Electronic Supplementary Material

Halide-free carbonylation of methanol with H-MOR supported $CuCeO_x$ catalysts

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Table S1. Textural properties of H-MOR and $CuCeO_x$/H-MOR catalyst.

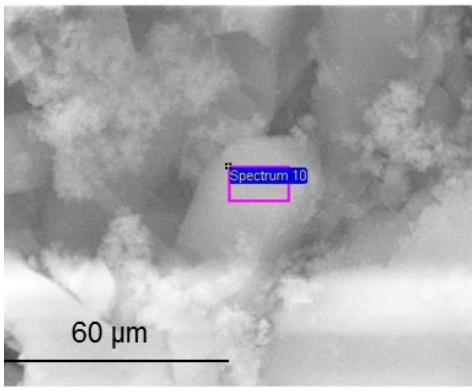
Catalyst	S_{BET} /$m^2\ g^{-1}$	$S_{micropore}$ /$m^2\ g^{-1}$	V_{pore} /mL g^{-1}	$V_{micropore}$ /mL g^{-1}	D_{pore} /nm
H-MOR	355	334	0.17	0.14	1.9
$CuCeO_x$/H-MOR	304	172	0.28	0.07	3.7

Table S2. The radius[1] of element Cu and Ce.

Element	Radius /nm	Element	Radius /nm
Cu	0.128	Ce	0.183
Cu^{2+}	0.073	Ce^{3+}	0.183

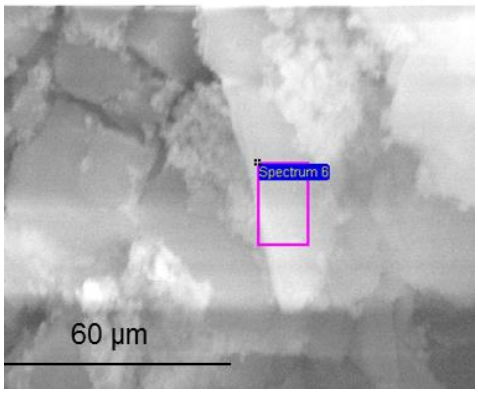
[1] Z. H. Li. Data manual of element properties [M]. Hebei People's publishing house, 1985.

Table S3. Element content in smooth region of $CuCeO_x$/H-MOR catalyst before calcination.



Element symbol	Atomic conc. /%
O	66.31
Si	28.06
Al	2.85
Cu	1.47
Ce	1.32

Table S4. Element content in smooth region of $CuCeO_x$/H-MOR catalyst after calcination at 500 °C for 4 h.



Element symbol	Atomic conc. /%
O	62.84
Si	31.34
Al	2.91
Cu	1.94
Ce	0.98

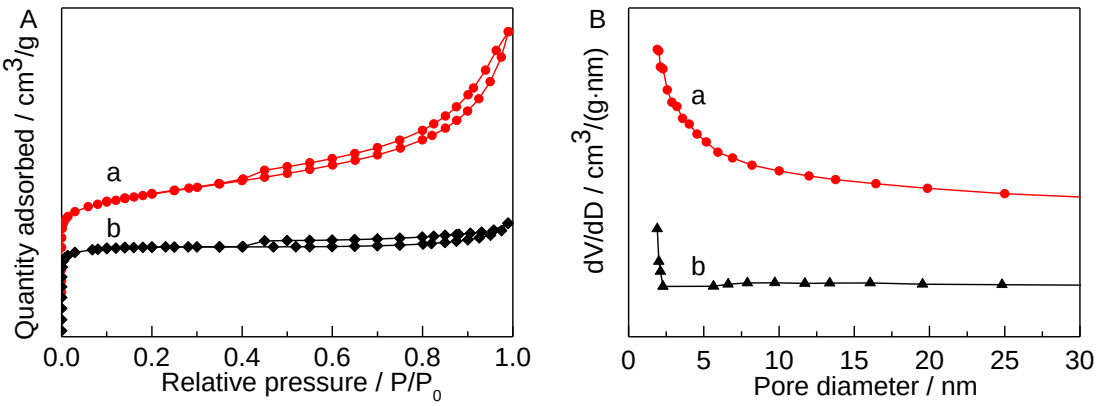


Fig. S1 (A) Ar adsorption−desorption isotherms and (B) pore-size distributions of (a) $CuCeO_x$/H-MOR and (b) H-MOR catalyst.

