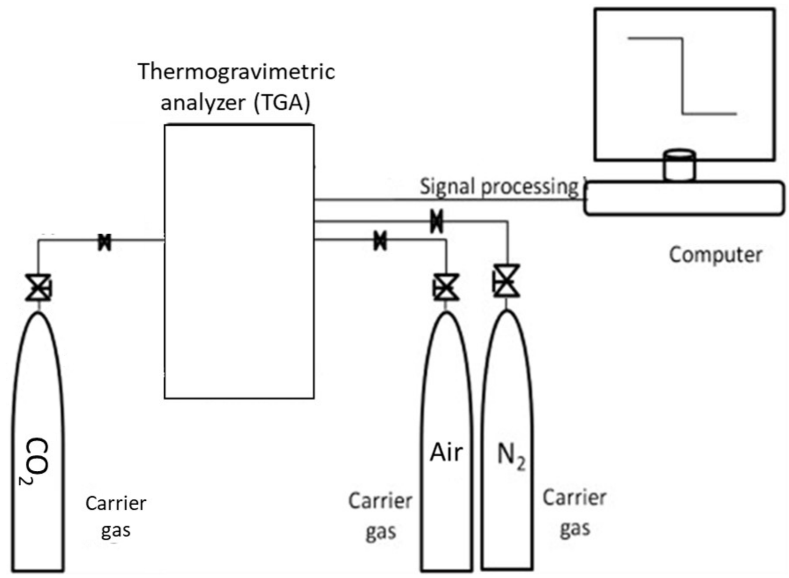

Figure S2. Schematic of the TGA apparatus.

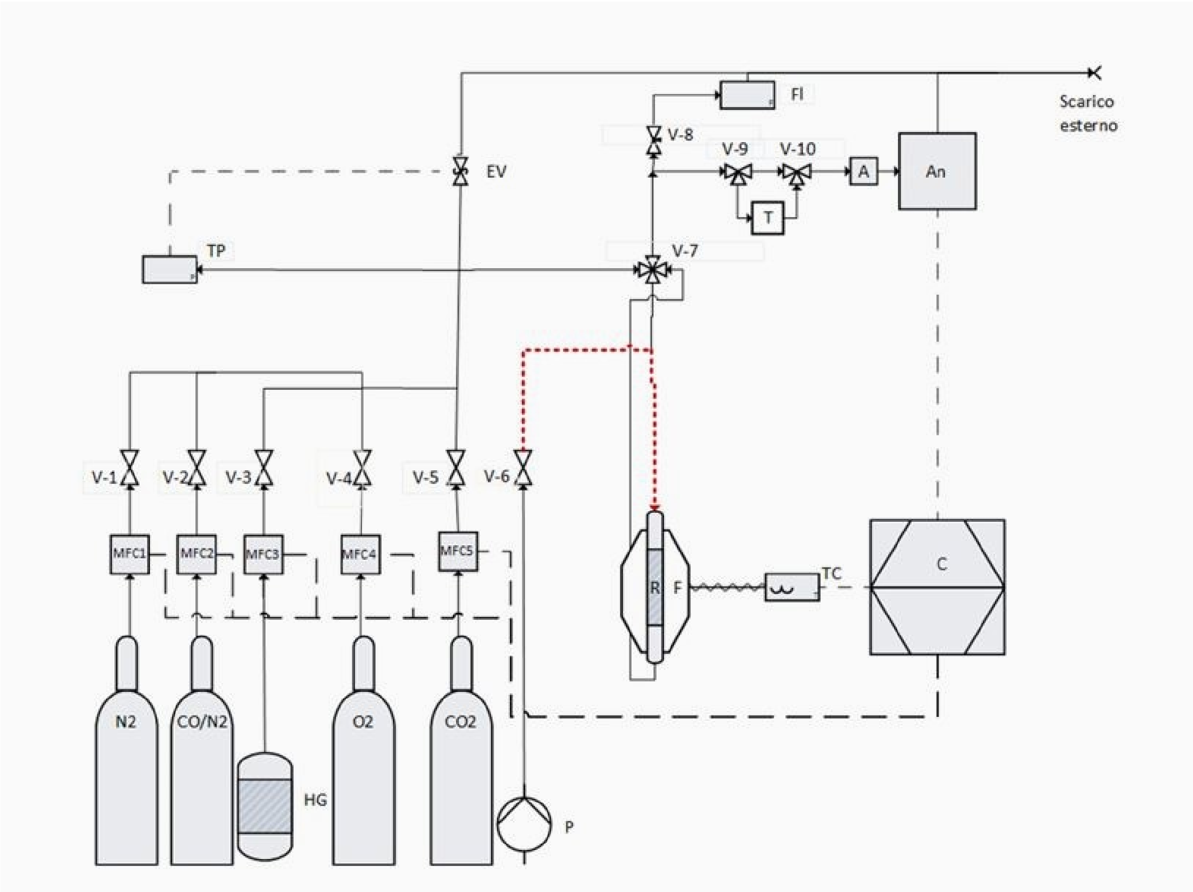

Figure S3. Schematic of the quartz reactor setup.

