Supporting information

Efficient methanol steam reforming over ZnCeZrOx: the unique role of cerium

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Table S1. Physicochemical parameters of the metal oxide catalysts.

Catalysts	S_{BET} (m^2/g)	Zn/Ce/Zr (mol/mol) by ICP	Zn/Ce/Zr (mol/mol) by XPS	Zn (at%) by XPS	Ce (at%) by XPS	Zr (at%) by XPS
ZrO_2 [1]	43	-	-	-	-	-
CeO_2	65	-	-	-	-	-
$Ce_1Zr_9O_x$	55	1.0:10.7 (Ce/Zr)	1.0:16.6 (Ce/Zr)	-	5.7	94.3
$Zn_1Ce_{10}O_x$	40	1.0:11.2	-	-	-	-
$Zn_1Ce_{0.5}Zr_9O_x$	55	1.0:0.5:10.3	-	-	-	-
$Zn_1Ce_1Zr_9O_x$	50	1.0:1.0:10.5	1.4:1.0:15.7	7.7	5.5	86.7
$Zn_1Ce_1Zr_9O_x$ [a]	43	-	1.5:1.0:4.3	22.1	14.7	63.2
$Zn_1Ce_2Zr_9O_x$	62	1.0:1.9:9.2	-	-	-	-
$Zn_1Zr_{10}O_x$	34	1.0:8.5 (Zn/Zr)	1.0:2.6 (Zn/Zr)	27.4	-	72.6

[a] data in the parenthesis refers to the spent catalysts.

Table S2. XPS results of fresh and spent mixed metal oxides catalysts.

Catalysts	Zn 2p (eV)	Zr 3d (eV)	Ce 3d (eV)					Ce^{3+} (%) [a]	O 1s (eV)		Ov (%) [b]
			Ce^{3+}		Ce^{4+}				Ov	O_L	
$Zn_1Zr_{10}O_x$	1021.7	182.1	-	-	-	-	-	-	531.2	529.9	39.6
$Zn_1Ce_1Zr_9O_x$	1021.1	181.6	881.4	884.7	881.6	888.1	897.9	33.6	530.4	529.0	53.2
Spent $Zn_1Ce_1Zr_9O_x$	1021.5	182.2	881.1	885.1	881.9	887.6	897.8	47.4	531.4	529.7	31.9

[a] Ce^{3+} (%) = Ce^{3+} ×100 / (Ce^{3+} + Ce^{4+}); [b] Ov (%) = Ov ×100 / (Ov+O_L).

