Supplementary information

Dual-engine-driven synthesis of unsaturated esters over channel-expanding Cu-Cs catalysts

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Supplementary Figures and Tables

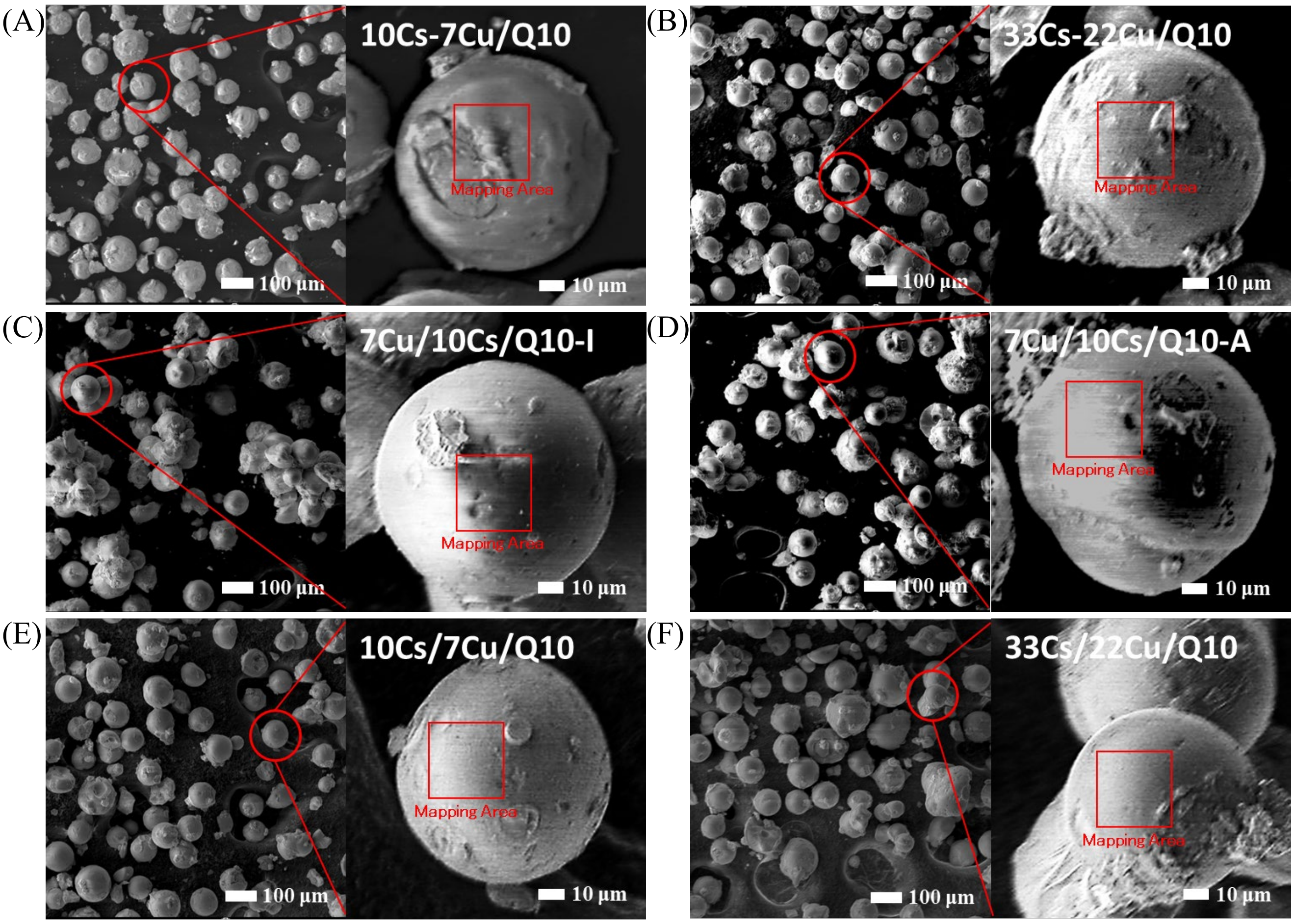

Figure S1. SEM images of (A) 10Cs-7Cu/Q10, (B) 33Cs-22Cu/Q10, (C) 7Cu/10Cs/Q10-I, (D) 7Cu/10Cs/Q10-A, (E) 10Cs/7Cu/Q10, (F) 33Cs/22Cu/Q10.