Table S1. XRD parameters evaluated from the (111) plane: (diffraction angle (2θ, °); cell parameter (a, nm); crystallite size (τ, nm) and specific surface area (SSA, m^2/g) of used samples (treated up to 1350 °C).

Sample	***2θ***	**a**	**τ**	**SSA**
CeZr	28.39	0.544	23	3
Fe-CeZr	28.18	0.548	27	3
Mn-CeZr	28.21	0.548	23	3
Cu-CeZr	28.58	0.541	24	5
K-CeZr	28.68	0.539	24	4
K-Fe-CeZr	28.83	0.536	70	4
K-Cu-CeZr	28.70	0.539	57	5

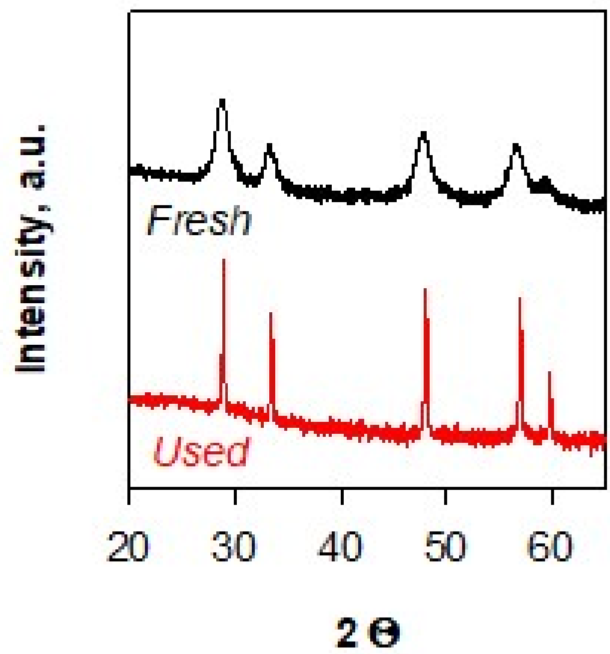

Figure S4. XRD profiles of fresh and used K-Fe-CeZr.

