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Supplementary Information

Combined halide-free Cu-based catalysts with tri-functions for heterogeneous conversion of methanol into methyl acetate

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Fig. S3. MA selectivity with time on stream over M+CuCeO||Cu-H-MOR catalysts with different dehydration catalysts (M = Cu-H-MOR, H-MOR, H-ZSM-5 and Al_2O_3) for CH_3OH conversion reaction. Reaction conditions: T = 200 °C, P_{co} = 1.0 MPa, MeOH/CO = 2.15 mol%, F = 10 mL/min.

Fig. S4. Catalytic performance of Cu-H-MOR+N||Cu-H-MOR catalysts with different WGSR catalysts (N = CuCeO, CuZnAl, CuMgO and CuMnO) for CH_3OH conversion reaction. Reaction conditions: T = 200 °C, P_{co} = 1.0 MPa, MeOH/CO = 2.15 mol%, F = 10 mL/min, time on stream = 3 h.

Fig. S5. MA selectivity with time on stream over Cu-H-MOR+N||Cu-H-MOR catalysts with

different WGSR catalysts (N = CuCeO, CuZnAl, CuMgO and CuMnO) for CH_3OH conversion reaction. Reaction conditions: T = 200 °C, P_{co} = 1.0 MPa, MeOH/CO = 2.15 mol%, F = 10 mL/min.

Fig. S6. Catalytic performance of Cu-H-MOR+CuCeO||Py-Cu-H-MOR catalysts for CH_3OH conversion reaction. Reaction conditions: T = 200 °C, P_{co} = 1.0 MPa, MeOH/CO = 2.15 mol%, F = 10 mL/min.

Fig. S7. Ar adsorption−desorption isotherms of different catalysts (A) upper catalyst, (B) lower catalyst.

Fig. S8. XRD patterns of different catalysts (A) upper catalyst, (B) lower catalyst. NH_3-TPD profiles of lower catalyst (C).

Table S1 Enthalpy changes ($\Delta_r H$) and Gibbs free energy changes ($\Delta_r G$) for some reactions related to conversions of methanol with CO

Reaction	$\Delta_r H$(298K) (kJ/mol)	$\Delta_r G$(473K) (kJ/mol)
$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$	−25	−34
$CO + H_2O \leftrightarrow CO_2 + H_2$	−41	−21
$CH_3OCH_3 + CO \leftrightarrow CH_3COOCH_3$	−113	−47

Table S2 Catalytic performance of catalysts in various combinations for the catalytic reaction

Combination	MeOH Conv. /%	Select. /%					STY_{MA} (mol/kg/h)	STY_{H2} [a] (mol/kg/h)
		MA	AA	DME	BT	CH_4		
1	86.7	13.9	0.3	84.7	0.4	0.6	0.07	0.0065
2	98.2	74.5	0.5	23.3	1.3	0.4	0.42	0.65
3	99.6	90.4	1.5	0.8	6.9	0.4	0.52	0.66
4	99.2	92.6	1.2	1.2	4.4	0.6	0.53	0.57
5	91.8	54.9	1.8	39.2	2.7	1.4	0.29	0.24

1: Cu-H-MOR, 2: Cu-H-MOR+CuCeO, 3: Cu-H-MOR+CuCeO||Cu-H-MOR,

4: Cu-H-MOR||CuCeO||Cu-H-MOR, 5: CuCeO||Cu-H-MOR.

a: The STY_{H2} calculation process was as follows:

Because there was no CuCeO in Combination 1 (Cu-H-MOR), it was assumed that the generation of trace CH_4 did not follow the Scheme 2 mechanism diagram, and the selectivity of CH_4 was 0.6% equal to the selectivity of CO_2. Then we calculated the STY_{CO2} of Combination 1. According to the area of CO_2 peak in different combinations, the STY_{CO2} of other combinations could be obtained, and the calculated STY_{CH4} indicated the consumption of hydrogen. Finally, the subtraction of the two was STY_{H2} ($STY_{H2} = STY_{CO2} - STY_{CH4}$).

