Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

Synergetic effect of Cu active sites and oxygen vacancies in Cu/CeO_2-ZrO_2 for water-gas shift reaction

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Table S1 CO conversion and turnover frequency (TOF) data of different $20CuCe_yZr_{1-y}$[a]

Catalyst	CO conversion (%)				TOF[a] (s^{-1})			
	240 ℃	260 ℃	280 ℃	300 ℃	240 ℃	260 ℃	280 ℃	300 ℃
20CuCe	2.2	3.9	5.9	8.2	0.0087	0.0155	0.0234	0.0325
$20CuCe_{0.8}Zr_{0.2}$	3.5	6.5	8.9	12.1	0.0069	0.0128	0.0175	0.0238
$20CuCe_{0.6}Zr_{0.4}$	4.8	7.5	11.3	14.9	0.0061	0.0095	0.0144	0.0189
$20CuCe_{0.4}Zr_{0.6}$	3.9	6.3	9.1	12.9	0.0055	0.0089	0.0128	0.0182
$20CuCe_{0.2}Zr_{0.8}$	1.6	2.5	4.1	5.9	0.0062	0.0096	0.0158	0.0227
20CuZr	0.1	0.3	0.5	0.7	0.0021	0.0047	0.0079	0.0113

[a] Reaction condition: H_2:CO:H_2O = 1:2:2 (molar ratio), P = 0.1 MPa, GHSV = 80000 h^{-1}.

Table S2 Raman analysis results for spent $20CuCe_yZr_{1-y}$

Catalyst	N (cm^{-3}) [a]
20CuCe	2.1×10^{21}
$20CuCe_{0.8}Zr_{0.2}$	3.9×10^{21}
$20CuCe_{0.6}Zr_{0.4}$	5.5×10^{21}
$20CuCe_{0.4}Zr_{0.6}$	4.2×10^{21}
$20CuCe_{0.2}Zr_{0.8}$	1.6×10^{21}
20CuZr	–

[a] Concentration of oxygen vacancies (N) is acquired by Raman analysis.

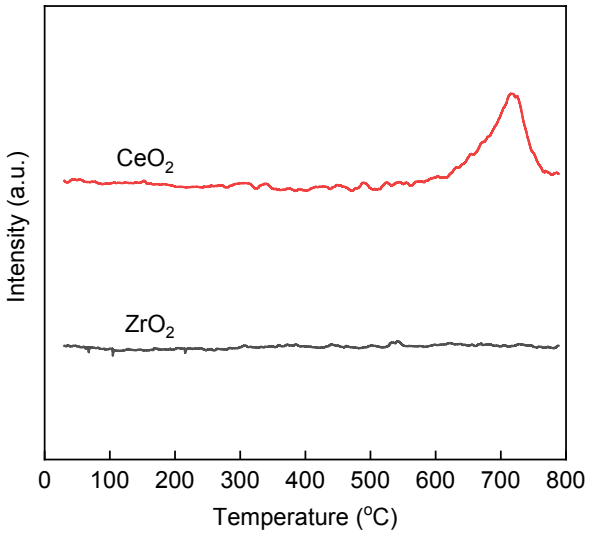

Fig. S1. H_2-TPR profiles of CeO_2 and ZrO_2.

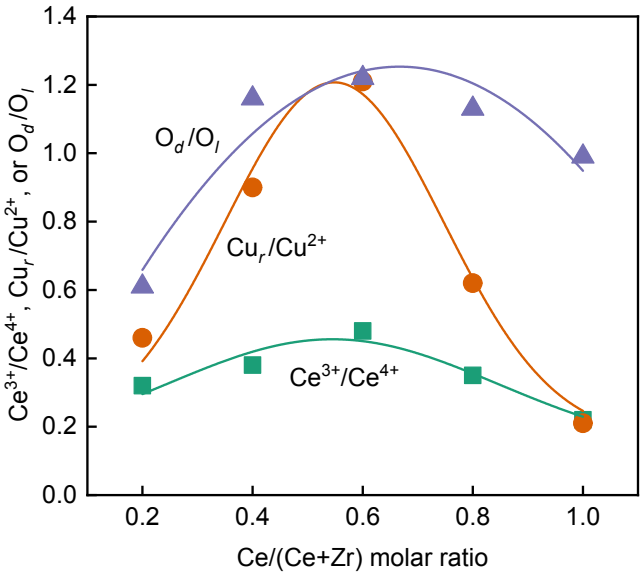

Fig. S2. Variation of Ce^{3+}/Ce^{4+}, Cu_r/Cu^{2+} and O_d/O_l ratios with Ce/(Ce+Zr) molar ratio for $20CuCe_yZr_{1-y}$ catalysts (symbols: experimental data; lines: fitted data by Gaussian function).

