Table S1. Effective bader charge of substituted metal atoms with oxygen atoms near oxygen vacancies when Zn and other metal atoms are co-substituted on the CeO_2 (111) surface.

Co-substituted metal	Zn	M	O_1	O_2	O_3
Zn-Rb	-1.29	-0.85	0.55	1.15	1.19
Zn-Nd	-1.23	-2.04	1.21	1.22	1.21
Zn-In	-1.25	-1.62	1.12	1.16	1.21
Zn-K	-1.34	-0.84	0.85	1.13	1.15
Zn-Pb	-1.24	-1.70	1.09	1.13	1.23
Zn-Na	-1.33	-0.84	0.81	1.15	1.15
Zn-Cd	-1.31	-1.26	0.86	1.17	1.16
Zn-Ag	-1.32	-1.06	0.97	1.05	1.20
Zn-Ca	-1.55	-1.30	0.92	1.22	1.16
Zn-Sc	-1.32	-2.10	1.17	1.25	1.20
Zn-Sr	-1.34	-1.59	0.98	1.21	1.16
Zn-Ba	-1.32	-1.58	0.97	1.19	1.16
Zn-Mn	-1.30	-1.67	1.09	1.15	1.22
Zn-Zr	-1.24	-2.31	1.23	1.23	1.21
Zn-Mg	-1.29	-1.68	0.84	1.26	1.19
Zn-Tl	-1.28	-1.19	1.01	1.08	1.19
Zn-Ti	-1.30	-1.99	1.17	1.19	1.21
Zn-Y	-1.24	-2.21	1.25	1.26	1.20
Zn-Hf	-1.24	-2.28	1.23	1.23	1.20
Zn-La	-1.30	-2.12	1.14	1.23	1.21
Zn-Ga	-1.29	-1.65	0.90	1.19	1.18
Zn-Fe	-1.32	-1.68	1.04	1.14	1.21
Zn-Al	-1.28	-2.43	0.89	1.37	1.17
Zn-Sn	-1.24	-2.17	1.18	1.19	1.19
Zn-Au	-1.31	-1.11	0.97	1.05	1.19
Zn-Pr	-1.22	-2.23	1.22	1.22	1.22
Zn-Rh	-1.30	-1.41	1.04	1.08	1.21

Zn-Bi	-1.24	-1.87	1.14	1.15	1.21
Zn-Ge	-1.24	-2.09	1.17	1.17	1.20
Zn-Cu	-1.30	-1.04	0.86	1.11	1.18
Zn-Pd	-1.31	-1.20	1.00	1.19	1.21
Zn-Cs	-1.28	-0.86	0.53	1.14	1.20
Zn-Cr	-1.27	-1.76	1.02	1.15	1.20
Zn-Nb	-1.28	-2.63	1.21	1.23	1.21
Zn-Ta	-1.28	-2.51	1.19	1.21	1.19
Zn-Pt	-1.30	-1.32	1.02	1.07	1.20
Zn-Co	-1.29	-1.46	0.90	1.18	1.19
Zn-Ru	-1.31	-1.51	1.09	1.11	1.21
Zn-Sb	-1.29	-2.18	1.17	1.19	1.20
Zn-V	-1.26	-1.85	1.03	1.18	1.21
Zn-Ni	-1.30	-1.14	0.90	1.11	1.18
Zn-W	-1.29	-2.58	1.07	1.21	1.23
Zn-Mo	-1.30	-2.30	0.99	1.21	1.21
Zn-Ir	-1.30	-1.51	1.05	1.10	1.19
Zn-Os	-1.30	-1.78	1.09	1.12	1.19