Table S3 Space time yield of different products

A_{CO2} (mV·s)[a]	STY_{CO2} (mol/kg/h)	STY_{CH4} (mol/kg/h)	STY_{H2} (mol/kg/h)
1.90	0.0065	–	0.0065
191.05	0.65	0.0045	0.65
193.59	0.66	0.0046	0.66
167.89	0.58	0.0068	0.57
74.77	0.25	0.015	0.24

a: CO_2 peak area in TCD.

Table S4 The coke content on the deactivated catalysts

Catalyst	Coke content (wt%)	Soft coke content (wt%)	Hard coke content (wt%)
upper layer	13.7	8.3	5.4
lower layer	10.2	1.2	9.0
mix	13.1	5.6	7.5

Table S5 The textural properties of different catalyst

Catalyst		S_{BET} (m^2/g)	$S_{micropore}$ (m^2/g)	V_{pore} (mL/g)	D_{pore} (nm)
upper layer	fresh	234	144	0.19	3.3
	deactivated	69	0	0.09	5.4
	regenerated	218	134	0.16	2.9
lower layer	fresh	420	363	0.21	2.0
	deactivated	22	0.2	0.04	7.1
	regenerated	404	361	0.20	1.9

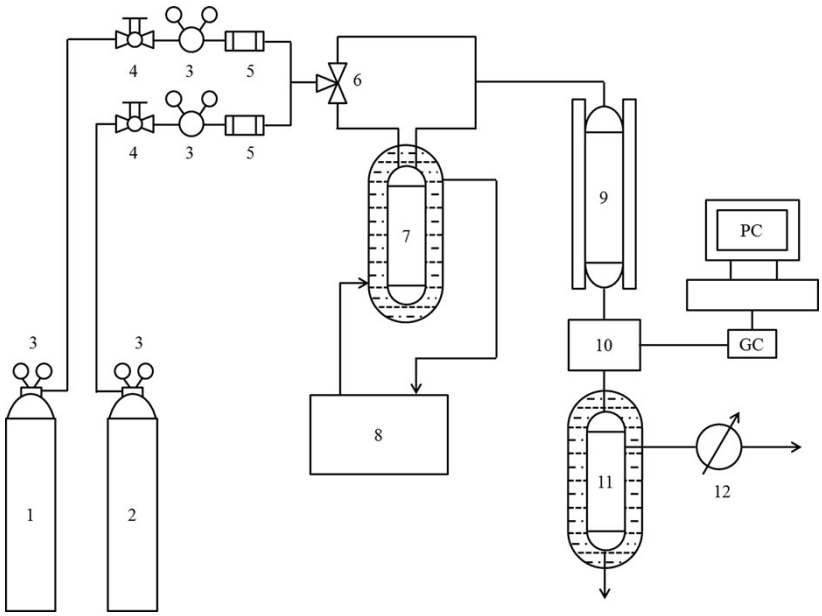


Fig. S1. Schematic representation of the experimental apparatus for the synthesis of MA from methanol. 1: 5% H_2/N_2 cylinder, 2: CO cylinder, 3: Pressure reducing valve, 4: Stop valve, 5: Mass flowmeter, 6: Ball valve, 7: Methanol tank, 8: Low temperature thermostatic bath, 9: Reactor, 10: Thermotank, 11: Gas−liquid separator, 12: Back pressure valve.