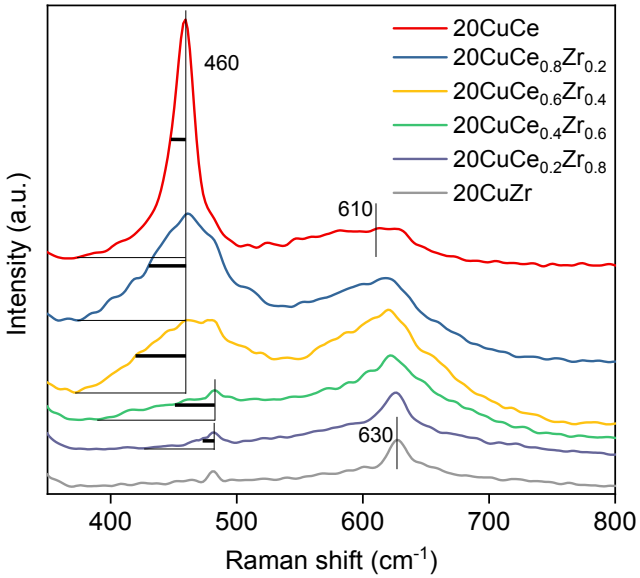

Fig. S3. Raman spectra of $20CuCe_yZr_{1-y}$ catalysts (HWHM is indicated by the thick solid black line).

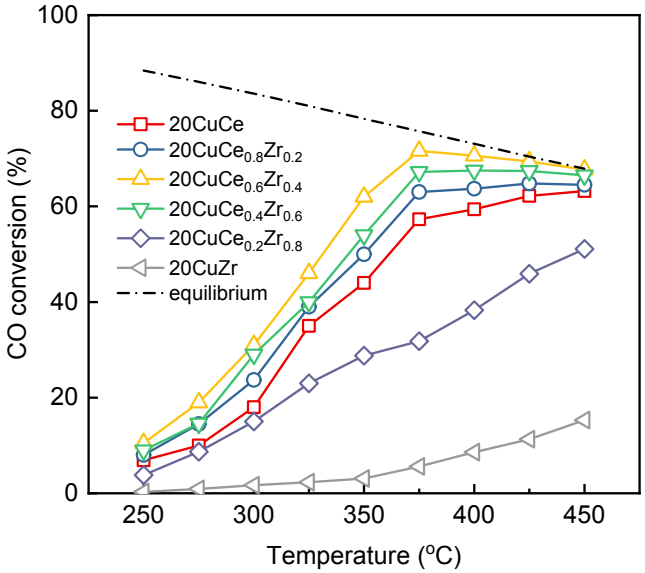

Fig. S4. Variation of CO conversion with temperature over $20CuCe_yZr_{1-y}$ catalysts. (reaction condition: H_2:CO:H_2O = 1:2:2 (molar ratio), P = 0.1 MPa, GHSV = 20000 h^{-1})

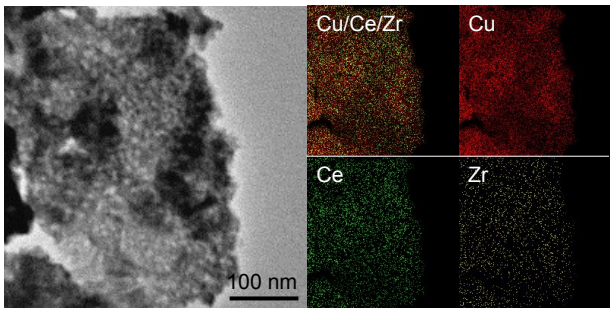

Fig. S5. HRTEM-EDS mappings of $50CuCe_{0.6}Zr_{0.4}$.

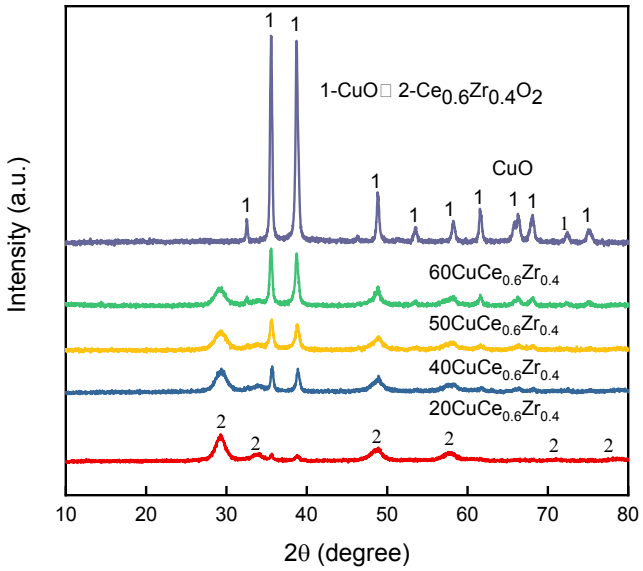

Fig. S6. XRD patterns of $xCuCe_{0.6}Zr_{0.4}$ catalysts with varying Cu loading.