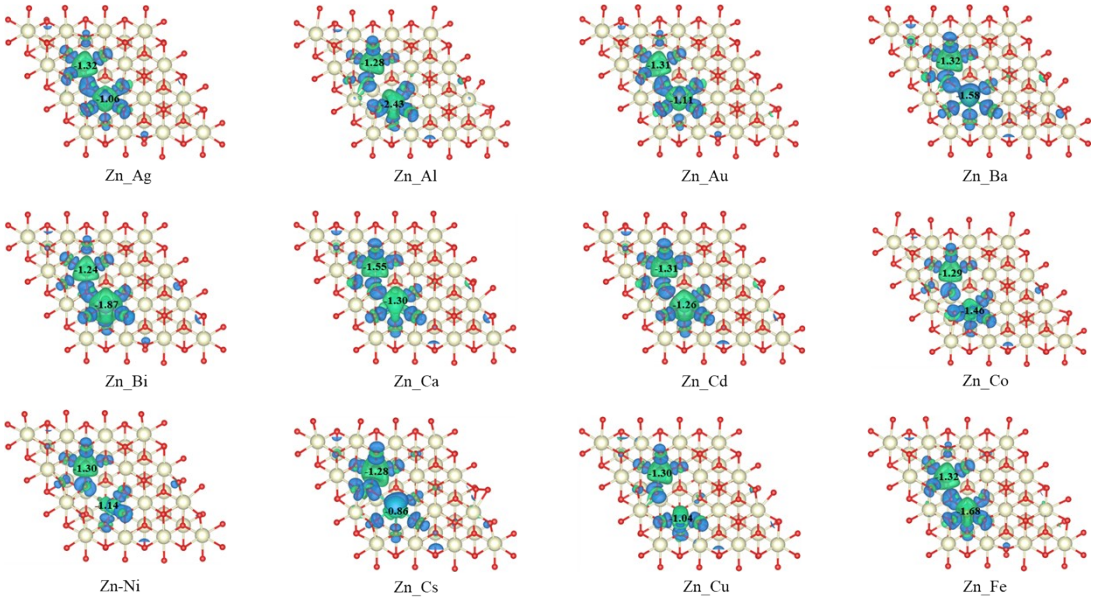

Fig. S1 DFT calculated the charge-density difference of Zn and other metal atoms co-substituted CeO_2 (111). (Other metal ions are Ag, Al, Au, Ba, Bi, Ca, Cd, Co, Ni, Cs, Cu and Fe.)

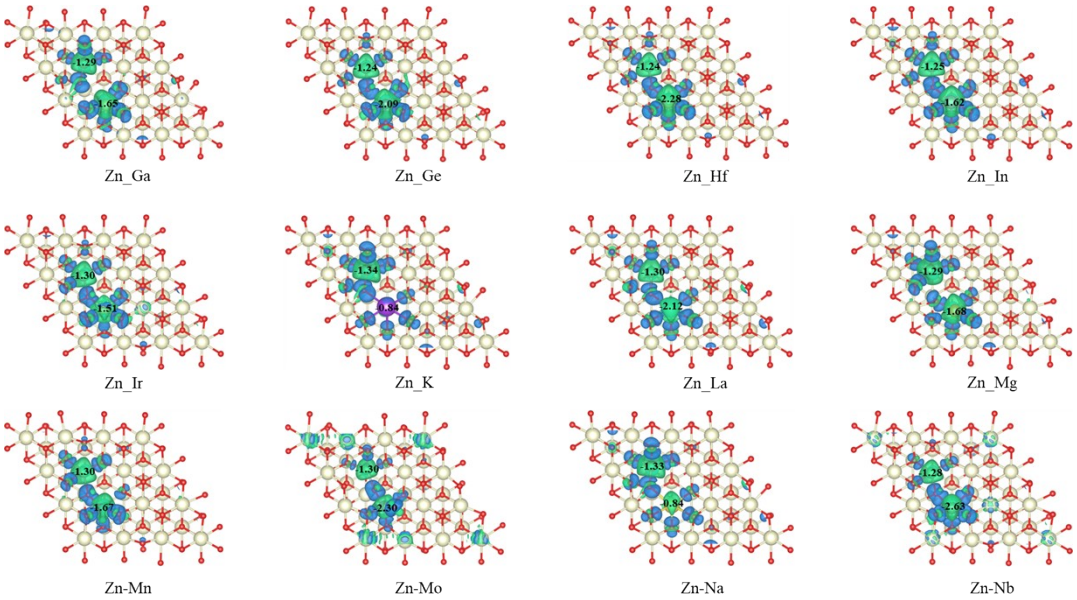

Fig. S2 DFT calculated the charge-density difference of Zn and other metal atoms co-substituted CeO_2 (111). (Other metal ions are Ga, Ge, Hf, In, Ir, K, La, Mg, Mn, Mo, Na and Nb.)