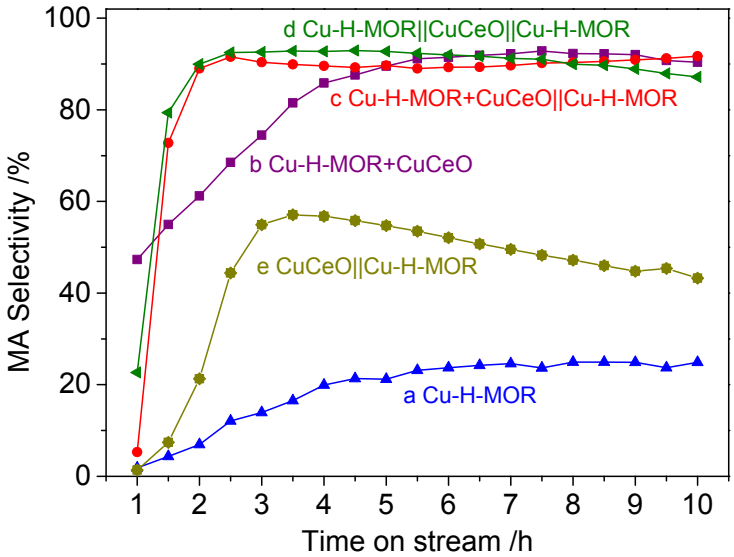
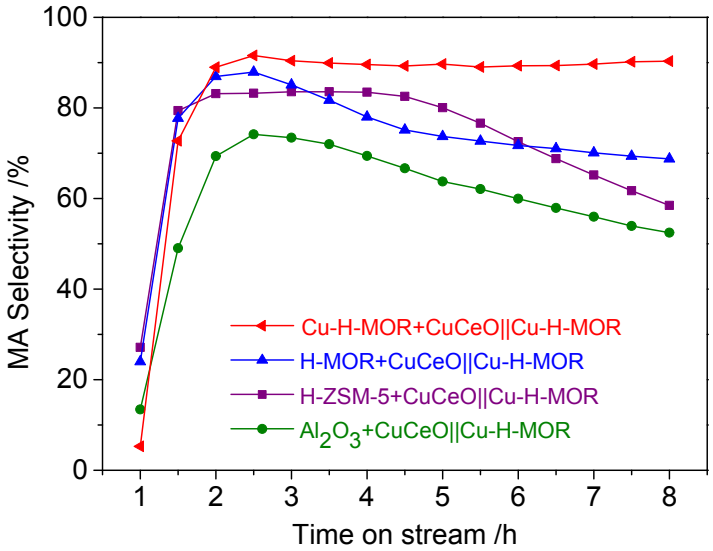


Fig. S2. MA selectivity with time on stream over various combined catalysts. Reaction conditions: $T = 200$ °C, $P_{co} = 1.0$ MPa, MeOH/CO = 2.15 mol%, $F = 10$ mL/min.



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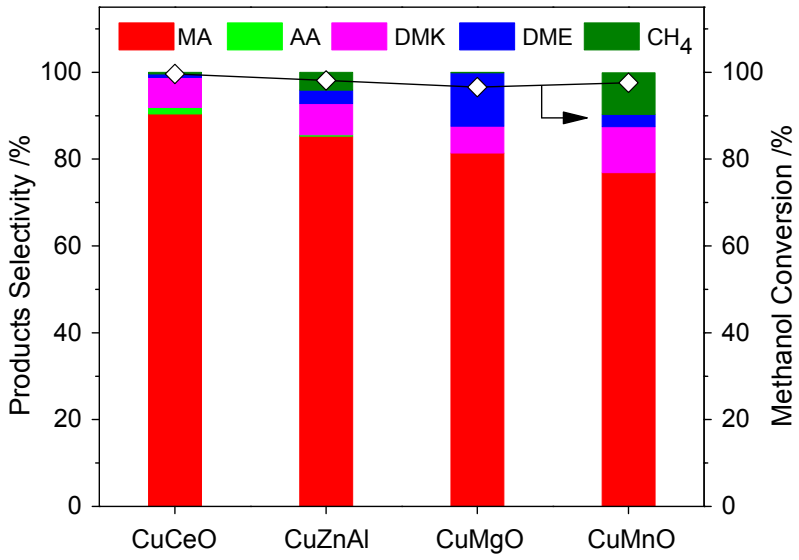