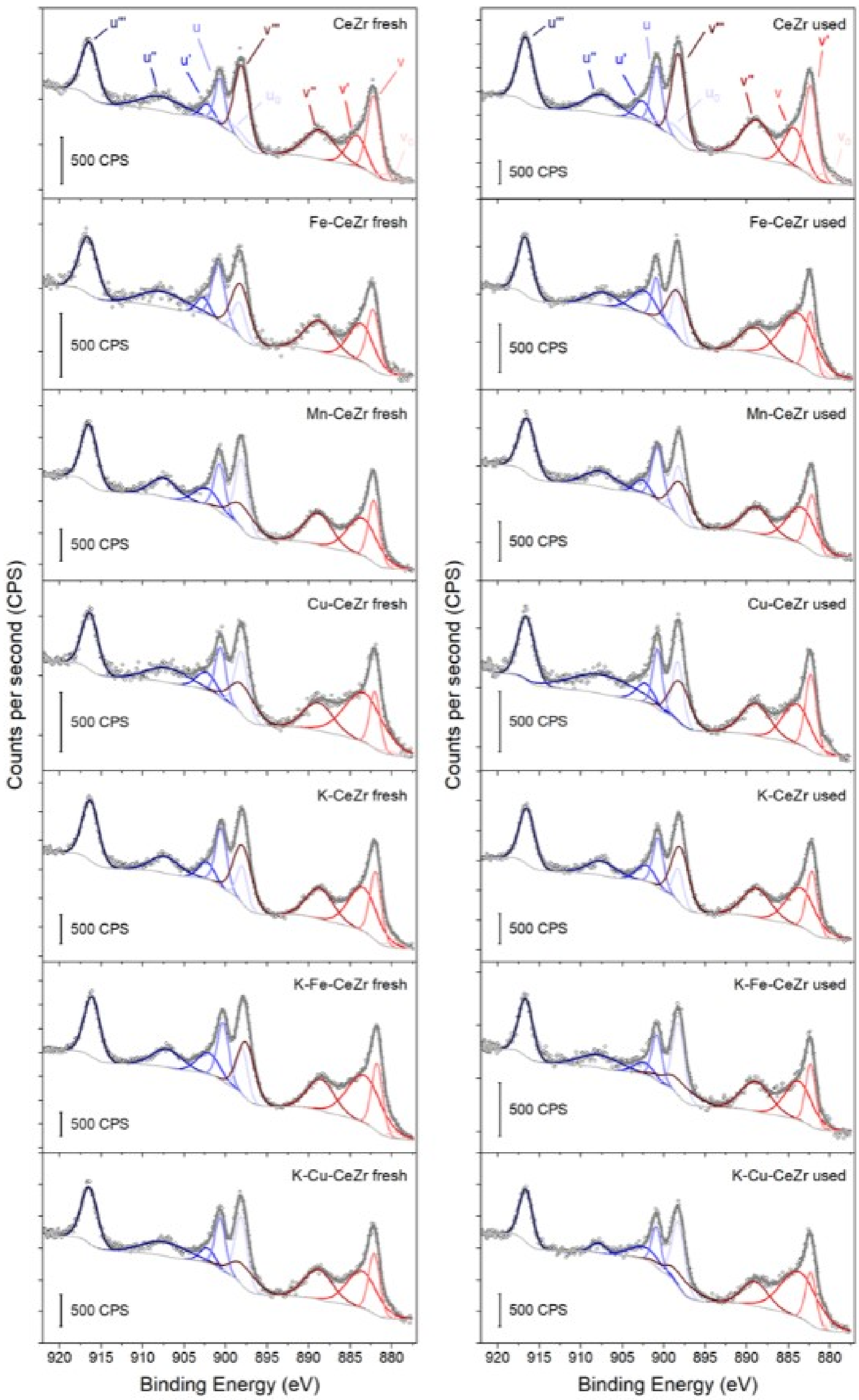

Figure S5. Ce 3d high-resolution XPS spectra with curve-fitting of the fresh (left) and used (right) catalysts.

Table S2. Content of surface labile oxygen (as ratio between labile oxygen (O_α) and bulk oxygen (O_β)) by XPS analysis.

Sample	Fresh	Used	Δ(Ce/Zr)	Δ(Ce^{3+}/Ce^{4+})
	O_α/O_β	O_α/O_β		
CeZr	1.33	0.57	0.96	***0.06***
Fe-CeZr	0.97	0.92	***-0.53***	***0.49***
Mn-CeZr	0.92	1.42	***-0.92***	-0.15
Cu-CeZr	1.04	1.10	***-1.32***	-0.31
K-CeZr	0.85	0.58	***-0.16***	***0.05***
K-Fe-CeZr	0.67	0.68	***-1.76***	***0.03***
K-Cu-CeZr	0.85	1.04	***-1.05***	***0.48***