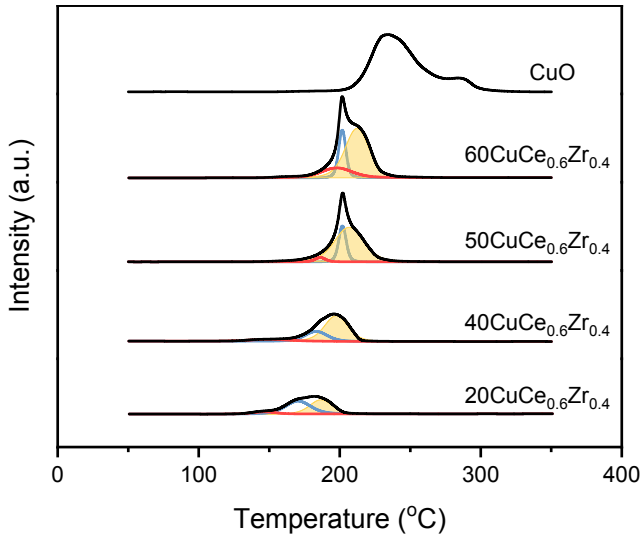

Fig. S7. H_2-TPR profiles of xCuCe$_{0.6}$Zr$_{0.4}$ catalysts with varying Cu loading.

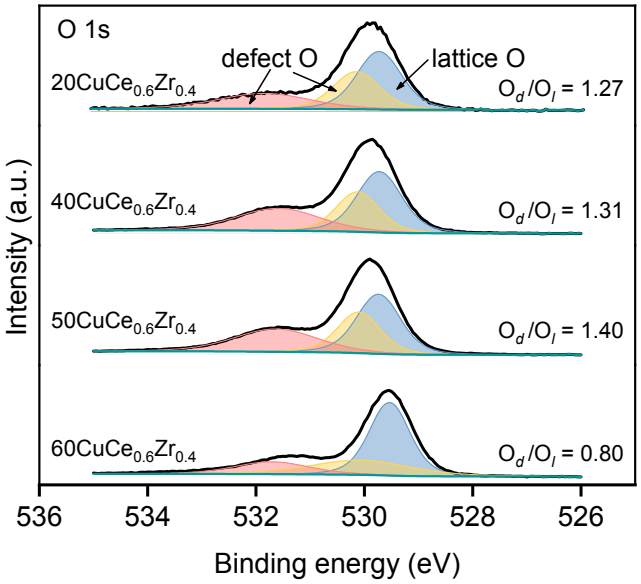

Fig. S8. XPS spectra of O 1s of xCuCe$_{0.6}$Zr$_{0.4}$ catalysts with varying Cu loading.

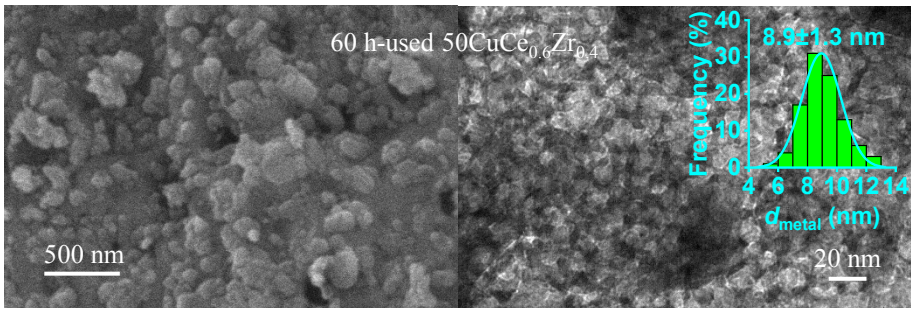

Fig. S9. FESEM (left) and HRTEM (right) images of 60 h-used 50CuCe$_{0.6}$Zr$_{0.4}$.

(reaction condition: H_2:CO:H_2O = 1:2:2 (molar ratio), T = 350 ºC, P = 0.1 MPa, GHSV = 20000 h^{-1})