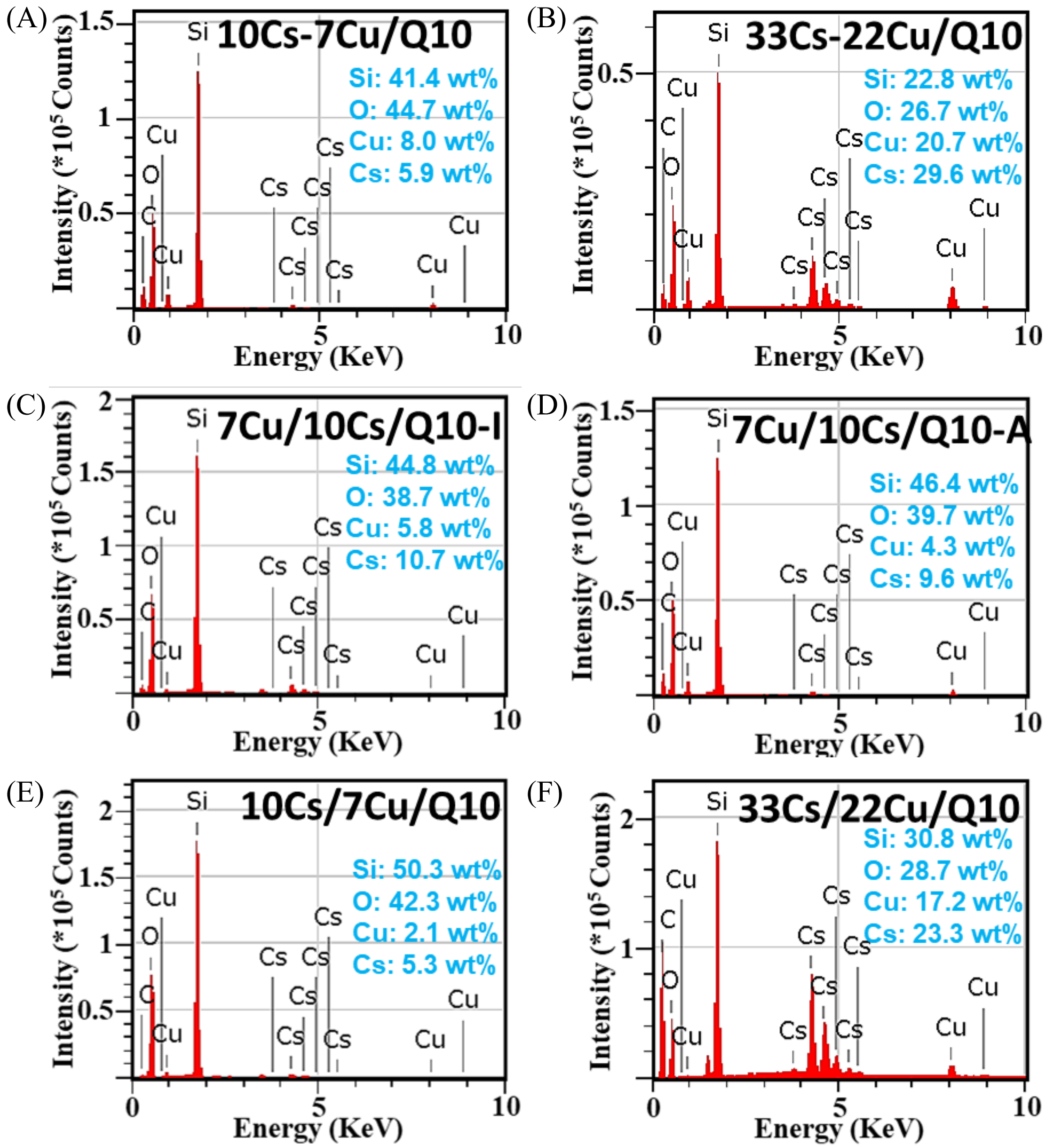

Figure S2. EDS mapping analysis of (A) 10Cs-7Cu/Q10, (B) 33Cs-22Cu/Q10, (C) 7Cu/10Cs/Q10-I, (D) 7Cu/10Cs/Q10-A, (E) 10Cs/7Cu/Q10, (F) 33Cs/22Cu/Q10.