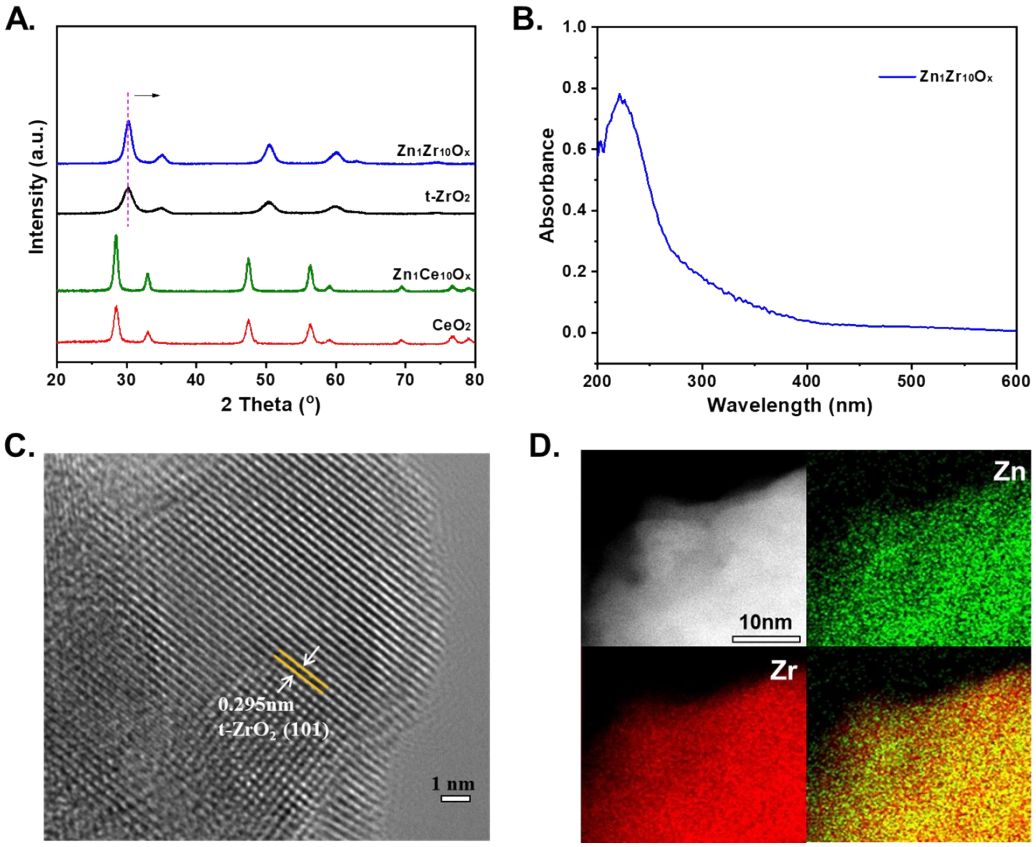

Figure S1. (A) XRD patterns of $Zn_1Ce_{10}O_x$, CeO_2, $Zn_1Zr_{10}O_x$ and ZrO_2; (B) UV-vis diffuse reflectance spectra of $Zn_1Zr_{10}O_x$; (C) HRTEM image and (D) High-angle annular dark field imaging in scanning transmission electron microscopy (HAADF-

STEM) micrographs and the corresponding Zn and Zr EDX mappings of $Zn_1Zr_{10}O_x$.

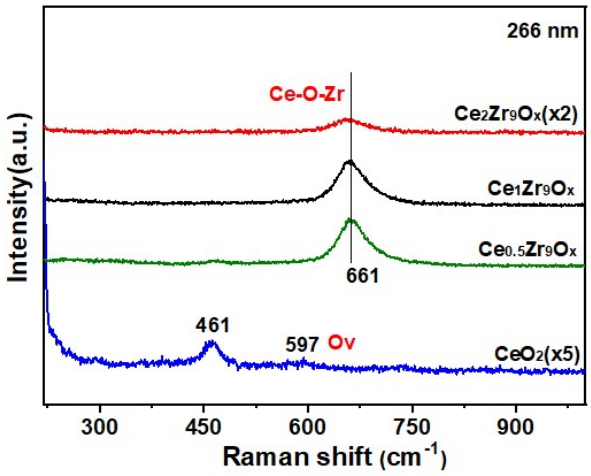

Figure S2. Raman spectra of $Ce_yZr_9O_x$ (y= 0.5, 1, 2) and CeO_2.

