Supplementary Information

Fast synthesis of Cu@zeolitic imidazolate framework-8 (ZIF-8) derived Cu/ZnO catalysts via a facile mechanical grinding method for CO_2 hydrogenation to methanol

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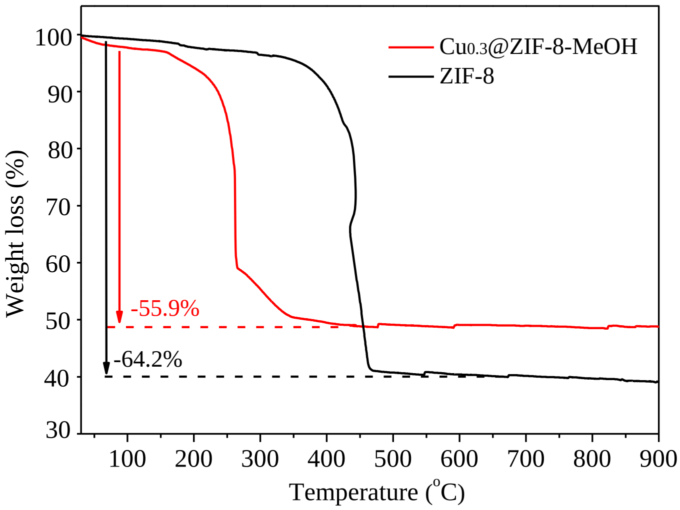

Fig. S1 TG curves of ZIF-8 and $Cu_{0.3}$@ZIF-8-MeOH precursors.

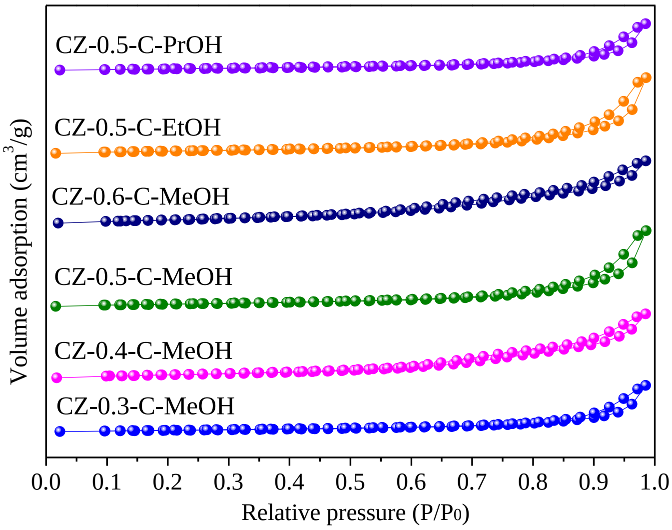

Fig. S2 N_2 adsorption-desorption isotherms of the calcined catalysts.

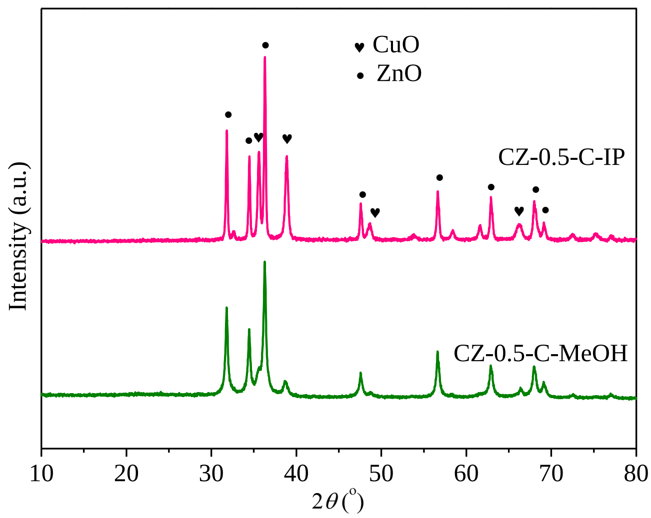

Fig. S3 XRD patterns of CZ-0.5-C-MeOH and CZ-0.5-C-IP catalysts.