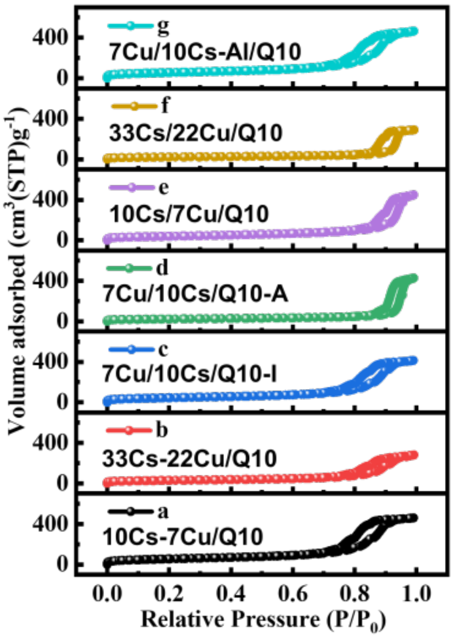

Figure S3. The N_2 adsorption-desorption isotherms of as-synthesized samples.

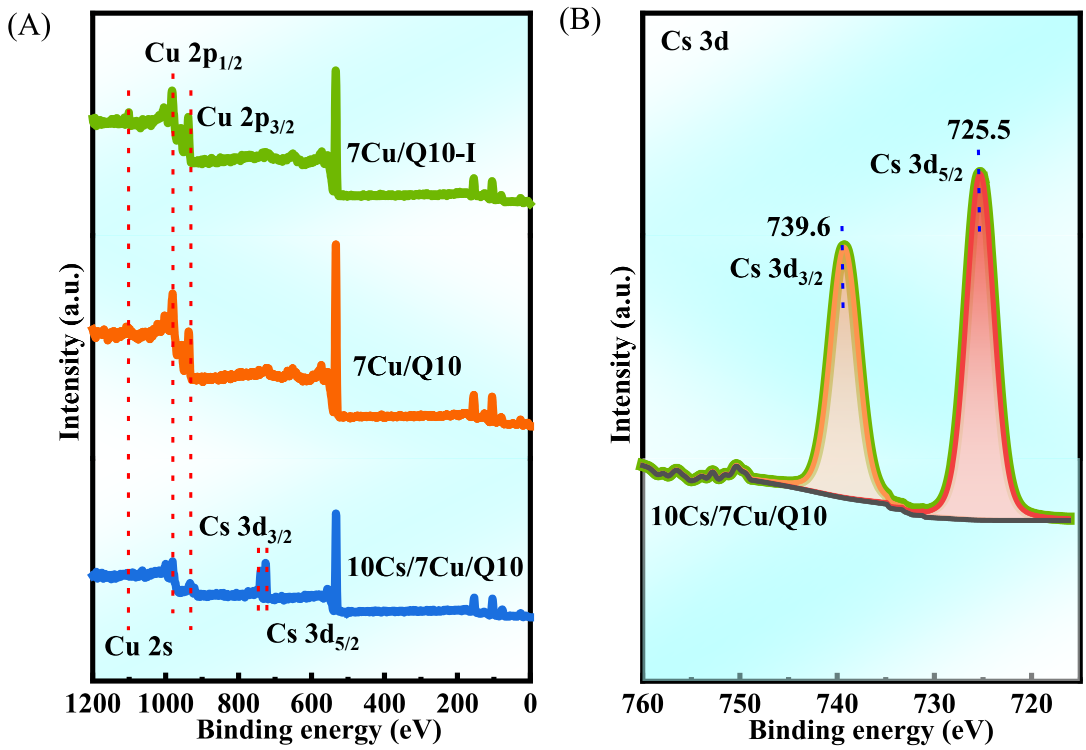

Figure S4. XPS of (A) Cu containing samples, (C) Cs 3d in 10Cs/7Cu/Q10.