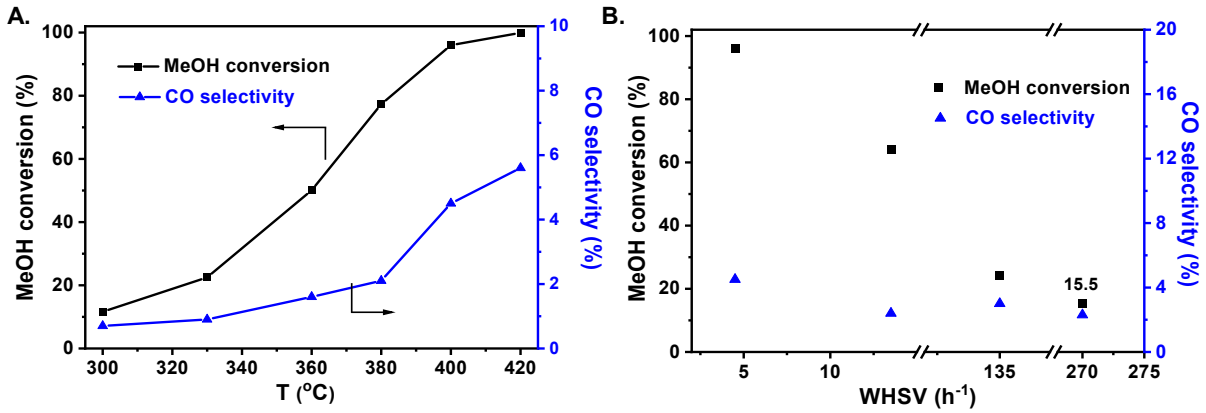

Figure S3. Methanol conversion and CO selectivity over $Zn_1Ce_1Zr_9O_x$ for the influence of (A) reaction temperature and (B) WHSV. Reaction conditions: 0.1 MPa, H_2O/MeOH = 1.0.

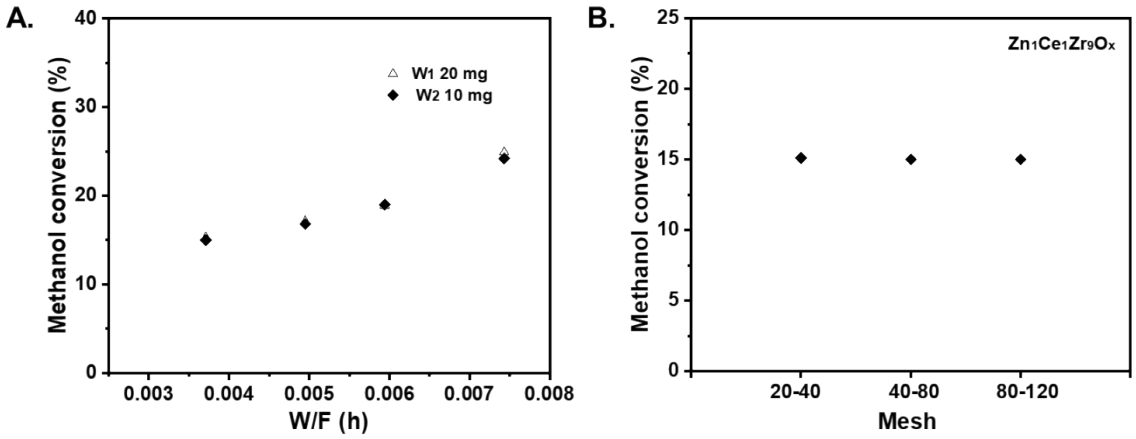

Figure S4. Diffusion effects over $Zn_1Ce_1Zr_9O_x$. (A) The relation of methanol conversion with residence time by using different mass catalysts (Reaction conditions: 400 °C; H_2O/MeOH = 1.0); (B) The relation of methanol conversion with catalysts particle size (Reaction conditions: 400 °C; H_2O/MeOH = 1.0; N_2 30 mL/min; 10 mg catalysts).

To eliminate the external diffusion, the methanol conversion was measured using different amounts of catalysts with the same contact time by adjusting the flow rate. The methanol conversion tends to a similar value with the same contact time as the flow rate increases, implying the external diffusion is eliminated. As for internal diffusion, the methanol conversion does not change with the particle sizes of the catalysts, indicating that the influence of the internal diffusion can be neglected.[2, 3]

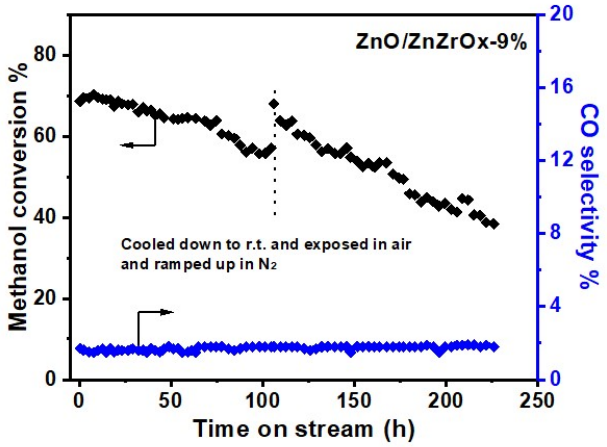

Figure S5. Stability test of ZnO/ZnZrOx-9% for SRM (reaction conditions: 400 °C, H_2O/MeOH 1.0, WHSV 9.0 h^{-1}).