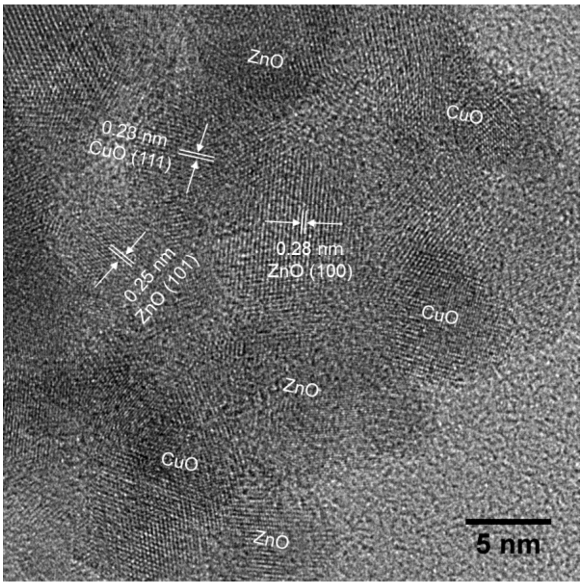

Fig. S4 HR-TEM image of CZ-0.5-C-MeOH catalsyt.

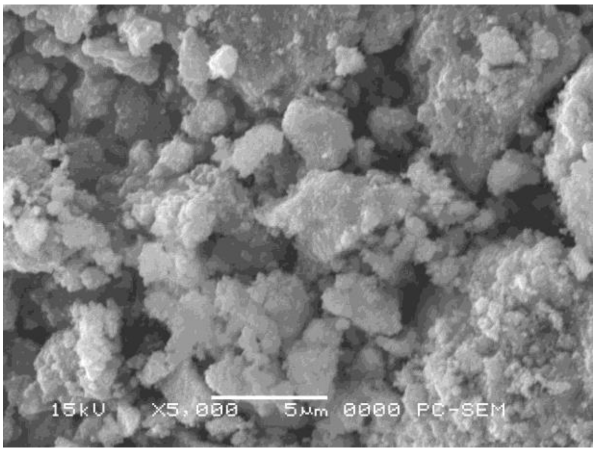

Fig. S5 SEM image of CZ-0.5-C-IP catalyst prepared by the conventional impregnation method.

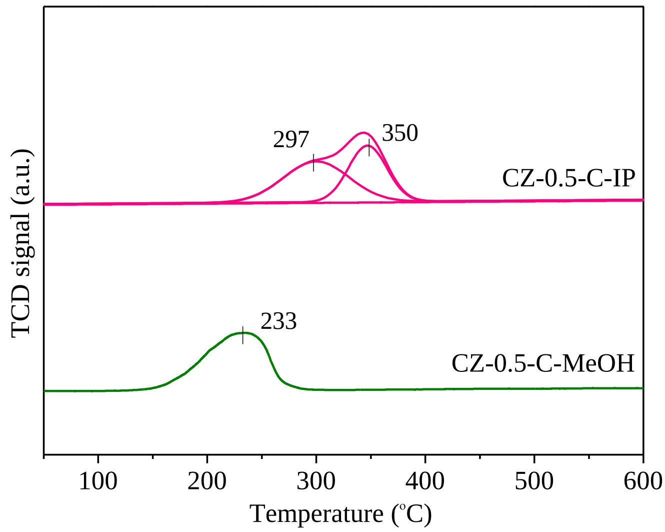

Fig. S6 H_2-TPR profiles of $Cu_{0.5}$@ZIF-8-MeOH derived CZ-0.5-C-MeOH catalyst and CZ-0.5-C-IP catalyst synthesized by the conventional impregnation method.

