Supporting Information

Thermo-Photo Catalysis for Methanol Synthesis from Syngas

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Reaction configuration

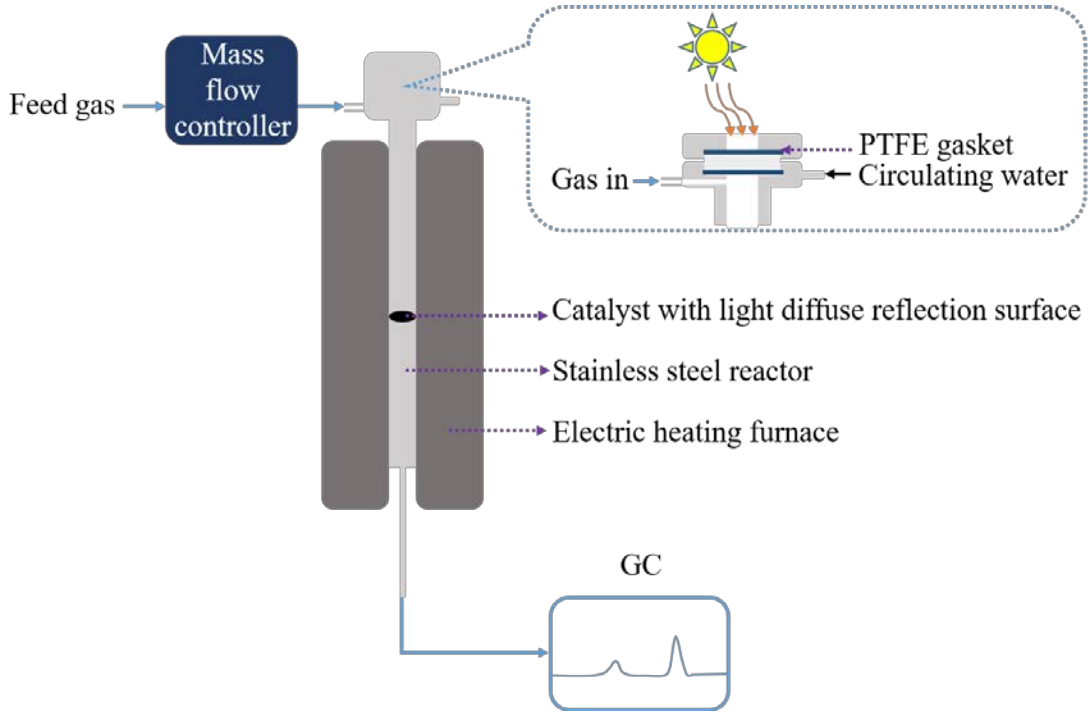

Figure S1. Thermo-photo catalytic reactor

To avoid possible leakage:

(1) The reactor is maintained at doubled reaction temperature (500 ^{o}C) and pressure (5Mpa) before use.

(2) The reactor top (where quartz window locates) is cooled by circulating water to prevent the overheating of the sealing PTFE gasket.

(3) A high-sensitive flammable gas detector is employed to avoid possible leakage.