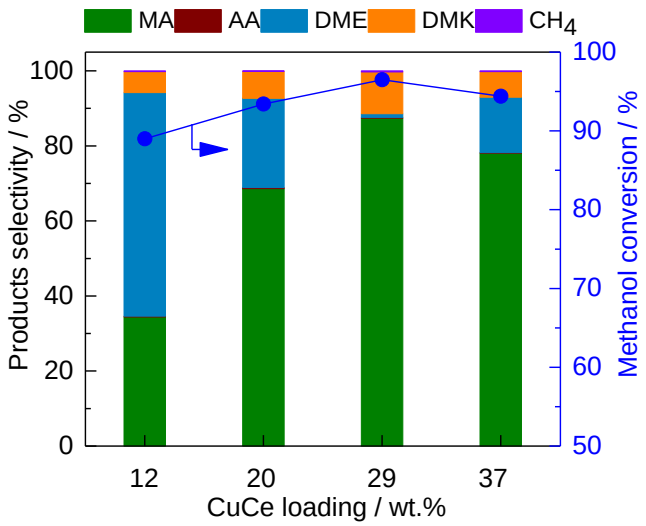


Fig. S2. Effect of the metal loadings on CuCe catalyst for methanol heterogeneous carbonylation reaction. Reaction conditions: T = 200 ℃, P_{CO} = 1.0 MPa, CH_3OH/CO = 2.15 mol%, F = 10 mL min^{-1}, time on stream = 3 h.

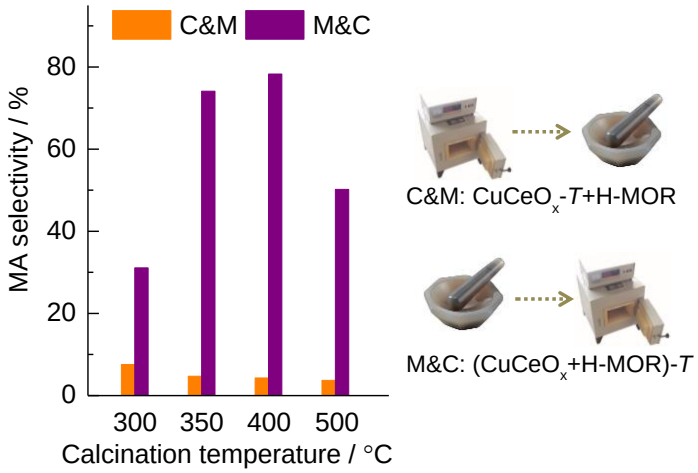


Fig. S3 MA selectivity of two comparative experiments at different calcination temperatures.

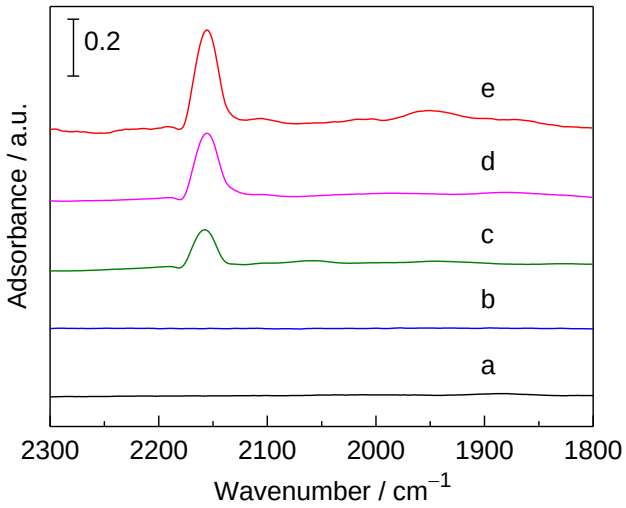


Fig. S4 FT-IR spectra of the chemisorbed CO on as-reduced catalyst after evacuation for 25 min (a) H-MOR, (b) $CuCeO_x$, (c) H-MOR+$CuCeO_x$, (d) Cu-H-MOR+$CuCeO_x$, and (e) $CuCeO_x$/H-MOR.