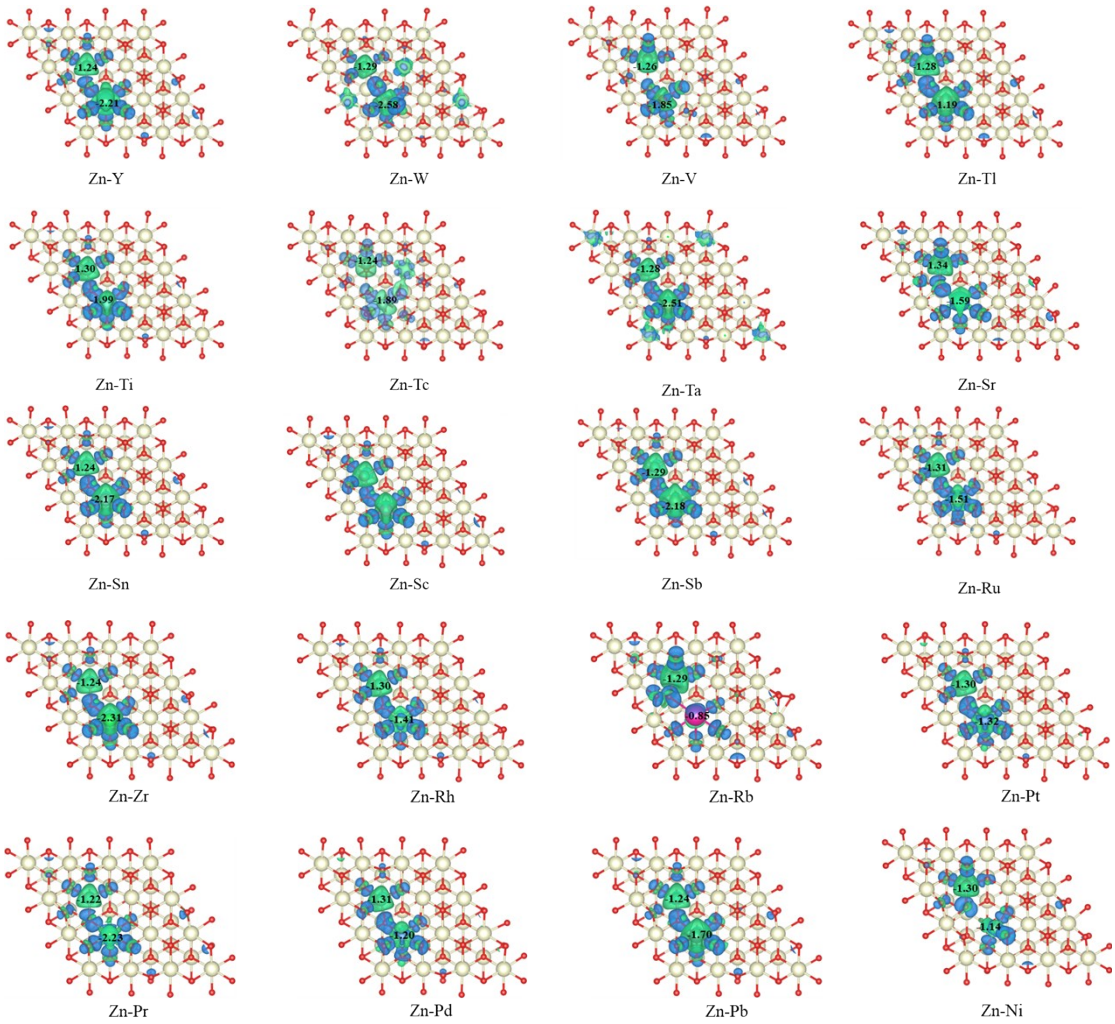

Fig. S3 DFT calculated the charge-density difference of Zn and other metal atoms co-substituted CeO_2 (111). (Other metal ions are Y, W, V, Tl, Ti, Tc, Ta, Sr, Sn, Sc, Sb, Ru, Zr, Rh, Rb, Pt, Pr, Pd, Pb and Ni.)