Characterizations of Cu/Zn/Al catalysts with various composition

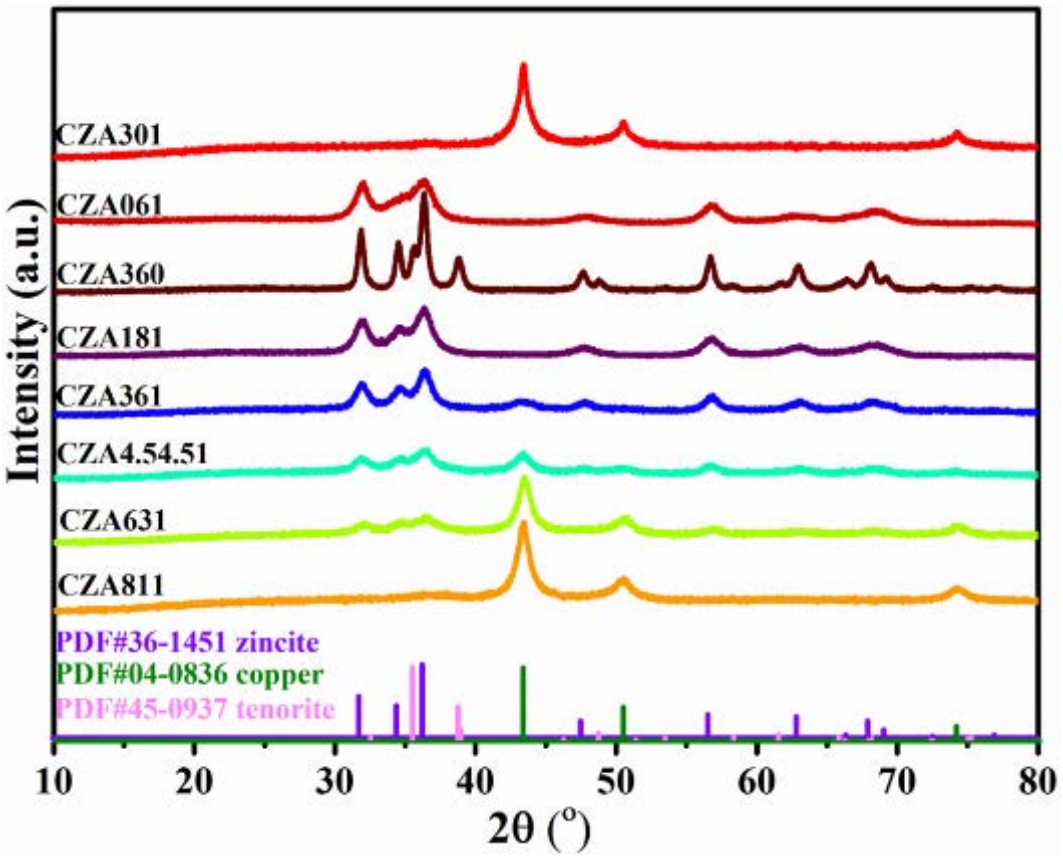

Figure S2. XRD patterns of hydrogen reduced catalysts in different compositions

Hydrogen treated Cu/Zn/Al catalyst was denoted as CZAlmn, where l, m and n represented the comparative molar ratio of Cu, Zn and Al, respectively. The main diffraction peaks of CZA061 were assigned to the planes of zincite, while the characteristic peaks of CZA301 have shown to be tenorite and copper. CZA360, CZA361, CZA4.54.51, CZA631 contained all aforementioned phases. In comparison, the comparatively less amount and low crystallinity of ZnO lead to the absence in diffraction peaks of zincite in CZA811. Similarly, the absence of tenorite and copper phases in CZA181 can also be ascribed to the less amount and low crystallinity of CuO

and metallic copper. Notably, Al_2O_3 might exist as amorphous phase as no such signal was observed.[1]

Table S1. The BET specific area and BJH pore volumes of hydrogen treated catalysts with different compositions

Catalyst	BET surface area (m^2/g)	BJH Desorption average pore diameter (Å)	BJH Desorption cumulative volume of pores (cm^3/g)
CZA301	44.53	239.87	0.23
CZA061	74.82	157.06	0.40
CZA360	40.22	323.86	0.37
CZA181	58.39	202.38	0.36
CZA361	50.18	387.25	0.53
CZA4.54.51	79.67	269.84	0.59
CZA631	46.28	388.33	0.49
CZA811	31.68	289.81	0.21

Temperature on surface of Cu/Zn/Al catalyst influenced by electrical-furnace-heating