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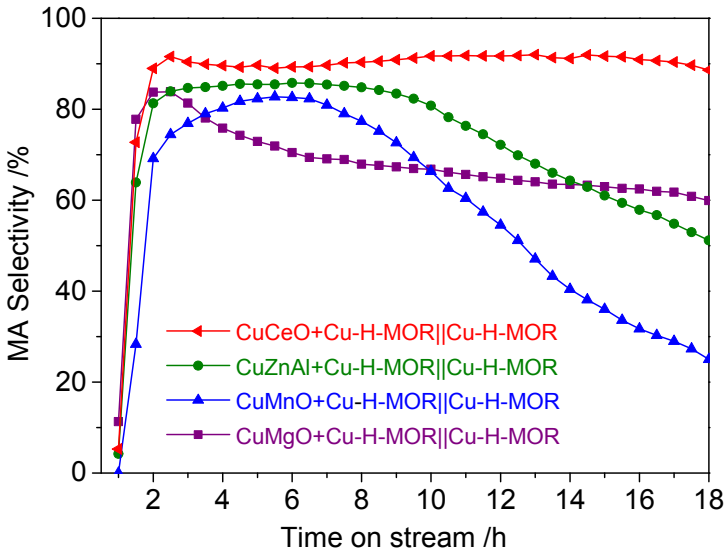

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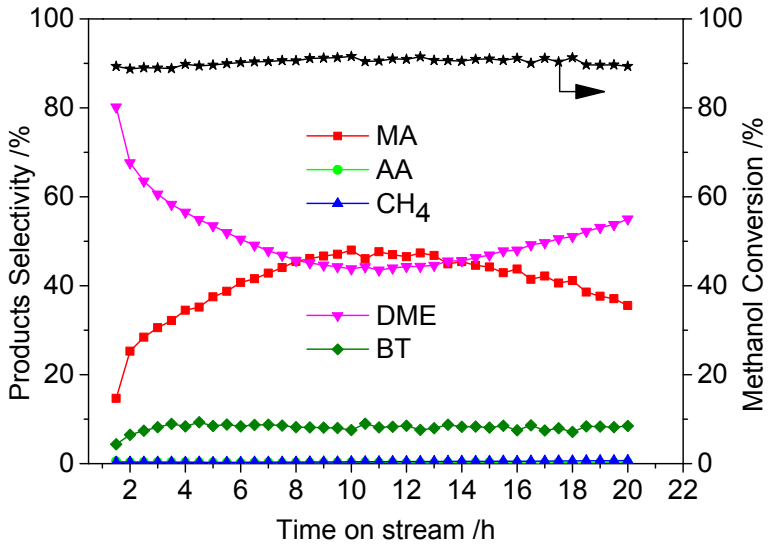

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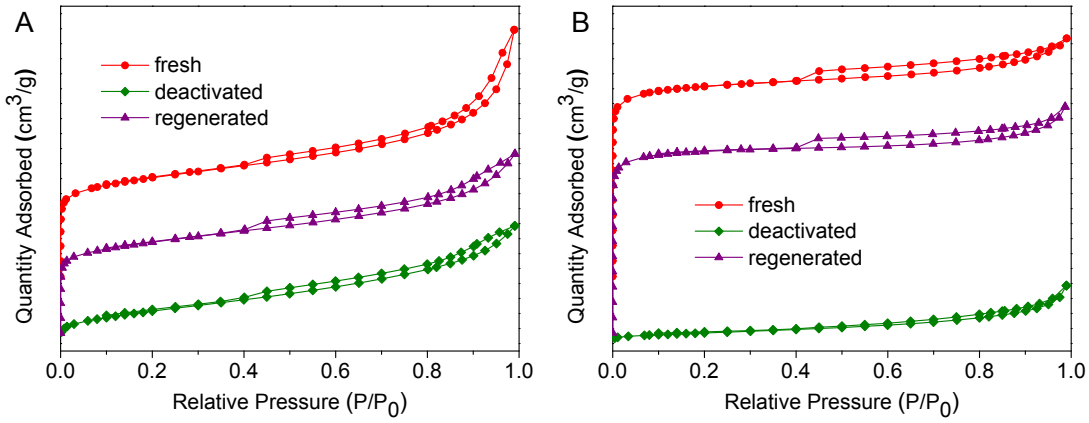