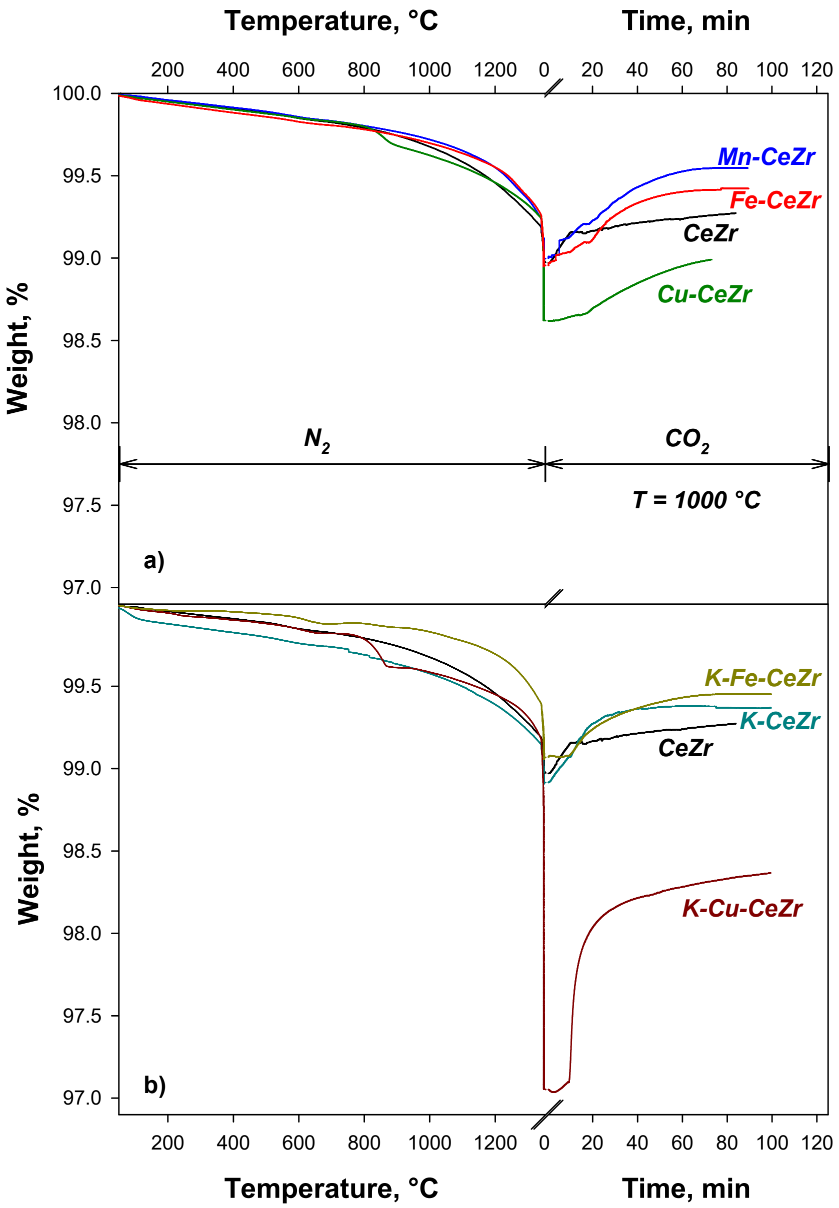

Figure S6. TG profiles of a CO_2 splitting cycle of M'-M-CeZr samples. a) undoped and transition metals doped samples; b) undoped and potassium doped and co-doped samples.