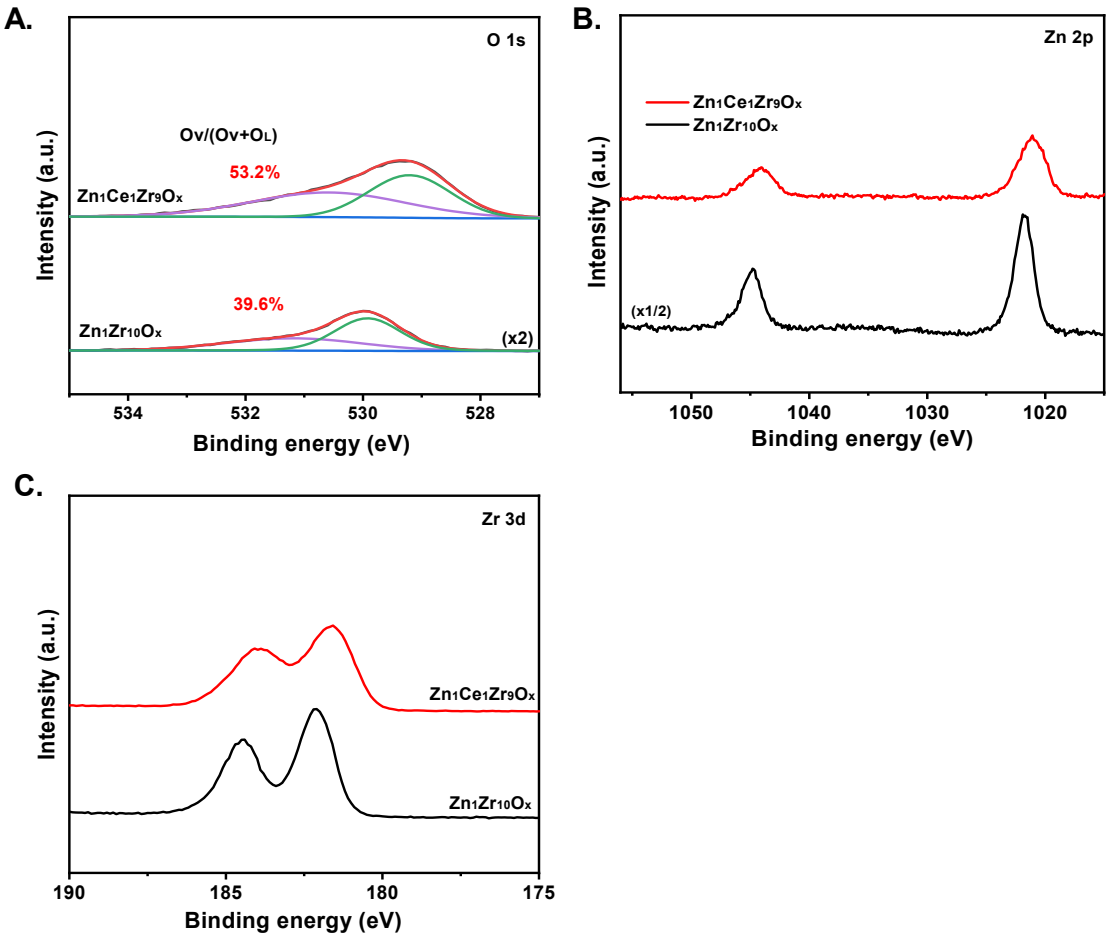

Figure S6. (A) O 1s, (B) Zn 2p, (C) Zr 3d XPS spectra of $Zn_1Ce_1Zr_9O_x$ and $Zn_1Zr_{10}O_x$.