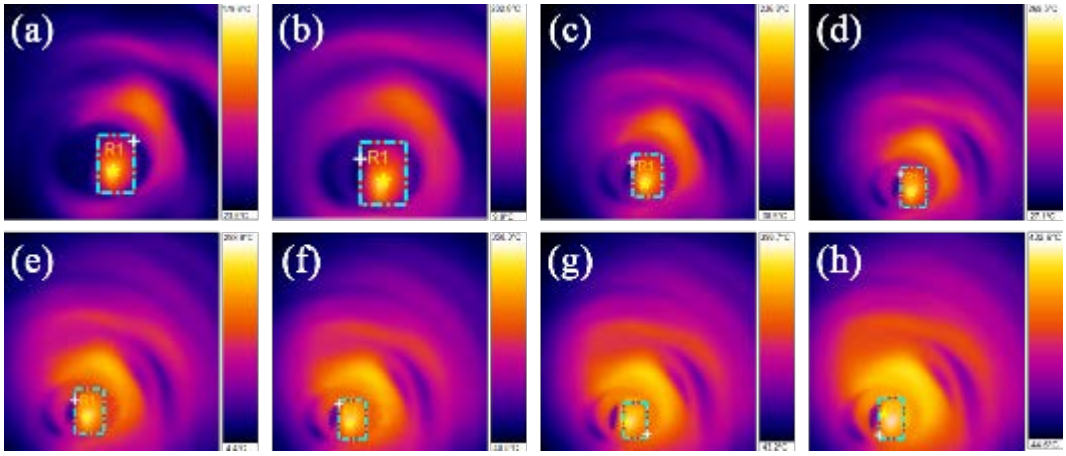

Figure S3. IR-thermographic images taken when the reactor was heated by external thermal field with light intensity maintained at 650 mW cm^{-2}. Specifically, the temperatures of syngas were (a) 25 ºC, (b) 50 ºC, (c) 100 ºC, (d) 150 ºC, (e) 200 ºC, (f) 250 ºC, (g) 300 ºC, and (h) 350 ºC.

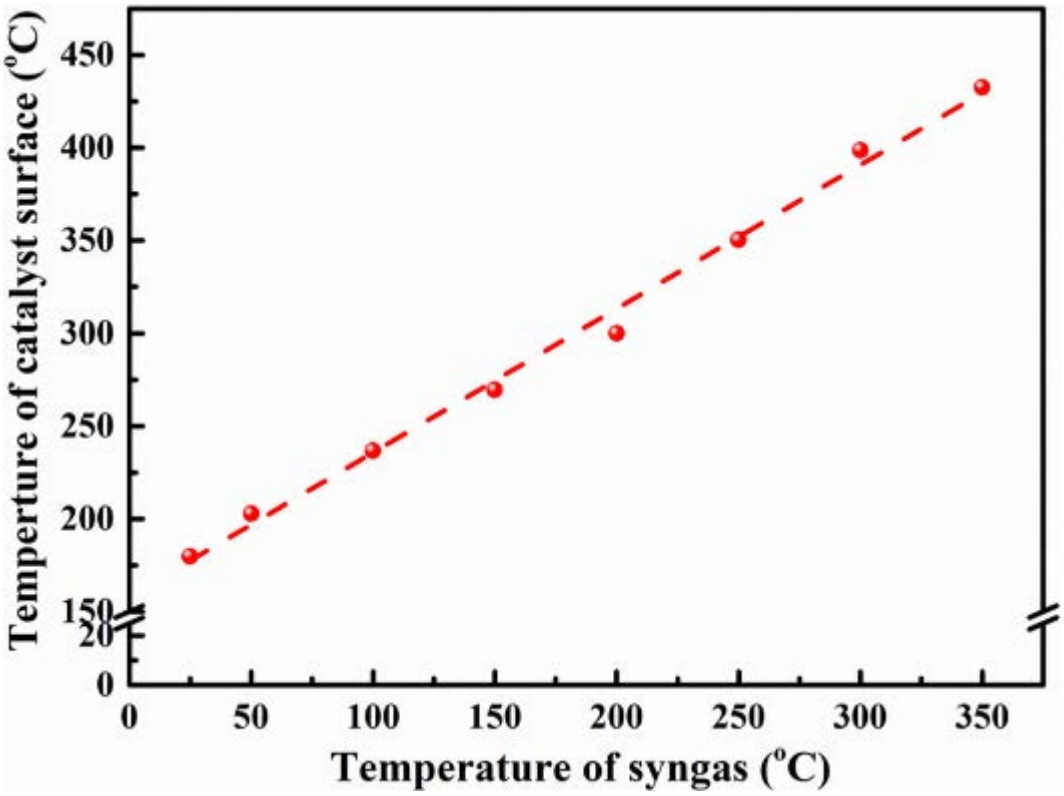

Figure S4. Temperature of catalyst surface at various syngas temperature with light intensity maintained at 650 mW cm^{-2}.