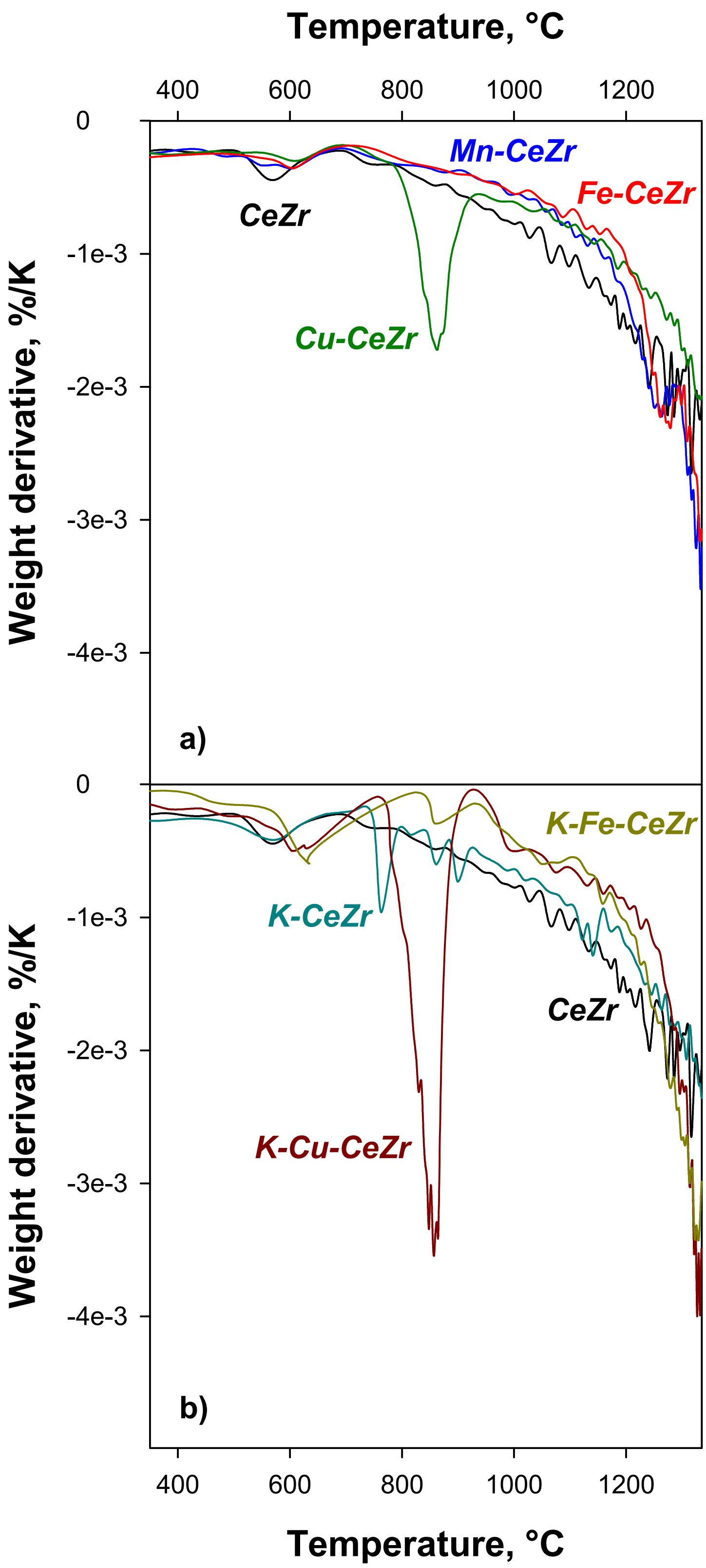

Figure S7. DTG profiles of self-reduction step of the studied samples

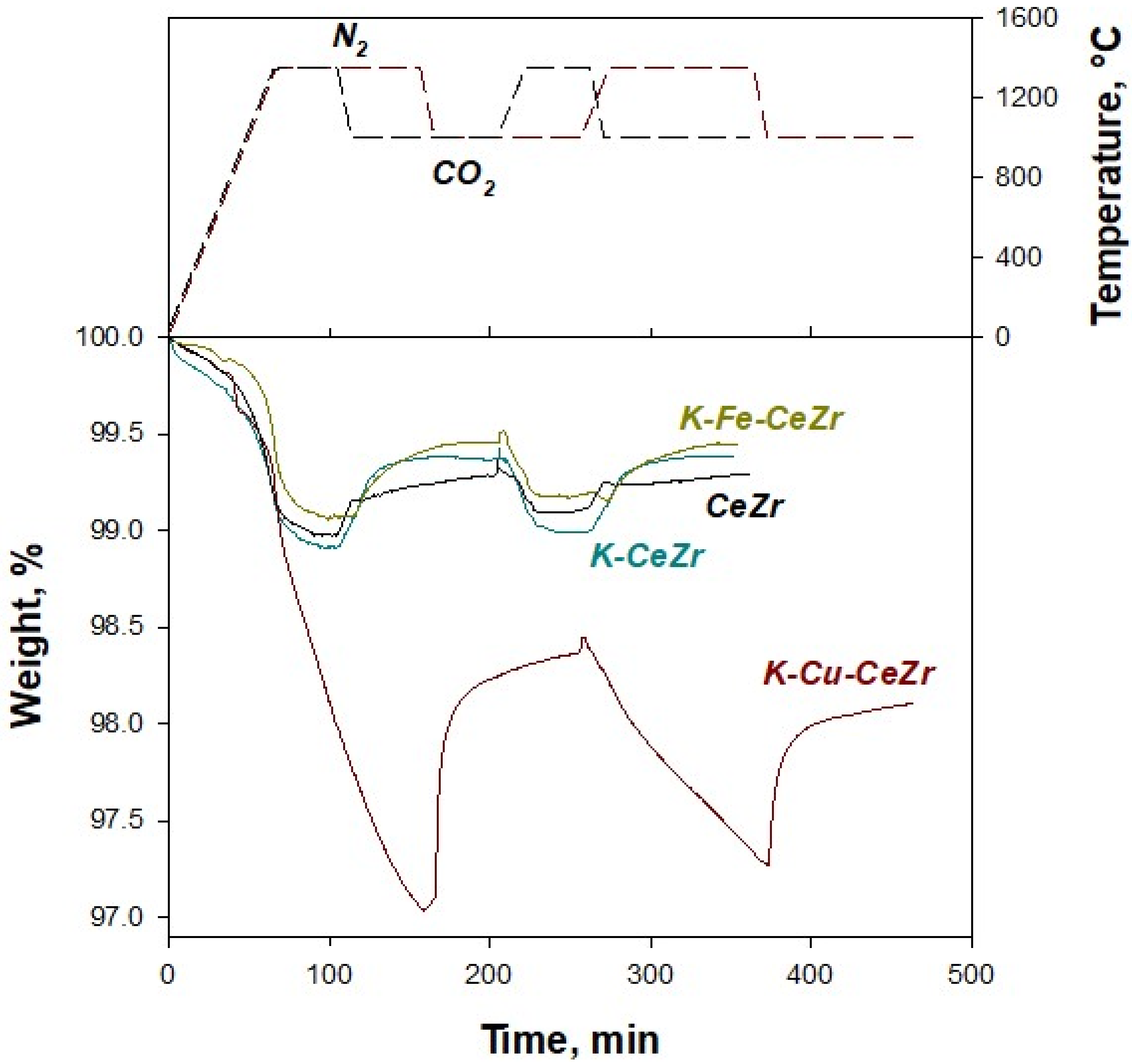

Figure S8. TG profiles of a double CO2 splitting cycle on bare and K-doped ceria/zirconia samples.