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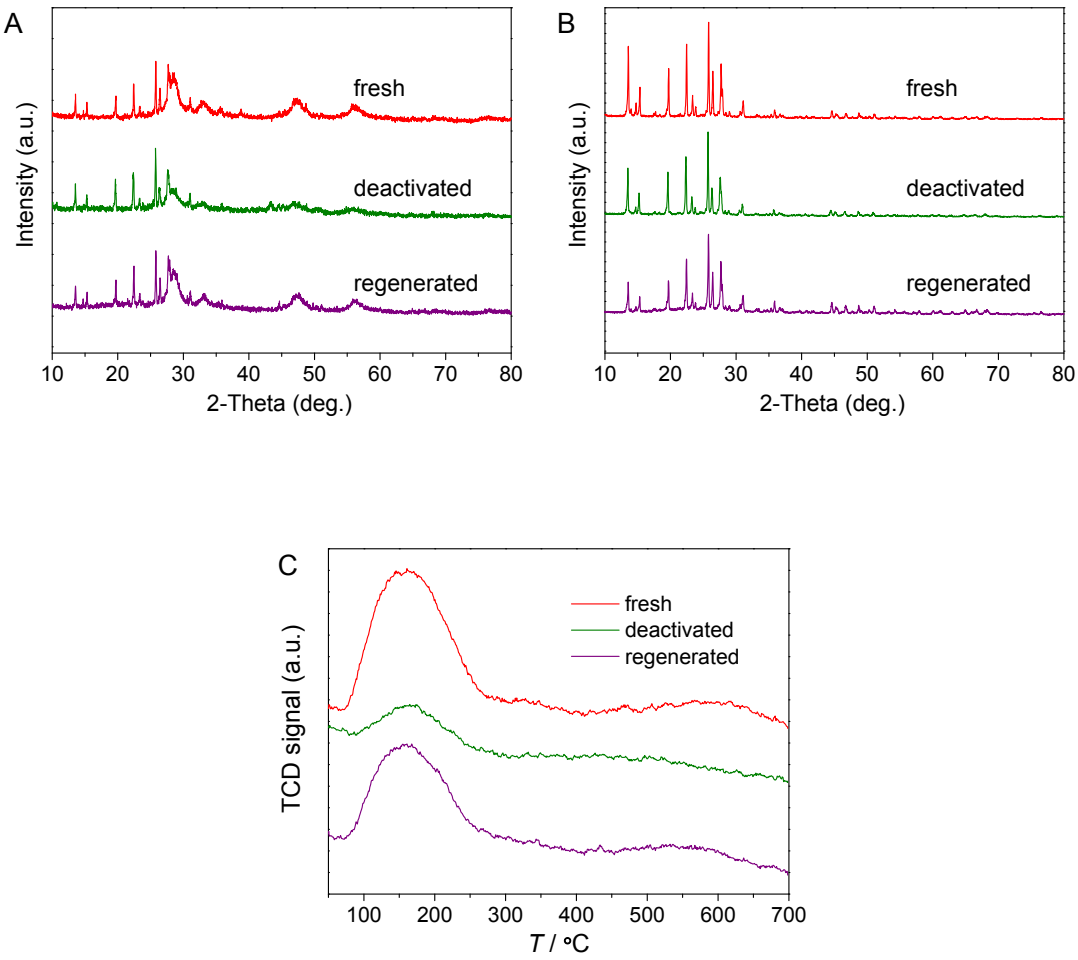

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