Table S2. Adsorption sites and adsorption energies (E_{ads}) of CH_4 in chemical looping dry reforming of methane on the surface of pristine CeO_2 (111) as well as on the surface of Zn and Nd co-substituted CeO_2 (111).

pristine CeO_2 (111)							
Adsorption sites	Ce-Top_1	Ce-Top_2	O-Top	Oxygen Vacancy	O-O-Bridge	Ce-O-Bridge	Hollow
E_{ads}/eV	-0.71	-0.53	-0.20	-0.83	-0.14	-0.15	-0.19
Zn and Nd co-substituted CeO_2 (111)							
Adsorption sites	Ce-Top	Zn-Top	Nd-Top	O-Top_1	O-Top_2	O-Top_3	O-Top_4
E_{ads}/eV	-0.28	-0.27	0.65	0.82	-0.16	0.98	0.77
Adsorption sites	Oxygen Vacancy	O-O-$Bridge_1$	O-O-$Bridge_2$	Ce-O-$Bridge_1$	Ce-O-$Bridge_2$	$Hollow_1$	$Hollow_2$
E_{ads}/eV	0.44	-0.20	0.95	-0.21	-0.18	-0.39	-0.29

Table S3. Adsorption sites and adsorption energies (E_{ads}) of CH_3 in chemical looping dry reforming of methane on the surface of pristine CeO_2 (111) as well as on the surface of Zn and Nd co-substituted CeO_2 (111).

pristine CeO_2 (111)							
Adsorption sites	Ce-Top_1	Ce-Top_2	O-Top	Oxygen Vacancy	O-O-Bridge	Ce-O-Bridge	Hollow
E_{ads}/eV	-1.88	-1.88	-2.59	-1.63	-0.59	-0.79	-1.88
Zn and Nd co-substituted CeO_2 (111)							
Adsorption sites	Ce-Top	Zn-Top	Nd-Top	O-Top_1	O-Top_2	O-Top_3	O-Top_4
E_{ads}/eV	-0.42	-4.22	0.48	-3.60	-3.69	-3.75	-4.26
Adsorption sites	Oxygen Vacancy	O-O-$Bridge_1$	O-O-$Bridge_2$	Ce-O-$Bridge_1$	Ce-O-$Bridge_2$	$Hollow_1$	$Hollow_2$
E_{ads}/eV	0.35	-3.71	-4.31	-2.61	-3.71	0.57	-0.56

Table S4. Adsorption sites and adsorption energies (E_{ads}) of CH_2 in chemical looping dry reforming of methane on the surface of pristine CeO_2 (111) as well as on the surface of Zn and Nd co-substituted CeO_2 (111).

pristine CeO_2 (111)							
Adsorption sites	Ce-Top$_1$	Ce-Top$_2$	O-Top	Oxygen Vacancy	O-O-Bridge	Ce-O-Bridge	Hollow
E_{ads}/eV	-2.54	-2.54	-3.81	-2.51	-2.54	-3.90	-2.54
Zn and Nd co-substituted CeO_2 (111)							
Adsorption sites	Ce-Top	Zn-Top	Nd-Top	O-Top$_1$	O-Top$_2$	O-Top$_3$	O-Top$_4$
E_{ads}/eV	-3.76	-4.81	-4.73	-3.62	-3.82	-3.64	-5.65
Adsorption sites	Oxygen Vacancy	O-O-Bridge$_1$	O-O-Bridge$_2$	Ce-O-Bridge$_1$	Ce-O-Bridge$_2$	Hollow$_1$	Hollow$_2$
E_{ads}/eV	-3.73	-4.82	-4.79	-3.76	-3.75	-3.77	-4.79