Table S3. . Reduction degree after each step (x_{red}, %), oxidation yield (α, %), and reduction yield (β, %) during thermochemical cycles in TG.

		CeZr	Fe-CeZr	Mn-CeZr	Cu-CeZr	K-CeZr	K-Fe-CeZr	K-Cu-CeZr
I cycle	x_{red}	25.6	25.6	22.9	31.4	26.6	20.5	43.1
	β	-	-	-	-	-	-	-
	x_{red}	22	16.7	13.8	26.6	12.2	9.7	30.2
	α	13.8	35	39.9	15.4	54.1	52.7	29.9
II cycle	x_{red}	27.4	-	-	-	18.4	13.1	42.8
	β	151.8	-	-	-	43.4	31.6	97.4
	x_{red}	26.3	-	-	-	11.5	8.6	40.5
	α	19.8	-	-	-	110.9	131.8	18.3
III cycle	x_{red}	-	-	-	-	17.8	12.6	48.9
	β	-	-	-	-	91.4	88	369.5
	x_{red}	-	-	-	-	12	8.9	48.2
	α	-	-	-	-	92.1	91.9	8.6
IV cycle	x_{red}	-	-	-	-	18.2	12.7	53.3
	β	-	-	-	-	106	103.9	699
	x_{red}	-	-	-	-	13.4	9.1	55
	α	-	-	-	-	77.3	94.7	0
V cycle	x_{red}	-	-	-	-	19.5	13.3	61.3
	β	-	-	-	-	127.1	116.8	0
	x_{red}	-	-	-	-	14.9	10	60.9
	α	-	-	-	-	76.2	79.4	7.5