Temperature on surface of Cu/Zn/Al catalyst affected by light intensities

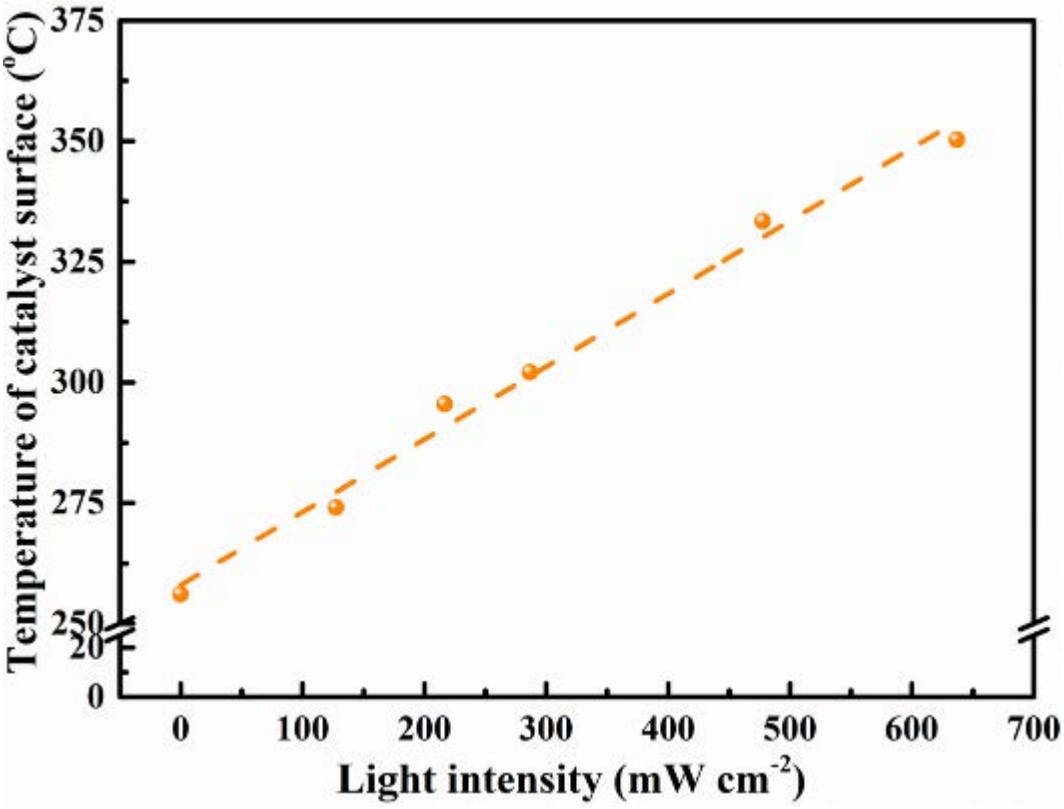

Figure S5. Heating effect of light irradiation on the temperature variation of catalyst surface with feed gas temperature maintained at 250 °C.