Table S5. Adsorption sites and adsorption energies (E_{ads}) of CH in chemical looping dry reforming of methane on the surface of pristine CeO_2 (111) as well as on the surface of Zn and Nd co-substituted CeO_2 (111).

pristine CeO_2 (111)							
Adsorption sites	Ce-Top_1	Ce-Top_2	O-Top	Oxygen Vacancy	O-O-Bridge	Ce-O-Bridge	Hollow
E_{ads}/eV	-3.34	-3.34	-5.16	-3.34	-3.34	-5.13	-3.34
Zn and Nd co-substituted CeO_2 (111)							
Adsorption sites	Ce-Top	Zn-Top	Nd-Top	O-Top_1	O-Top_2	O-Top_3	O-Top_4
E_{ads}/eV	-5.21	-7.21	-5.11	-5.04	-5.93	-5.97	-6.21
Adsorption sites	Oxygen Vacancy	O-O-$Bridge_1$	O-O-$Bridge_2$	Ce-O-$Bridge_1$	Ce-O-$Bridge_2$	$Hollow_1$	$Hollow_2$
E_{ads}/eV	-6.04	-5.20	-6.77	-5.04	-5.22	-5.99	-5.22

Table S6. Adsorption sites and adsorption energies (E_{ads}) of C in chemical looping dry reforming of methane on the surface of pristine CeO_2 (111) as well as on the surface of Zn and Nd co-substituted CeO_2 (111).

pristine CeO_2 (111)							
Adsorption sites	Ce-Top_1	Ce-Top_2	O-Top	Oxygen Vacancy	O-O-Bridge	Ce-O-Bridge	Hollow
E_{ads}/eV	-2.92	-2.92	-6.50	-2.92	-6.50	-6.58	-2.91
Zn and Nd co-substituted CeO_2 (111)							
Adsorption sites	Ce-Top	Zn-Top	Nd-Top	O-Top_1	O-Top_2	O-Top_3	O-Top_4
E_{ads}/eV	-4.90	-8.24	-6.68	-7.01	-7.47	-7.29	-8.48
Adsorption sites	Oxygen Vacancy	O-O-$Bridge_1$	O-O-$Bridge_2$	Ce-O-$Bridge_1$	Ce-O-$Bridge_2$	$Hollow_1$	$Hollow_2$
E_{ads}/eV	-7.28	-7.46	-8.48	-7.35	-7.46	-8.24	-3.97

Table S7. Adsorption sites and adsorption energies (E_{ads}) of H in chemical looping dry reforming of methane on the surface of pristine CeO_2 (111) as well as on the surface of Zn and Nd co-substituted CeO_2 (111).

pristine CeO_2 (111)							
Adsorption sites	Ce-Top_1	Ce-Top_2	O-Top	Oxygen Vacancy	O-O-Bridge	Ce-O-Bridge	Hollow
E_{ads}/eV	-2.32	-2.32	-3.44	-2.13	-0.52	-3.75	-2.30
Zn and Nd co-substituted CeO_2 (111)							
Adsorption sites	Ce-Top	Zn-Top	Nd-Top	O-Top_1	O-Top_2	O-Top_3	O-Top_4
E_{ads}/eV	0.84	-5.13	-0.17	-4.58	-4.72	-4.76	-5.12
Adsorption sites	Oxygen Vacancy	O-O-$Bridge_1$	O-O-$Bridge_2$	Ce-O-$Bridge_1$	Ce-O-$Bridge_2$	$Hollow_1$	$Hollow_2$
E_{ads}/eV	-4.25	0.79	-5.20	-4.58	-4.73	-3.39	0.29

Table S8. Adsorption sites and adsorption energies (E_{ads}) of O in chemical looping dry reforming of methane on the surface of pristine CeO_2 (111) as well as on the surface of Zn and Nd co-substituted CeO_2 (111).