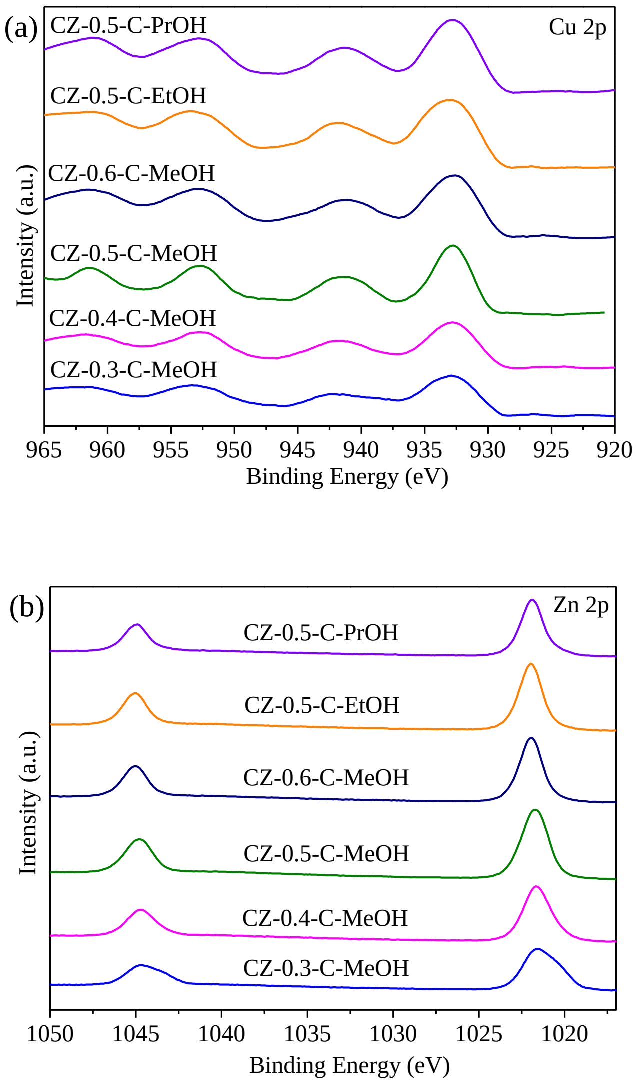

Fig. S7 Cu 2p (a) and Zn 2p (b) spectra of the calcined catalysts.

Table S1 XPS parameters of the calcined catalysts

Catalysts	Binding Energy (eV)				O_{vac}/O_{lat}
	Cu $2p_{3/2}$	Cu $2p_{1/2}$	Zn $2p_{3/2}$	Zn $2p_{1/2}$	
CZ-0.3-C-MeOH	932.8	953.3	1021.8	1044.8	0.702
CZ-0.4-C-MeOH	932.9	953.2	1021.7	1044.7	0.740
CZ-0.5-C-MeOH	932.8	953.2	1021.7	1044.8	0.775
CZ-0.6-C-MeOH	932.8	953.3	1021.8	1044.9	0.699
CZ-0.5-C-EtOH	932.8	953.2	1021.8	1044.9	0.771
CZ-0.5-C-PrOH	932.7	953.2	1021.8	1044.9	0.722

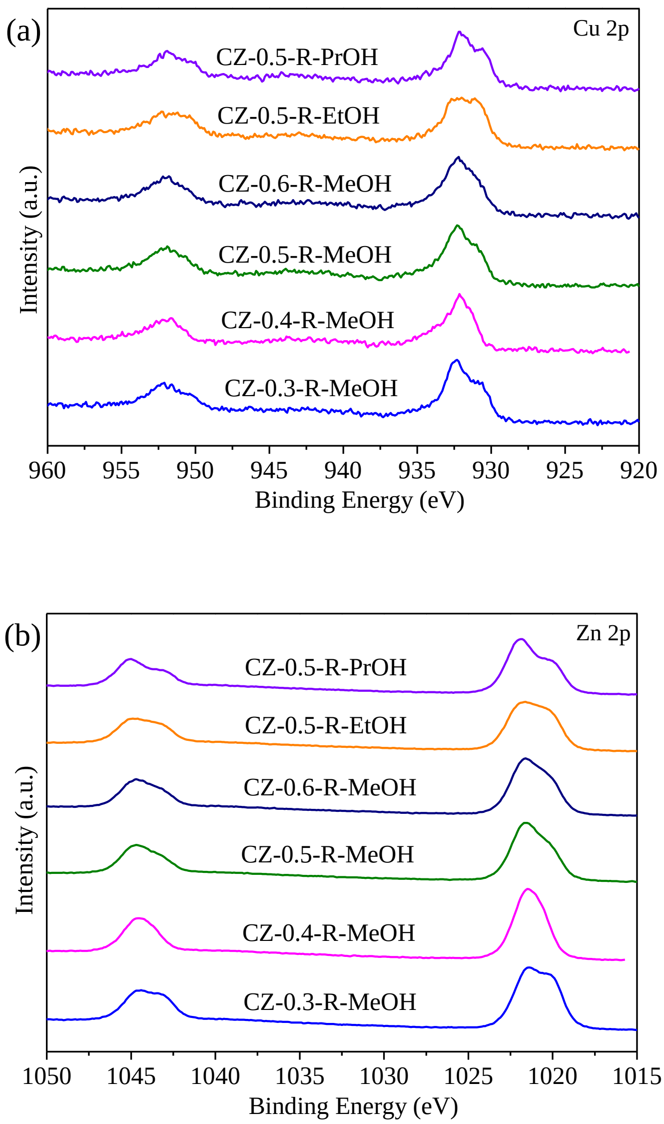

Fig. S8 Cu 2p (a) and Zn 2p (b) spectra of the reduced catalysts.