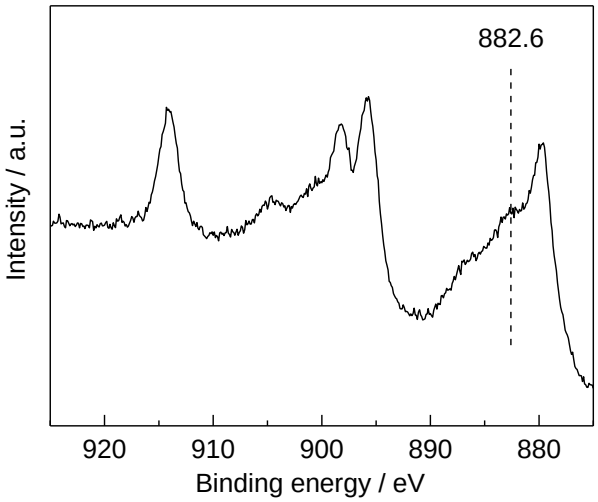


Fig. S5 Ce 3d XPS of in situ reduced $CuCeO_x$/H-MOR.

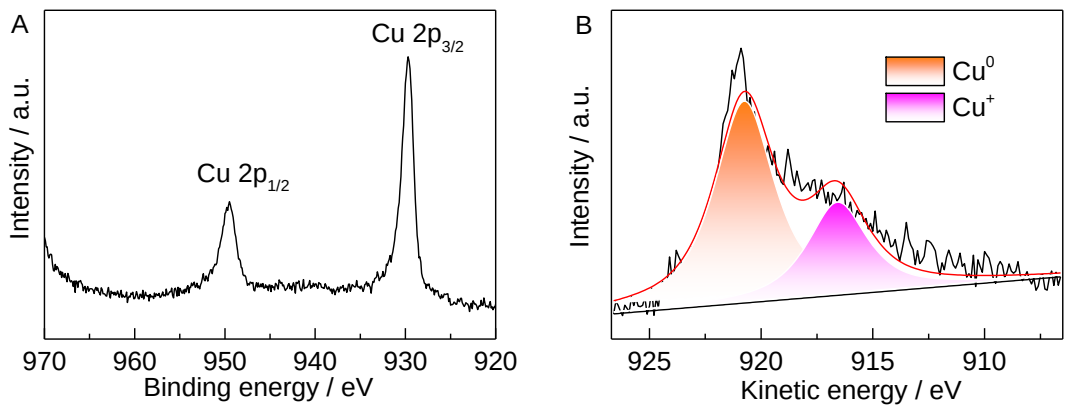


Fig. S6 (A) Cu 2p XPS and (B) Cu LMM AES of in situ reduced $CuCeO_x$/H-MOR.

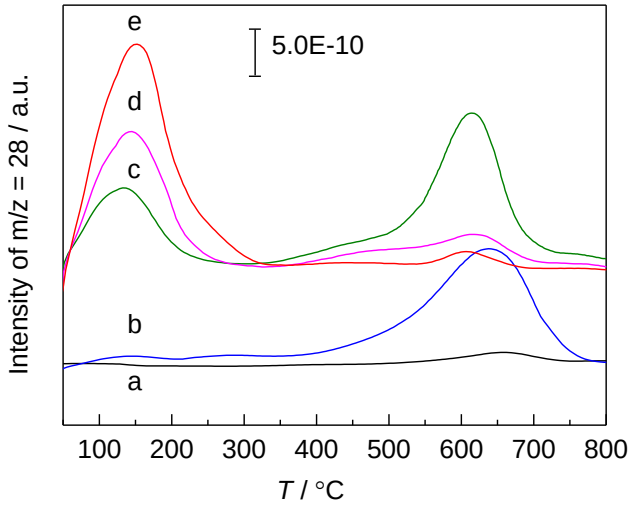


Fig. S7 CO–TPD profiles of different catalysts (a) H-MOR, (b) $CuCeO_x$, (c) H-MOR+$CuCeO_x$, (d) Cu-H-MOR+$CuCeO_x$, and (e) $CuCeO_x$/H-MOR.

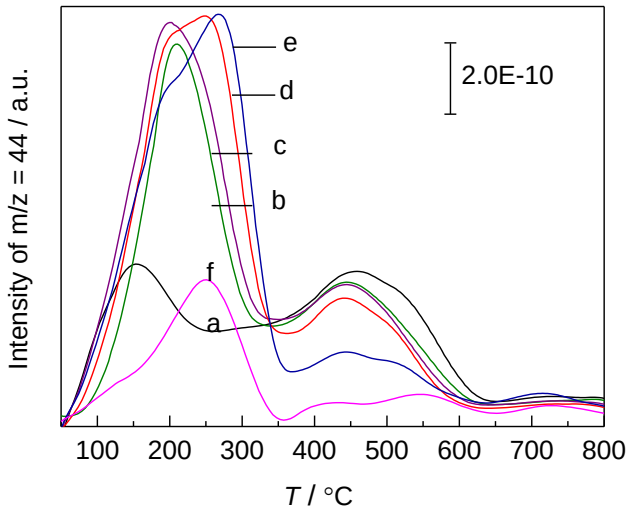


Fig. S8 CO_2 signal from CO–TPD profiles of $CuCeO_x$/H-MOR catalyst treated in air by different calcination temperatures: (a) 300 °C, (b) 350 °C, (c) 400 °C, (d) 500 °C, (e) 600 °C, and (f) 700 °C. Cu: 9.2 wt.%, Ce: 19.6 wt.%.