pristine CeO_2 (111)					
Adsorption sites	Ce-Top_1	Ce-Top_2	Oxygen Vacancy	Ce-O-Bridge	Hollow
E_{ads}/eV	-6.26	-6.25	-6.26	-3.53	-6.26

Zn and Nd co-substituted CeO_2 (111)							
Adsorption sites	Ce-Top	Zn-Top	Nd-Top	O-Top_1	O-Top_2	O-Top_3	O-Top_4
E_{ads}/eV	-2.67	-3.16	-1.35	-3.25	-2.62	-3.38	-3.30
Adsorption sites	Oxygen Vacancy	O-O-$Bridge_1$	O-O-$Bridge_2$	Ce-O-$Bridge_1$	Ce-O-$Bridge_2$	$Hollow_1$	$Hollow_2$
E_{ads}/eV	-1.29	-2.47	-0.46	-2.51	-3.62	-0.70	-1.47

Table S9. Adsorption sites and adsorption energies (E_{ads}) of CO in chemical looping dry reforming of methane on the surface of pristine CeO_2 (111) as well as on the surface of Zn and Nd co-substituted CeO_2 (111).

pristine CeO_2 (111)							
Adsorption sites	Ce-Top$_1$	Ce-Top$_2$	O-Top	Oxygen Vacancy	O-O-Bridge	Ce-O-Bridge	Hollow
E_{ads}/eV	-0.81	-0.65	-0.45	-0.77	-0.30	-0.48	-0.31
Zn and Nd co-substituted CeO_2 (111)							
Adsorption sites	Ce-Top	Zn-Top	Nd-Top	O-Top$_1$	O-Top$_2$	O-Top$_3$	O-Top$_4$
E_{ads}/eV	0.53	-0.59	-0.38	0.43	-0.17	-0.17	-3.67
Adsorption sites	Oxygen Vacancy	O-O-Bridge$_1$	O-O-Bridge$_2$	Ce-O-Bridge$_1$	Ce-O-Bridge$_2$	Hollow$_1$	Hollow$_2$
E_{ads}/eV	-0.46	-0.39	-0.33	0.44	-0.41	-0.35	0.44

Table S10. Adsorption sites and adsorption energies (E_{ads}) of CO_2 in chemical looping dry reforming of methane on the surface of pristine CeO_2 (111) as well as on the surface of Zn and Nd co-substituted CeO_2 (111).

pristine CeO_2 (111)							
Adsorption sites	Ce-Top_1	Ce-Top_2	O-Top	Oxygen Vacancy	O-O-Bridge	Ce-O-Bridge	Hollow
E_{ads}/eV	-0.86	-0.81	-0.68	-0.23	-0.79	-0.62	-0.91
Zn and Nd co-substituted CeO_2 (111)							
Adsorption sites	Ce-Top	Zn-Top	Nd-Top	O-Top_1	O-Top_2	O-Top_3	O-Top_4
E_{ads}/eV	0.60	0.44	-0.43	0.69	-0.44	-0.28	-0.26
Adsorption sites	Oxygen Vacancy	O-O-$Bridge_1$	O-O-$Bridge_2$	Ce-O-$Bridge_1$	Ce-O-$Bridge_2$	$Hollow_1$	$Hollow_2$
E_{ads}/eV	0.38	0.71	-0.59	0.51	0.40	0.35	0.41

Table S11. Adsorption sites and adsorption energies (E_{ads}) of H_2 in chemical looping dry reforming of methane on the surface of pristine CeO_2 (111) as well as on the surface of Zn and Nd co-substituted CeO_2 (111).