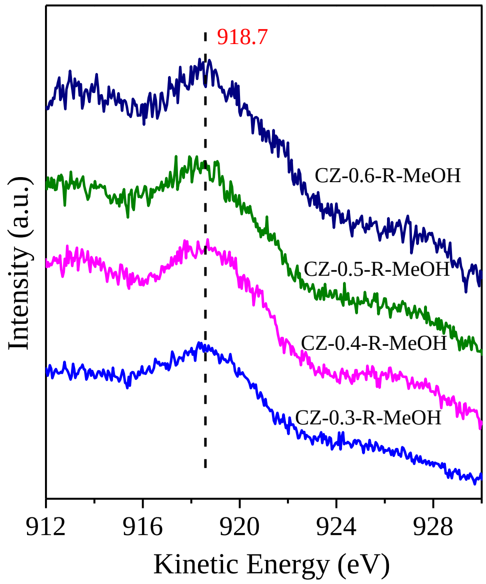

Fig. S9 Cu LMM spectra of the reduced catalysts with different Cu/(Cu+Zn) molar ratios.

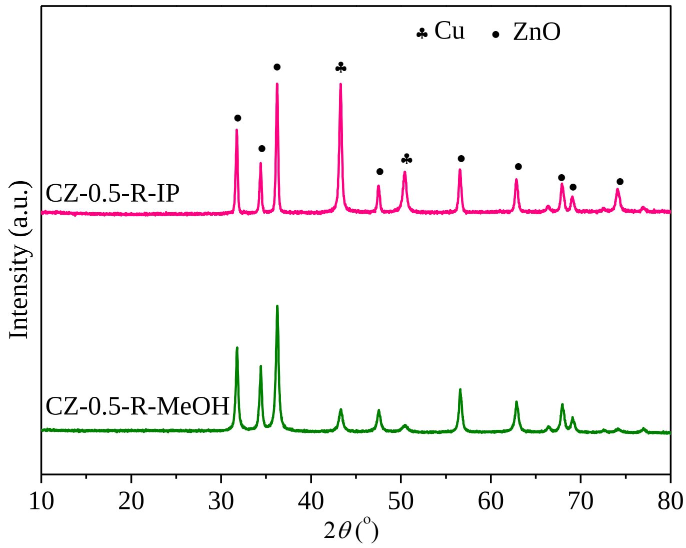

Fig. S10 XRD patterns of CZ-0.5-R-MeOH and CZ-0.5-R-IP catalysts.

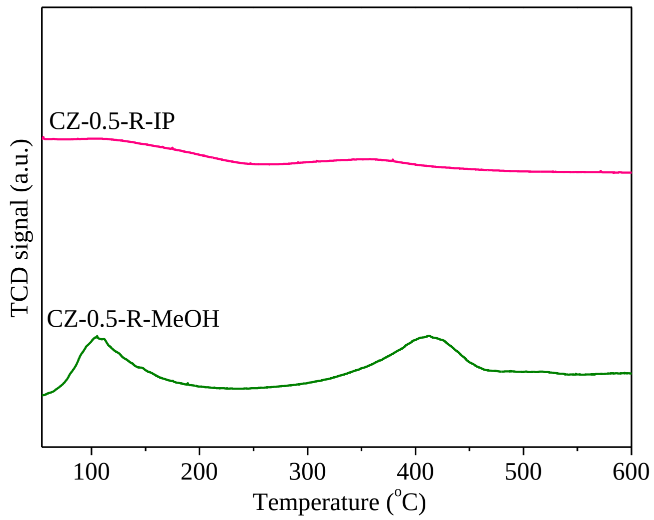

Fig. S11 CO_2-TPD profiles of CZ-0.5-R-MeOH and CZ-0.5-R-IP catalysts.