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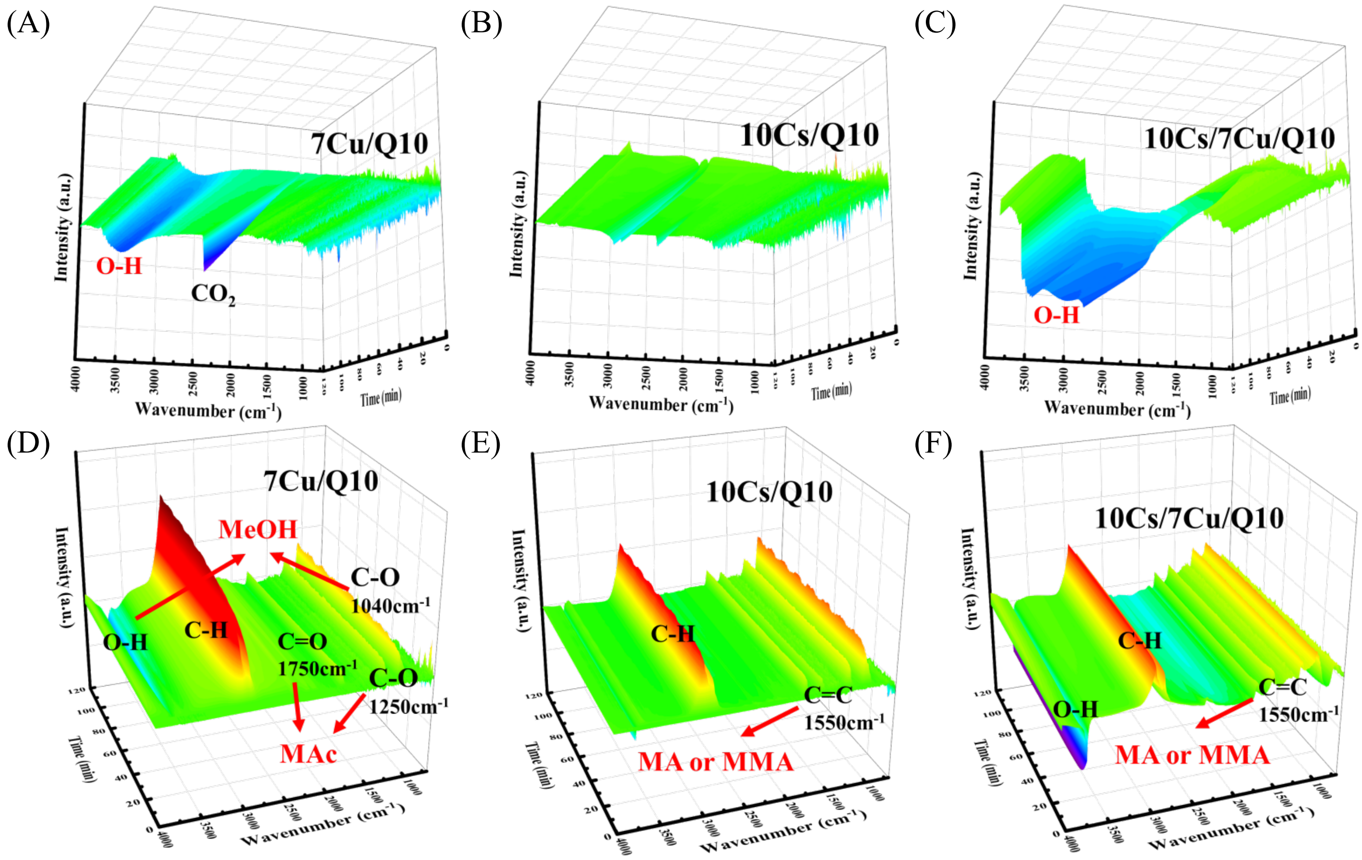

Figure S5. 3D In-situ FTIR spectra of as-synthesized samples during reduction and reaction; Reduction of 7Cu/Q10 (A), 10Cs/Q10 (B), and 10Cs/7Cu/Q10 (C); Reaction over 7Cu/Q10 (D), 10Cs/Q10 (E), and 10Cs/7Cu/Q10 (F).

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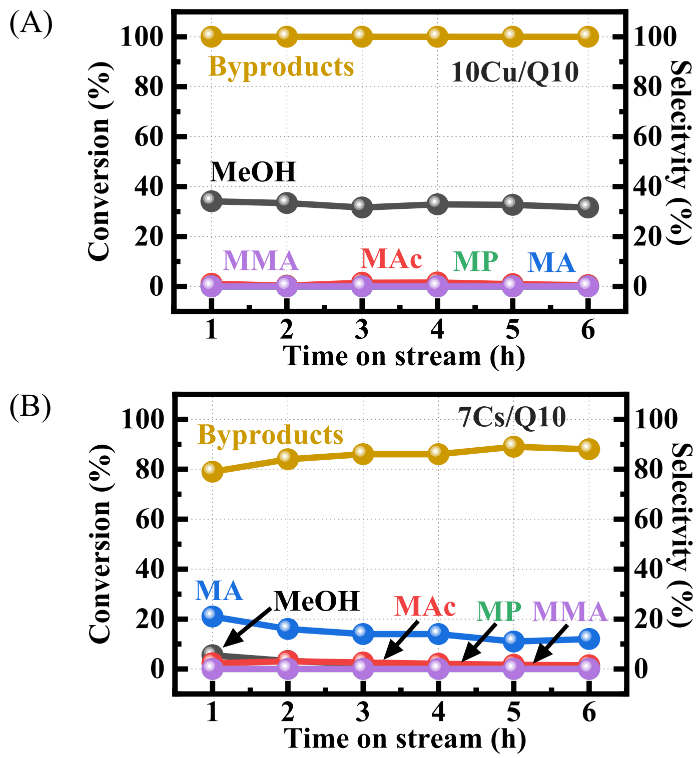