pristine CeO_2 (111)							
Adsorption sites	Ce-Top_1	Ce-Top_2	O-Top	Oxygen Vacancy	O-O-Bridge	Ce-O-Bridge	Hollow
E_{ads}/eV	-0.51	-0.58	-0.04	-0.04	-0.50	-0.54	-0.14
Zn and Nd co-substituted CeO_2 (111)							
Adsorption sites	Ce-Top	Zn-Top	Nd-Top	O-Top_1	O-Top_2	O-Top_3	O-Top_4
E_{ads}/eV	-0.20	-0.15	0.72	0.87	0.80	0.80	0.76
Adsorption sites	Oxygen Vacancy	O-O-$Bridge_1$	O-O-$Bridge_2$	Ce-O-$Bridge_1$	Ce-O-$Bridge_2$	$Hollow_1$	$Hollow_2$
E_{ads}/eV	0.68	0.78	0.74	0.78	0.77	0.71	0.77

Table S12. Adsorption sites and adsorption energies (E_{ads}) of CH_3O in chemical looping dry reforming of methane on the surface of pristine CeO_2 (111) as well as on the surface of Zn and Nd co-substituted CeO_2 (111).

pristine CeO_2 (111)							
Adsorption sites	Ce-Top$_1$	Ce-Top$_2$	O-Top	Oxygen Vacancy	O-O-Bridge	Ce-O-Bridge	Hollow
E_{ads}/eV	-4.04	-4.05	-4.04	-4.06	-4.06	-4.06	-4.05
Zn and Nd co-substituted CeO_2 (111)							
Adsorption sites	Ce-Top	Zn-Top	Nd-Top	O-Top$_1$	O-Top$_2$	O-Top$_3$	O-Top$_4$
E_{ads}/eV	-1.97	-1.02	-1.91	-0.89	-0.66	-1.98	-1.44
Adsorption sites	Oxygen Vacancy	O-O-Bridge$_1$	O-O-Bridge$_2$	Ce-O-Bridge$_1$	Ce-O-Bridge$_2$	Hollow$_1$	Hollow$_2$
E_{ads}/eV	-1.03	0.95	-1.37	-0.61	-1.97	-1.96	-1.83

Table S13. Adsorption sites and adsorption energies (E_{ads}) of CH_2O in chemical looping dry reforming of methane on the surface of pristine CeO_2 (111) as well as on the surface of Zn and Nd co-substituted CeO_2 (111).

pristine CeO_2 (111)							
Adsorption sites	Ce-Top$_1$	Ce-Top$_2$	O-Top	Oxygen Vacancy	O-O-Bridge	Ce-O-Bridge	Hollow
E_{ads}/eV	-1.34	-1.34	-1.87	-1.37	-1.34	-2.03	-2.02

Zn and Nd co-substituted CeO_2 (111)							
Adsorption sites	Ce-Top	Zn-Top	Nd-Top	O-Top$_1$	O-Top$_2$	O-Top$_3$	O-Top$_4$
E_{ads}/eV	-0.01	-0.22	-1.17	0.01	-0.02	-0.28	-5.15
Adsorption sites	Oxygen Vacancy	O-O-Bridge$_1$	O-O-Bridge$_2$	Ce-O-Bridge$_1$	Ce-O-Bridge$_2$	Hollow$_1$	Hollow$_2$
E_{ads}/eV	0.20	-0.19	-1.11	-0.29	-0.11	-0.20	-0.05

Table S14. Adsorption sites and adsorption energies (E_{ads}) of CHO in chemical looping dry reforming of methane on the surface of pristine CeO_2 (111) as well as on the surface of Zn and Nd co-substituted CeO_2 (111).

pristine CeO_2 (111)							
Adsorption sites	Ce-Top$_1$	Ce-Top$_2$	O-Top	Oxygen Vacancy	O-O-Bridge	Ce-O-Bridge	Hollow
E_{ads}/eV	-1.72	-0.90	-4.10	-1.71	-0.95	-3.99	-1.70
Zn and Nd co-substituted CeO_2 (111)							
Adsorption sites	Ce-Top	Zn-Top	Nd-Top	O-Top$_1$	O-Top$_2$	O-Top$_3$	O-Top$_4$
E_{ads}/eV	-4.75	-4.62	-2.94	-3.81	-4.92	-3.91	-4.62
Adsorption sites	Oxygen Vacancy	O-O-Bridge$_1$	O-O-Bridge$_2$	Ce-O-Bridge$_1$	Ce-O-Bridge$_2$	Hollow$_1$	Hollow$_2$
E_{ads}/eV	5.99	-4.97	-5.57	-3.80	-4.00	-4.23	-2.84