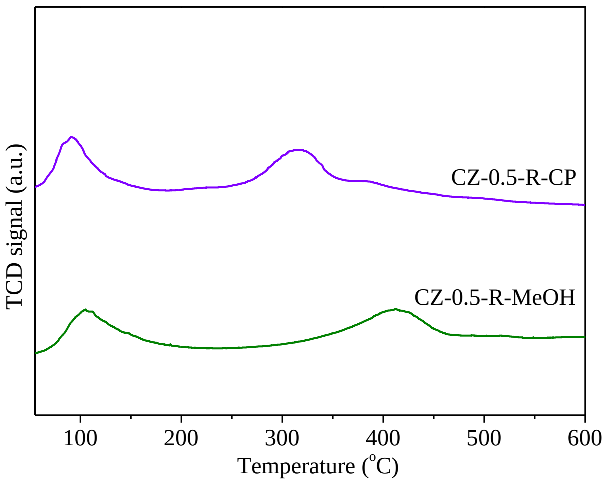

Fig. S12 CO_2-TPD profiles of CZ-0.5-R-MeOH and CZ-0.5-R-CP catalysts.

Table S2 The surface basicity and contribution of basic sites over CZ-0.5-R-MeOH and CZ-0.5-R-CP catalysts

Catalysts	Number of basic sites and contribution (mmol/g) [b]		Total number of basic sites (mmol/g)
	Weakly basic sites	Moderately basic sites	
CZ-0.5-R-MeOH	0.084 (38.7)	0.133 (61.3)	0.217
CZ-0.5-R-CP [a]	0.123 (56.4)	0.095 (43.6)	0.218

[a] Prepared by the conventional coprecipitation method.
[b] The value in the parentheses is the proportion of single basic sites to total basic sites.

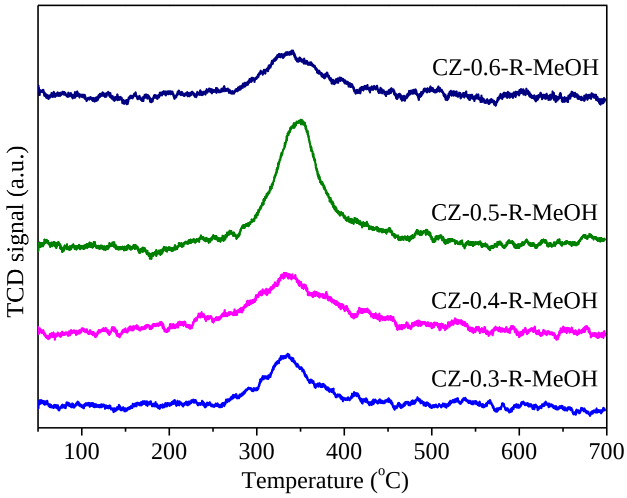

Fig. S13 H_2-TPD profiles of the reduced CZ-x-R-MeOH catalysts, where x represented Cu/(Cu+Zn) molar ratio (x = 0.3, 0.4, 0.5, 0.6).

Table S3 The amount of H_2 desorption over CZ-x-R-MeOH catalysts with different Cu/(Cu+Zn) molar ratios

Catalysts	Desorbed H_2 amount (mmol/g)
CZ-0.3-R-MeOH	0.116
CZ-0.4-R-MeOH	0.177
CZ-0.5-R-MeOH	0.287
CZ-0.6-R-MeOH	0.101