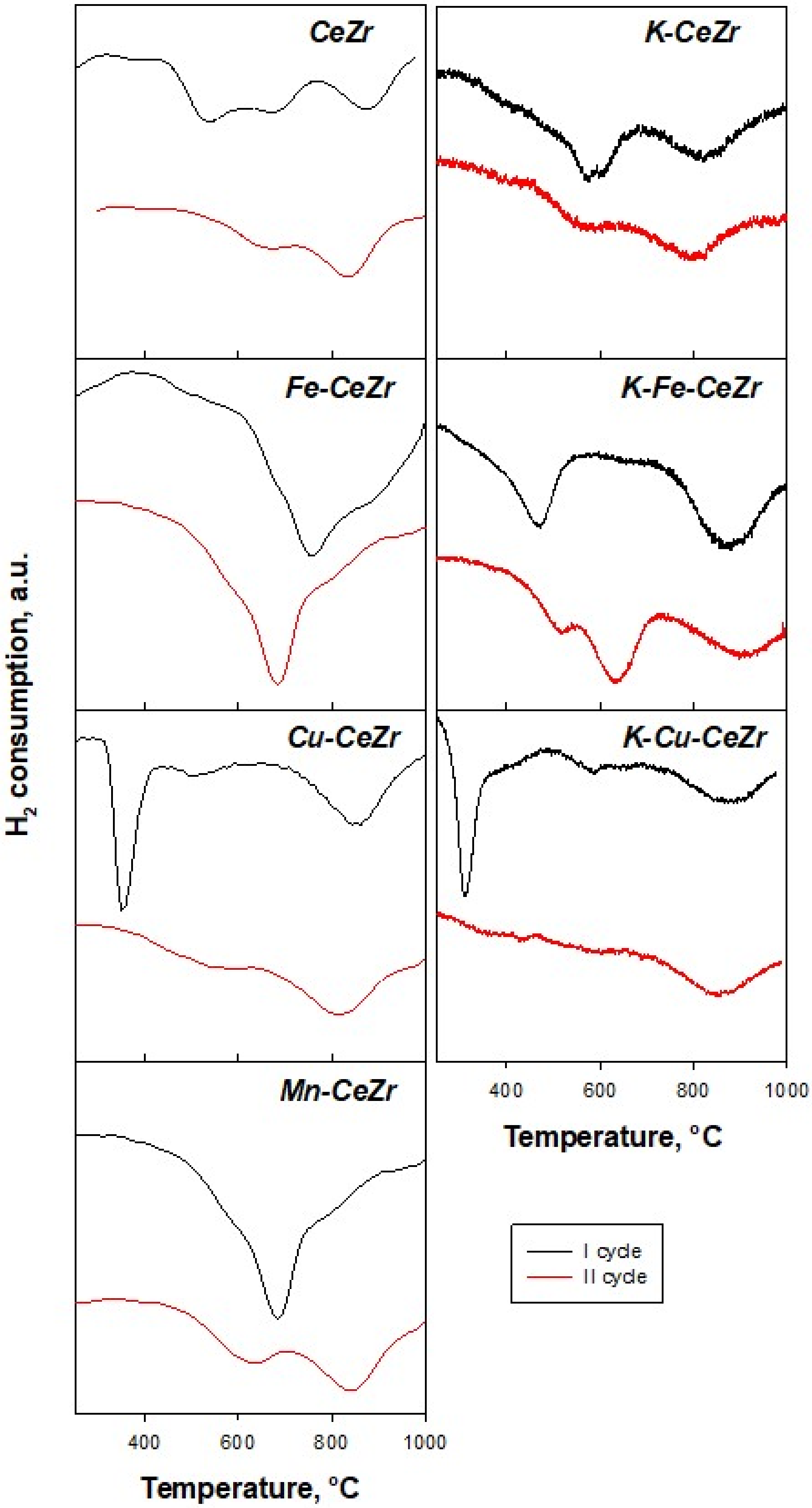

Figure S9. Reduction profiles of the studied samples for two reduction-oxidation cycles.

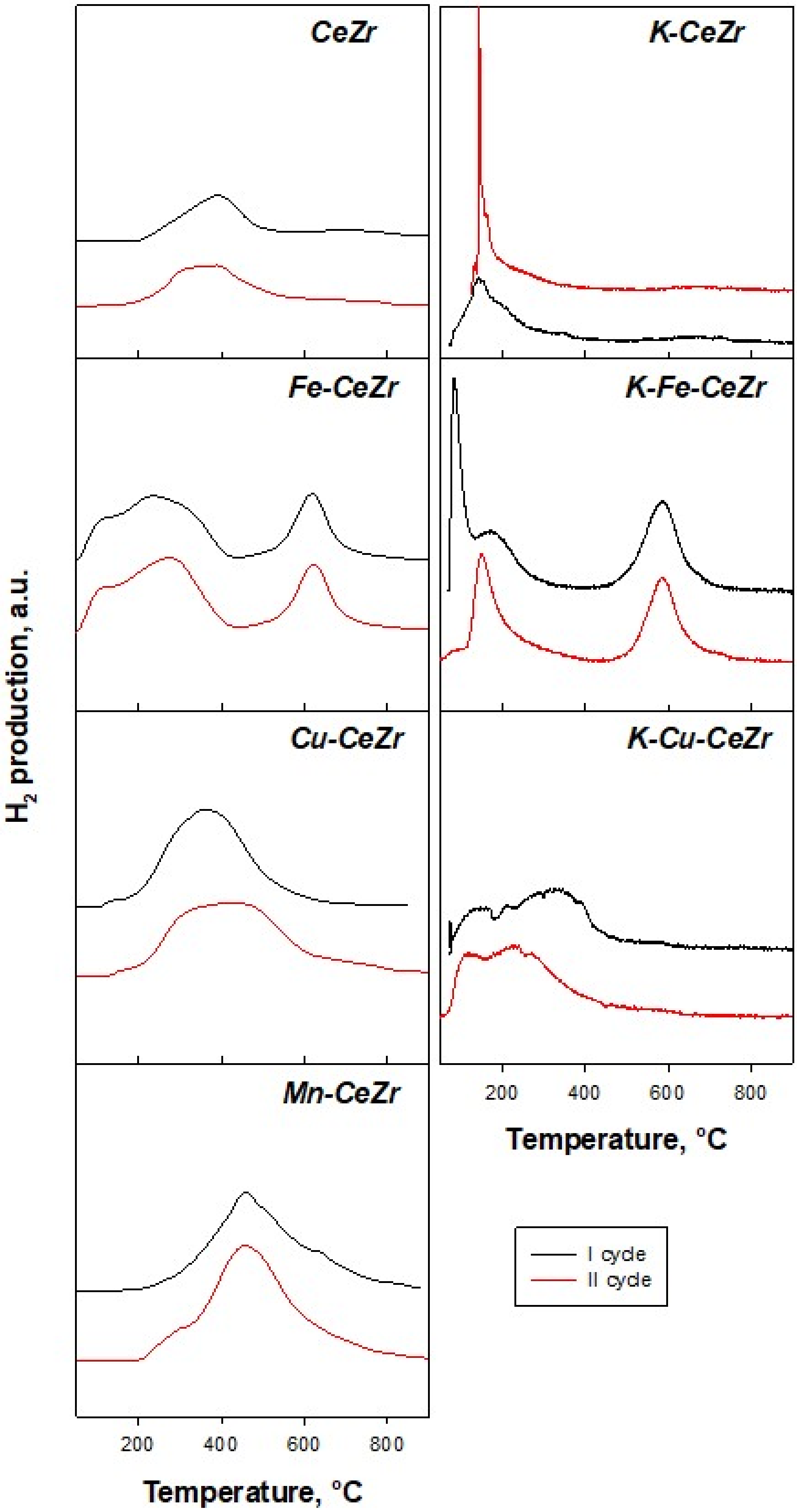

Figure S10. Oxidation profiles of the studied samples for two reduction-oxidation cycles.