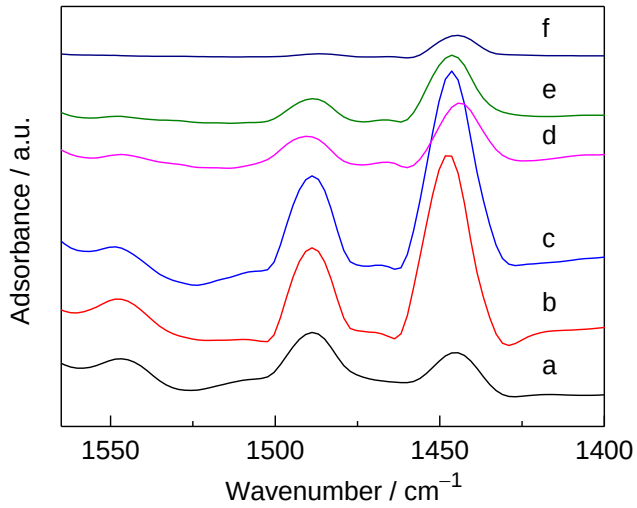


Fig. S9 Pyridine-adsorbed FT-IR spectra of $CuCeO_x$/H-MOR catalyst treated by different calcination temperature (a) 300 °C, (b) 350 °C, (c) 400 °C, (d) 500 °C, (e) 600 °C, and (f) 700 °C (1540 cm^{-1} = B acid sites, 1450 cm^{-1} = L acid sites).

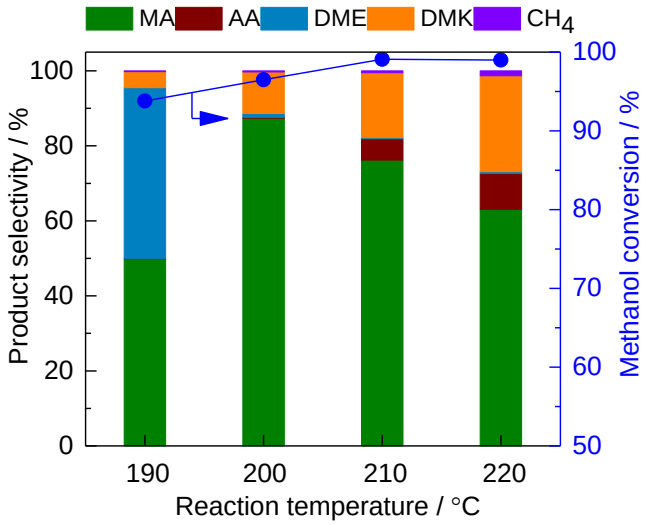


Fig. S10 Catalytic performance of $CuCeO_x$/H-MOR catalyst with different reaction temperatures for heterogeneous methanol carbonylation. Reaction conditions: P_{CO} = 1.0 MPa, CH_3OH/CO = 2.15 mol%, F = 10 mL min^{-1}, time on stream = 3 h.

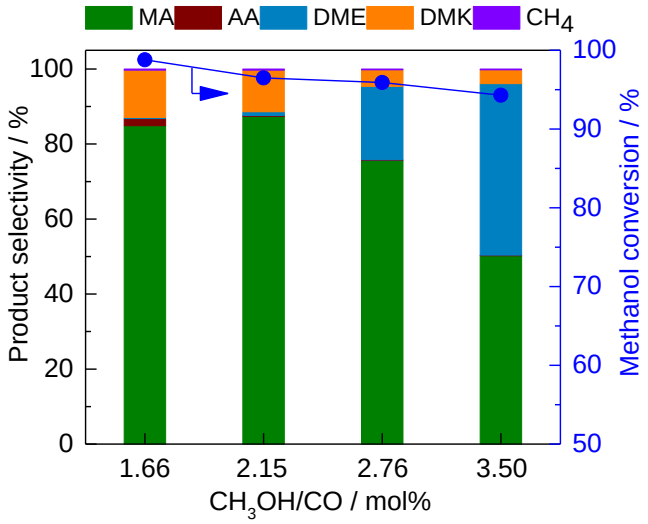


Fig. S11 Catalytic performance of $CuCeO_x$/H-MOR catalyst with different CH_3OH/CO ratios for heterogeneous methanol carbonylation. Reaction conditions: T = 200 °C, P_{CO} = 1.0 MPa, F = 10 mL min^{-1}, time on stream = 3 h.