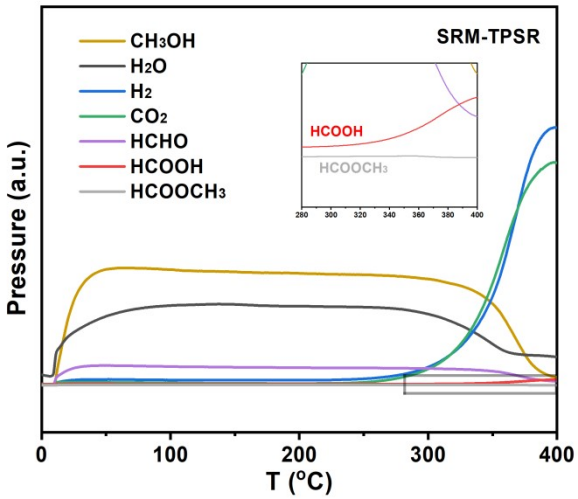

Figure S7. SRM-TPSR over $Zn_1Ce_1Zr_9O_x$. The sample is reduced in hydrogen for 1 h at 400 °C. In SRM-TPSR, the catalyst is exposed to a mixture of H_2O/MeOH of 1.0 at 20 mL/min Ar flow and the temperature is increased linearly at 5 °C/min.

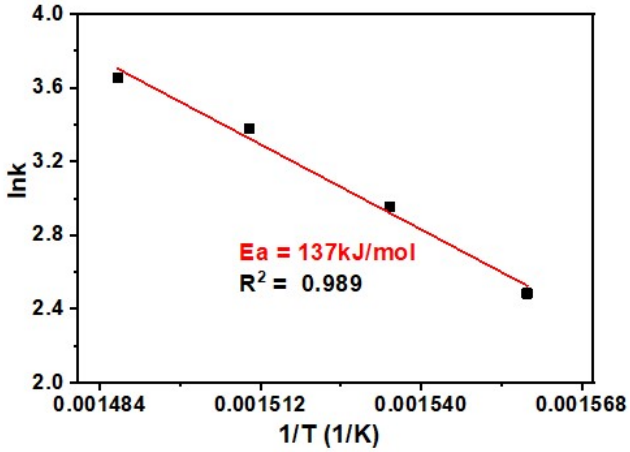

Figure S8. Arrhenius-type plots for SRM on $Zn_1Ce_1Zr_9O_x$.

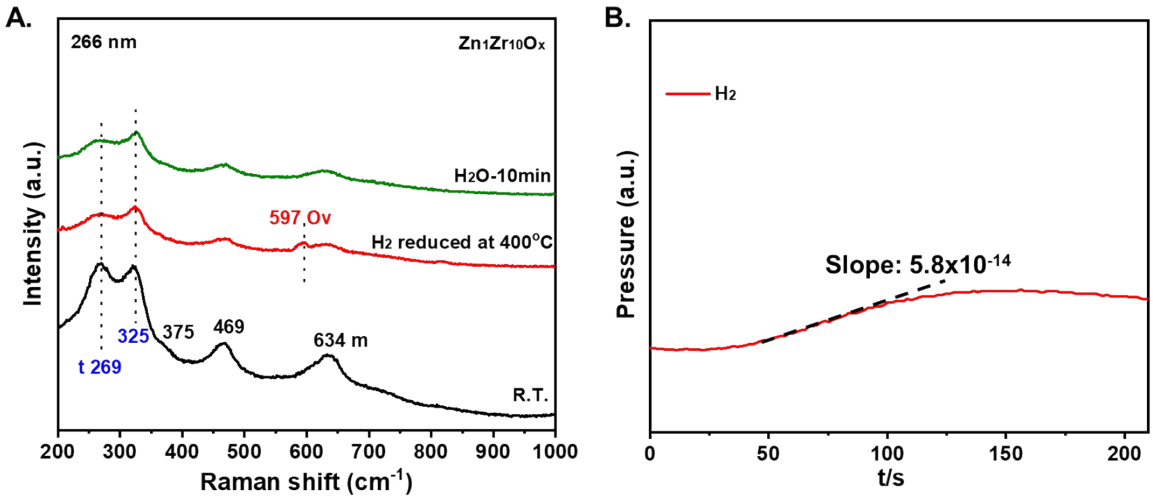

Figure S9. (A) *In situ* Raman spectra over $Zn_1Zr_{10}O_x$ (266 nm laser), the sample is reduced in hydrogen at 400 °C and then exposed to water, (B) Corresponding MS signal.