Figure S6. The catalytic performance of 10Cu/Q10 (A) and 7Cs/Q10 (B).
Reaction conditions: 0.1 g catalyst loaded, GHSV = 3000 ml/gh, 400 ℃, 0.1 MPa, MeOH/MAc = 2/1, N_2 flow rate 20 mL/min.

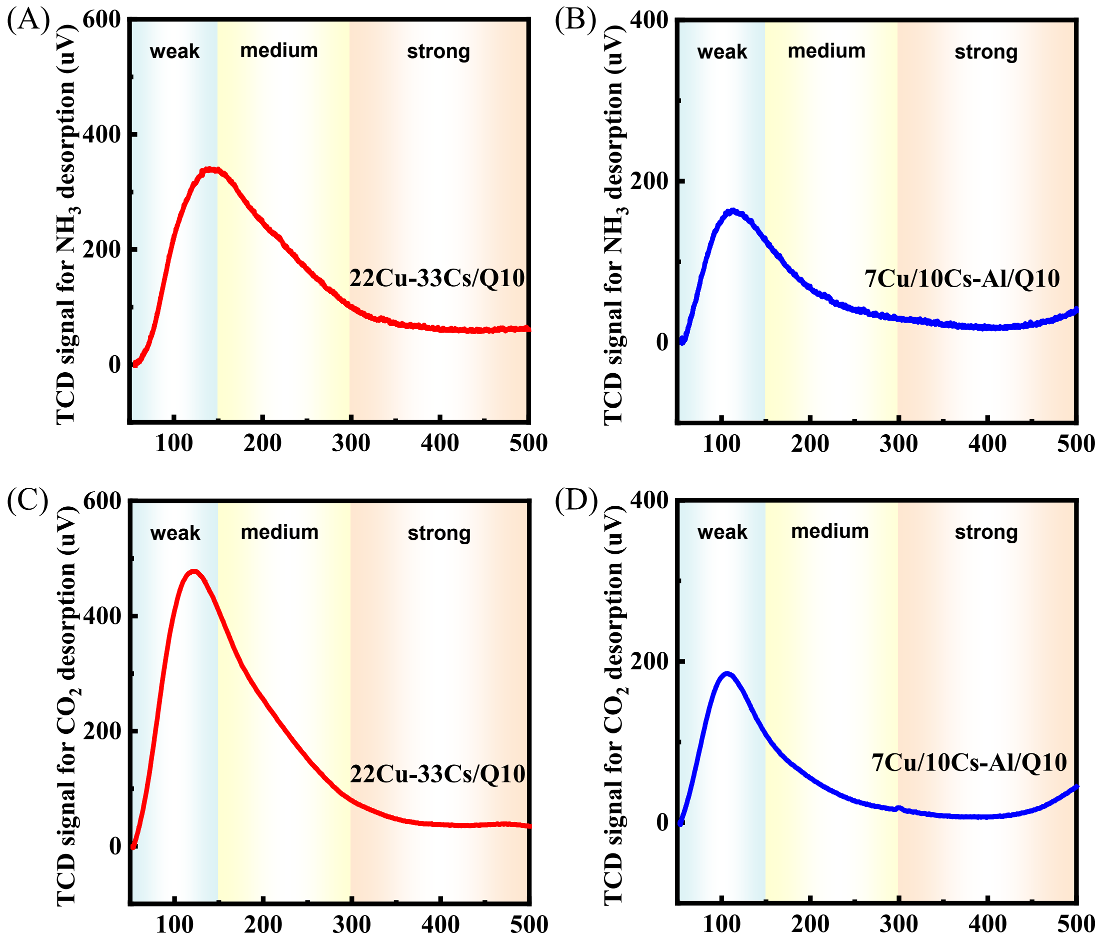

Figure S7. NH_3-TPD profiles of (A) 22Cu-33Cs/Q10, (B) 7Cu/10Cs-Al/Q10; CO_2-TPD profiles of (C) 22Cu-33Cs/Q10, (D) 7Cu/10Cs-Al/Q10.