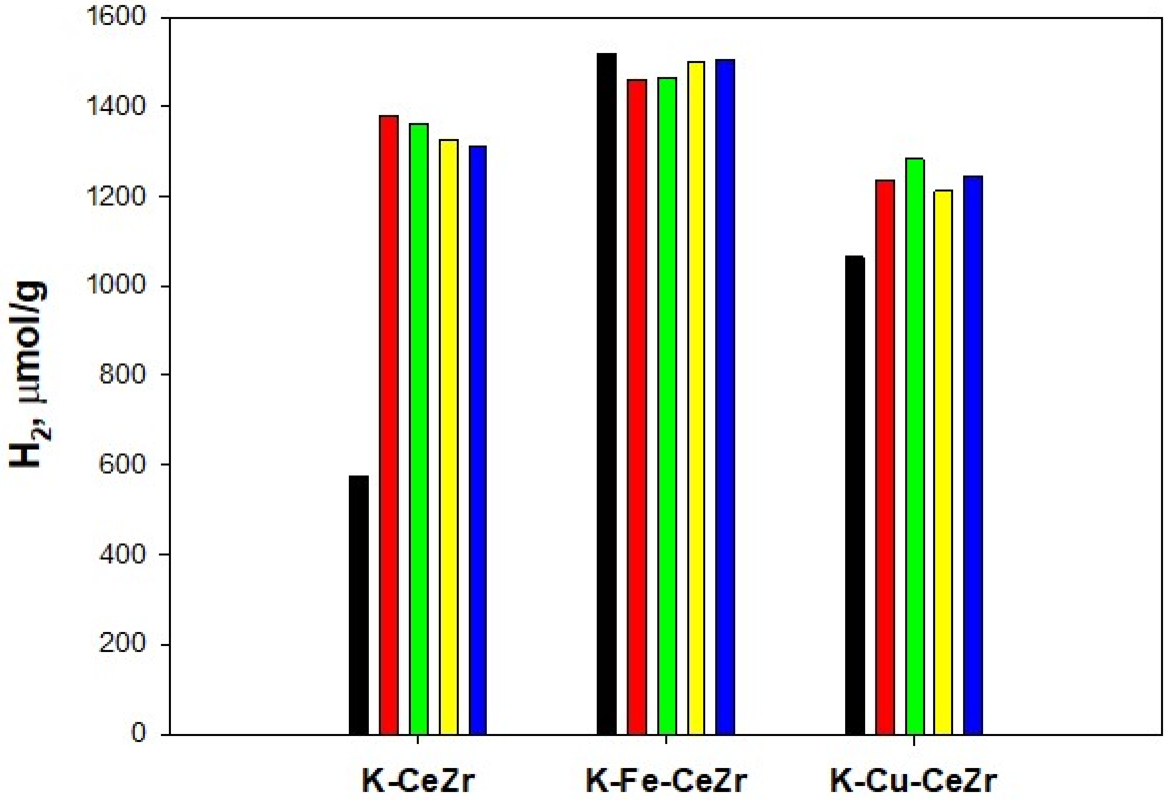

Figure S11. H_2 production during TPO with water of five consecutive TPR/TPO cycles by K containing materials.

Table S4. Reduction degree after each step (x_{red}, %), oxidation yield (α, %), and reduction yield (β, %) during TPR and TPO cycling.

	Sample	CeZr	Fe-CeZr	Mn-CeZr	Cu-CeZr	K-CeZr	K-Fe-CeZr	K-Cu-CeZr
I cycle	x_{red}	36.5	63.1	66.7	60.5	44.6	49.9	78.9
	β	-	-	-	-	-	-	-
	x_{red}	18	10.6	7.5	17.1	19.9	-6.1	37.2
	α	50.9	83.1	88.8	71.8	55.5	112.2	52.8
II cycle	x_{red}	56.3	72.3	68	61.5	67.4	49.1	81
	β	206.4	117.6	102.1	102.2	191.6	98.5	105.2
	x_{red}	34.6	20	12.9	20.2	7.7	-4.8	32.6
	α	56.5	84.8	91.1	92.9	125.7	97.6	110.5