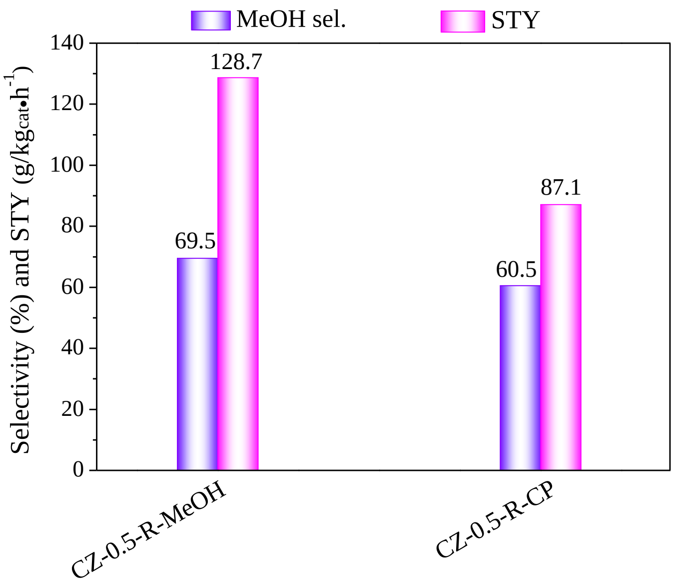

Fig. S14 Catalytic activity comparison of $Cu_{0.5}$@ZIF-8-MeOH derived CZ-0.5-R-MeOH catalyst and catalyst prepared by the conventional coprecipitation method (marked as CZ-0.5-R-CP). Reaction conditions: catalyst weight = 0.25 g, reaction temperature = 200 ℃, reaction pressure = 5.0 MPa, GHSV = 6000 mL g_{cat}^{-1} h^{-1}, feed gas: Ar/CO_2/H_2 = 4/24/72.

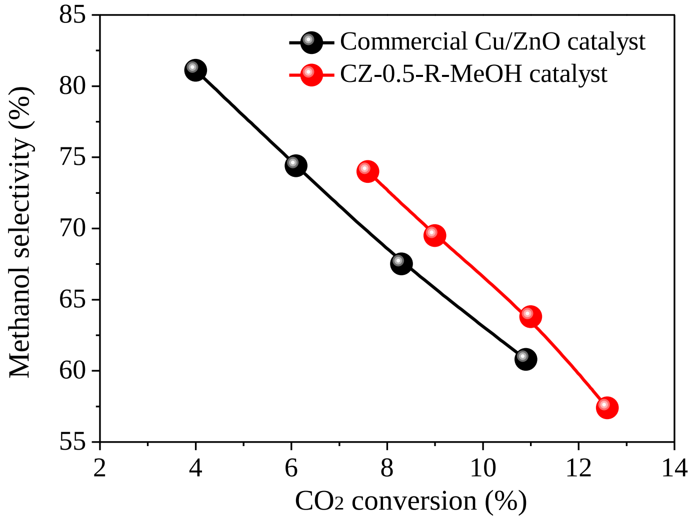

Fig. S15 The relationship between CO_2 conversion and methanol selectivity for CZ-0.5-R-MeOH catalyst and the commercial Cu/ZnO catalyst. Reaction conditions: catalyst weight = 0.25 g, reaction pressure = 5.0 MPa, GHSV = 6000 mL g_{cat}^{-1} h^{-1}, feed gas: $Ar/CO_2/H_2$ = 4/24/72.

Table S4 Catalytic activity comparison between MOFs derived Cu/ZnO catalyst reported in this work and previously reported catalysts with similar Cu/Zn compositions

Catalysts	Cu/Zn molar ratio	Preparation method	T (°C)	P (MPa)	H_2/CO_2 ratio	GHSV (mL g_{cat}^{-1} h^{-1})	STY (g/kg_{cat}·h^{-1})	Ref.
CZ-0.5-R-MeOH	1	mechanical grinding	200	5.0	3	6000	128.7	This work
CZ-0.5-R-MeOH	1	mechanical grinding	220	5.0	3	6000	148.8	This work
Cu/ZnO/C	1.3	Impregnation	260	4.0	3	6000	92.5	1
10NG-CZA	1.3	Co-precipitation	200	3.0	3	2240.7	52.9	2
CZZ-flower	1	Urea hydrolysis	250	3.0	3	3600	137.6	3
$Cu/ZnO/Ga_2O_3$	1	Co-precipitation	200	3.0	3	6000	48.3	4
CZ@UiO-66	1	Deposition-precipitation	240	3.0	5	2400	12.8	5
Cu/Zn-2mM	1	Solid-state grinding	200	7.0	3	6000	87.17	6
Cu/ZnO	1	hydrothermal	240	3.0	3	30000	115.5	7
$Er_{0.2}CuZnO$	1	Co-precipitation	190	5.0	3	6000	103.4	8
CZZ	1	Co-precipitation	240	3.0	3	4500	105.55	9