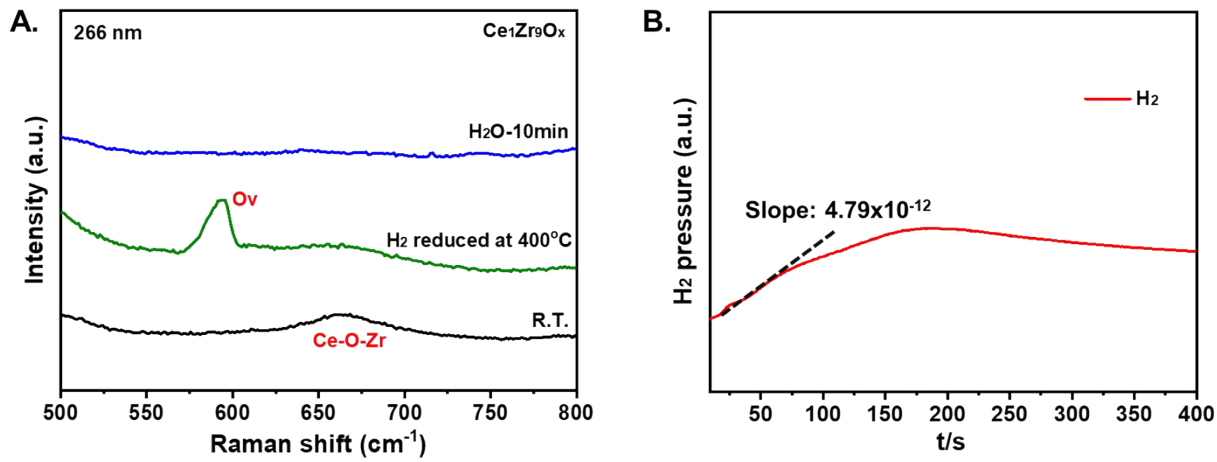

Figure S10. (A) *In situ* Raman spectra over $Ce_1Zr_9O_x$ (266 nm laser), the $Ce_1Zr_9O_x$ is reduced in hydrogen at 400 °C and then exposed to water, (B) Corresponding MS signal.

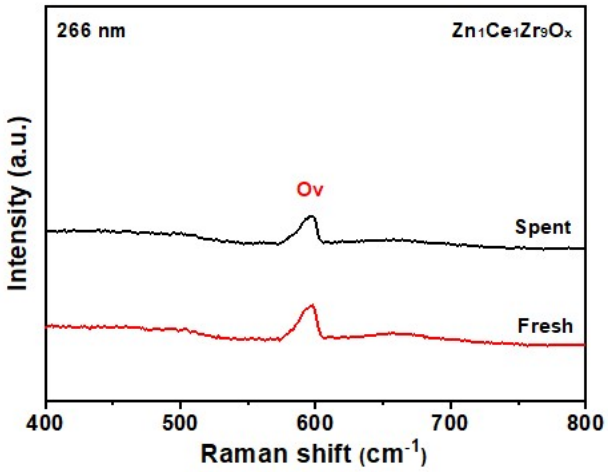

Figure S11. *In situ* Raman spectra (266 nm laser) of fresh and spent $Zn_1Ce_1Zr_9O_x$ reduced in hydrogen for 1 h at 400 °C.

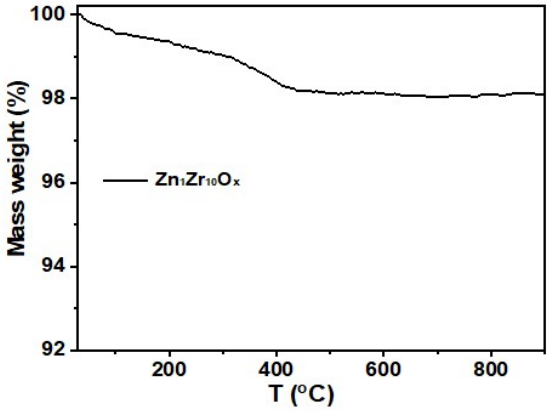

Figure S12. TG curve spent $Zn_1Zr_{10}O_x$.

References

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