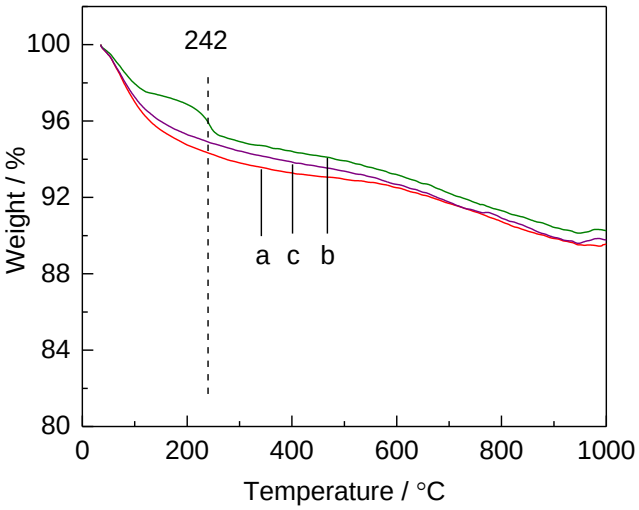


Fig. S12 TG curves of (a) as-calcined $CuCeO_x$/H-MOR, (b) spent $CuCeO_x$/H-MOR, and (c) regenerated $CuCeO_x$/H-MOR by burning coke.

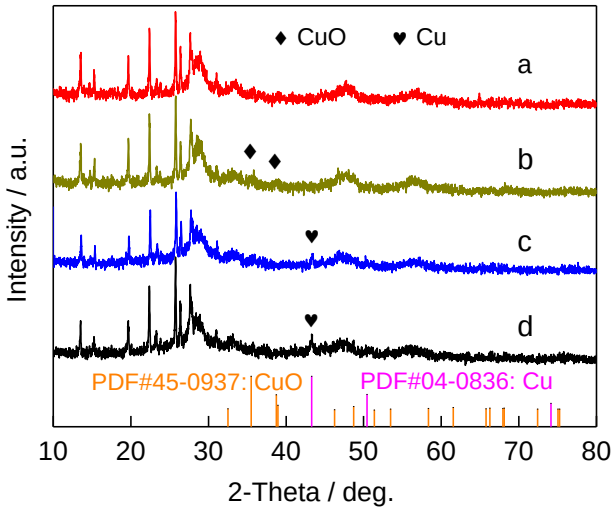


Fig. S13 XRD patterns of (a) as-calcined $CuCeO_x$/H-MOR, (b) regenerated $CuCeO_x$/H-MOR by burning coke, (c) as-reduced $CuCeO_x$/H-MOR by 5% H_2/Ar, and (d) spent $CuCeO_x$/H-MOR.

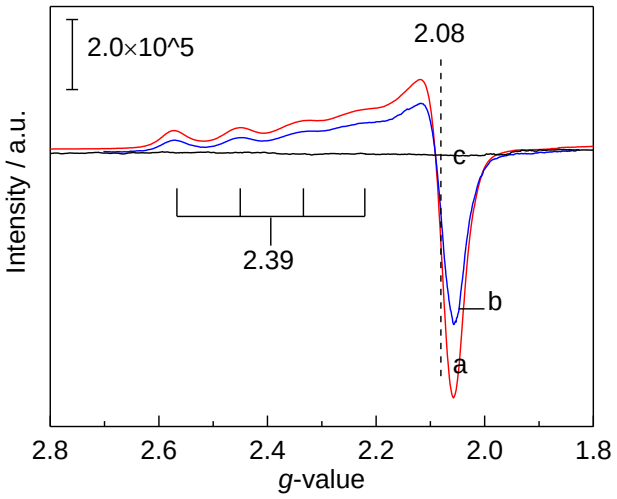


Fig. 14 ESR profiles of (a) as-calcined $CuCeO_x$/H-MOR, (b) regenerated $CuCeO_x$/H-MOR by burning coke, and (c) $CuCeO_x$.