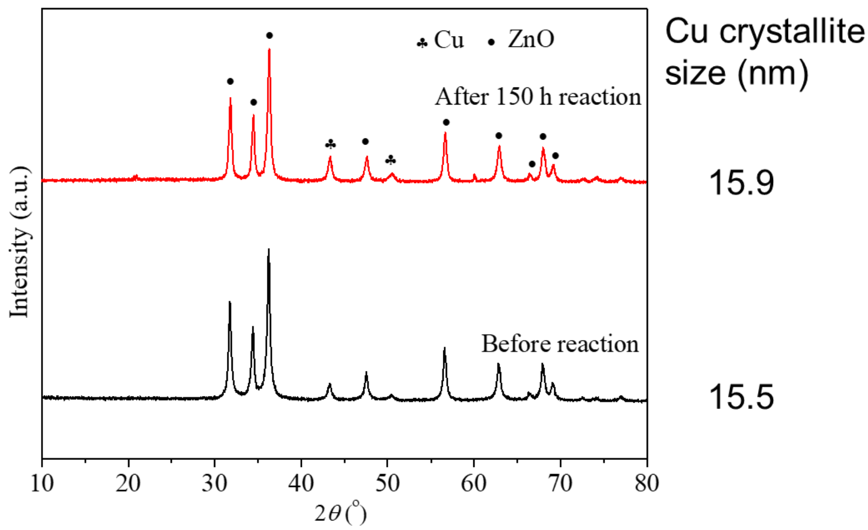

Fig. S16 XRD patterns of the CZ-0.5-R-MeOH catalyst before and after 150 h reaction.

Table S5 Cu^0 surface area and Cu dispersion before and after stability testing

	Cu^0 surface area (m^2/g)	Cu dispersion
Before reaction	9.0	3.1
After stability testing	8.8	3.0

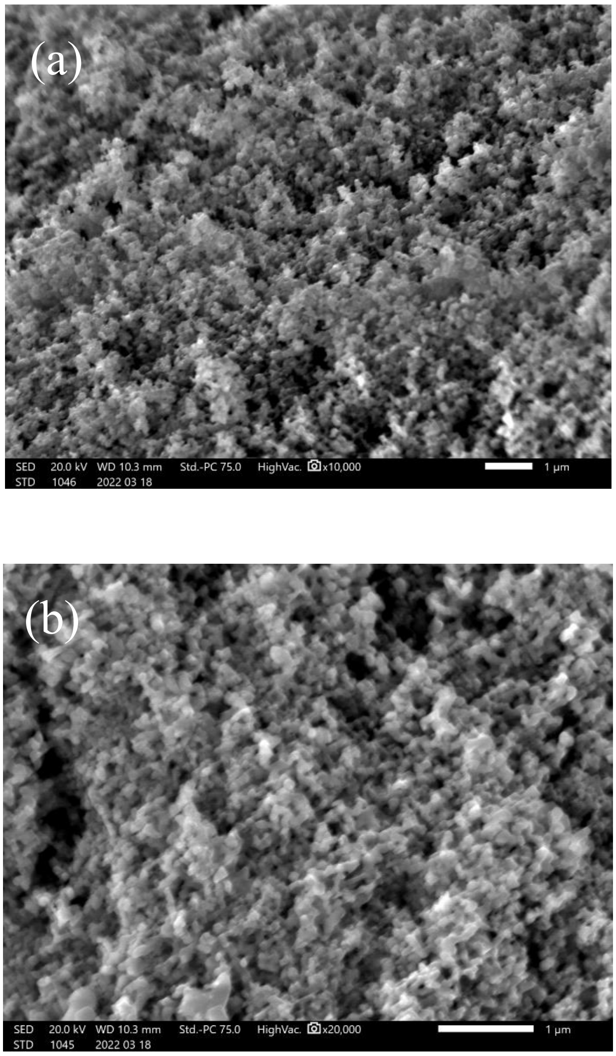

Fig. S17 SEM images of the fresh (a) and the spent (b) CZ-0.5-R-MeOH catalyst.

Table S6 The vibration bands assignment for the surface species on CZ-0.5-R-MeOH catalyst at 220 ℃ and 0.1 MPa

Wavenumber (cm^{-1})	Assignment	Species
2975, 2920, 2840	ν(C-H)	
1056, 1030, 1008	ν(C-O)	CH_3OH
1440	δ(C-H)	
1587	ν_{as}(O=C-O)	$HCOO^*$
1370	ν_s(O=C-O)	

ν_{as}: asymmetrical stretching vibration; ν_s: symmetrical stretching vibration; δ: deformation vibration

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