Table S15. The zero-point energies (ZPE), the product of the vibrational entropy and temperature (TS), the optimized structural energies (E_{SCF}), the Gibbs free energy correction values ($G_{correction}$), the Gibbs free energies (G) for gas-phase molecules have been obtained from the frequency calculations at 1073.15K.

intermediates	Gas molecule				
	ZPE	TS	E_{SCF}	$G_{correction}$	G
CH_4	1.19, 1.19[1]	2.81	-24.03, -24.03[1]	-1.07	-25.10
CO	0.13, 0.13[1]	2.70	-14.79, -14.79[1]	-2.23	-17.02
O_2	0.10, 0.10[1]	2.78	-9.86, -9.86[1]	-2.34	-12.19
H_2	0.27, 0.27[1]	1.86	-6.76, -6.76[1]	-1.27	-8.03
CO_2	0.31, 0.31[1]	3.20	-22.99, -22.99[1]	-2.40	-25.40

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Table S16. The zero-point energies (ZPE), the product of the vibrational entropy and temperature (TS), the optimized structural energies (E_{SCF}), the Gibbs free energy correction values ($G_{correction}$), the Gibbs free energies (G) for gas-phase molecules adsorbed on the surface of pristine CeO_2 (111) have been obtained from the frequency calculations at 1073.15K.

intermediates	pristine CeO_2 (111)				
	ZPE	TS	E_{SCF}	$G_{correction}$	G
CH_4	1.23	1.83	-677.57	0.09	-677.48
CH_3	1.00	1.04	-673.49	0.39	-673.11
CH_2	0.67	0.97	-668.71	0.13	-668.58
CH	0.38	0.43	-663.97	0.17	-663.81
C	0.11	0.55	-660.61	-0.24	-660.84
H	0.29	0.27	-657.58	0.15	-657.42
O	0.06	0.51	-660.56	-0.23	-660.79
CO	0.16	1.07	-668.32	-0.55	-668.87
CO_2	0.32	1.50	-676.60	-0.66	-677.26
H_2	0.33	1.16	-660.05	-0.43	-660.48
CH_3O	1.07	1.95	-681.24	-0.14	-681.38
CH_2O	0.83	1.25	-676.88	0.15	-676.73
CHO	0.55	1.11	-673.90	-0.10	-674.00

Table S17. The zero-point energies (ZPE), the product of the vibrational entropy and temperature (TS), the optimized structural energies (E_{SCF}), the Gibbs free energy correction values ($G_{correction}$), the Gibbs free energies (G) for gas-phase molecules adsorbed on the surface of Zn and Nd co-substituted CeO_2 (111) have been obtained from the frequency calculations at 1073.15K.

intermediates	Zn and Nd co-substituted CeO_2 (111)				
	ZPE	TS	E_{SCF}	$G_{correction}$	G
CH_4	1.21	1.34	-667.58	0.40	-667.18
CH_3	1.01	1.25	-665.66	0.27	-665.39
CH_2	0.69	1.07	-660.92	0.04	-660.88
CH	0.38	0.70	-656.04	-0.01	-656.06
C	0.10	0.36	-652.96	-0.15	-653.11
H	0.28	0.32	-649.40	0.10	-649.30
O	0.03	0.42	-647.92	-0.23	-648.15
CO	0.26	0.34	-661.33	0.11	-661.22
CO_2	0.33	1.79	-666.74	-0.86	-667.60
H_2	0.33	1.16	-650.12	-0.43	-650.55
CH_3O	1.11	1.44	-669.62	0.29	-669.33
CH_2O	0.75	1.49	-666.48	-0.17	-666.65
CHO	0.55	1.03	-665.83	-0.01	-665.84