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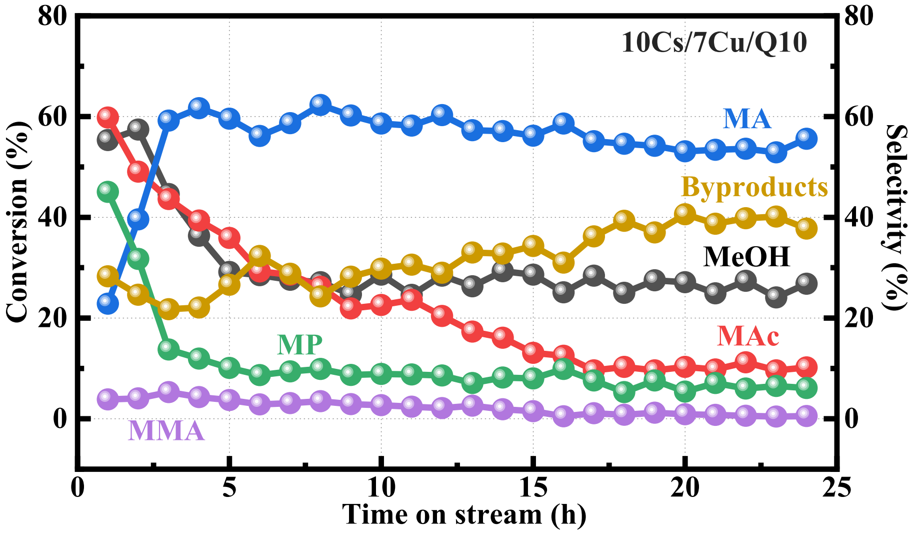

Figure S8. Stability of 10Cs/7Cu/Q10 catalyst in the synthesis system of unsaturated esters.

Reaction conditions: dual layer catalytic bed with 0.1 g sample loaded in upper layer and 0.2 g Cs-Al/Q10 in lower layer, GHSV = 3000 ml/gh, 400 °C, 0.1 MPa, MeOH/MAc = 2/1, N_2 flow rate 20 mL/min.

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Table S1. The concentration of Cu in the samples determined by ICP-OES.

Samples	m_0 (g)[a]	V_0 (ml)[b]	Element	C_0 (ppm)[c]	f[d]	C_1 (mg/L)[e]	C_x mg/kg[f]
Fresh 10Cs/7Cu/Q10	0.2533	25	Cu	3.776	100	377.562	37264.3
Fresh 10Cs/7Cu/Q10	0.1503	25	Cs	5.057	100	505.685	84112.6
Spent 10Cs/7Cu/Q10	0.2533	25	Cu	3.572	100	357.205	35255.1
Spent 10Cs/7Cu/Q10	0.1522	25	Cs	5.105	100	510.521	83856.9

[a] Mass of samples.
[b] Constant volume.
[c] Concentration of diluted liquid.
[d] Factor of dilution.
[e] Concentration of original solution.
[f] Elemental content.

Table S2. Fragment m/z values for relevant chemicals and their relative intensities in MS.[1, 2]

Chemicals	M_r	Fragment m/z (relative intensities, %)
CH_3OH	32	31 (100 %), 32 (75 %), 29 (45 %), 15 (14 %), 30 (8 %)
CH_3COOCH_3	74	43 (100 %), 74 (26 %), 42 (15 %)
CH_2=$CHCOOCH_3$	86	55 (100 %), 27 (44 %), 15 (13 %), 85 (12 %)
$CH_3CH_2COOCH_3$	88	57 (100 %), 29 (77 %), 59 (32 %), 88 (32 %), 27 (20 %),
CH_2=$C(CH_3)COOCH_3$	100	41 (100 %), 69 (63 %), 39 (37 %), 100 (32 %)

M_r: Relative molecular mass. The m/z values of the species employed in this work were marked in red.

References

[1] L. Yang, C. Wang, W. Dai, G. Wu, N. Guan, L. Li, Progressive steps and catalytic cycles in methanol-to-hydrocarbons reaction over acidic zeolites, Fundamental Research, 2 (2022) 184-192.

[2] J.-M. Jehng, I.E. Wachs, G.S. Patience, Y.-M. Dai, Experimental methods in chemical engineering: Temperature programmed surface reaction spectroscopy—TPSR, The Canadian Journal of Chemical Engineering, 99 (2021) 423-434.