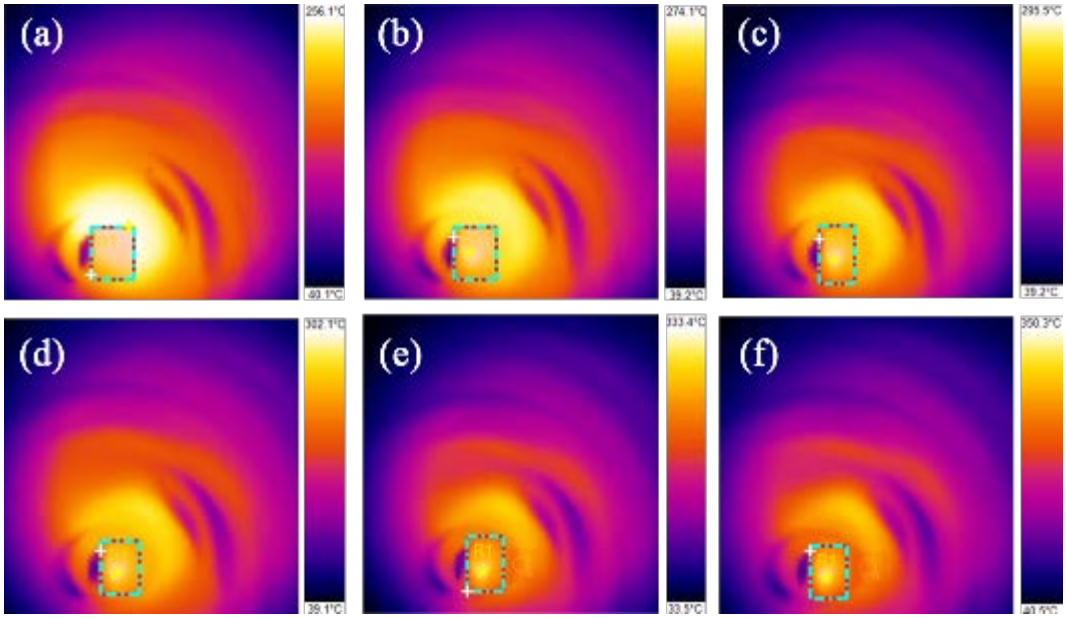

Figure S6. IR-thermographic images captured when the reactor was irradiated by exterior light field with feed gas temperature maintained at 250 ºC. Specifically, the light intensities were (a) 0 mW cm^{-2} (light off), (b) 127 mW cm^{-2}, (c) 217 mW cm^{-2}, (d) 287 mW cm^{-2}, (e) 478 mW cm^{-2}, and (f) 637 mW cm^{-2}.

TPC performance of Cu/Zn/Al at different light intensity and light source

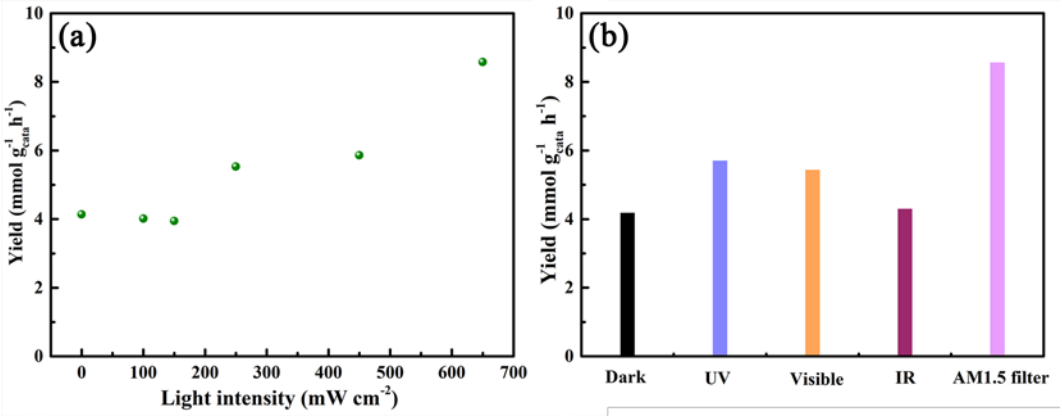

Figure S7. (a) Effect of light intensity on methanol yield for TPC process and (b) TPC production of methanol under various wave ranges (Reaction condition: Temperature of reactants=250 ^{o}C, H_2:CO=2:1, P=3MPa, GHSV=20 L $h^{-1}g_{cata}^{-1}$).

Effect of CO_2 blending in TC and TPC processes

Table S2. Methanol yields with/without CO_2 blending in TC and TPC processes.

Catalytic process	MeOH Yield (mmol g_{cata}^{-1} h^{-1})	
	$CO:H_2$=33:67	**$CO:CO_2:H_2$=27:5:68**
TC	3	8.1
TPC	8.3	15.9

(Reaction condition: P = 3 MPa, GHSV = 20 L h^{-1} g_{cata}^{-1}, Temperature of catalyst surface = 350 ^oC; Temperature of syngas = 350 ^oC for the TC process and 260 ^oC for the TPC process.)

Adsorption spectra of Cu/Zn/Al catalyst

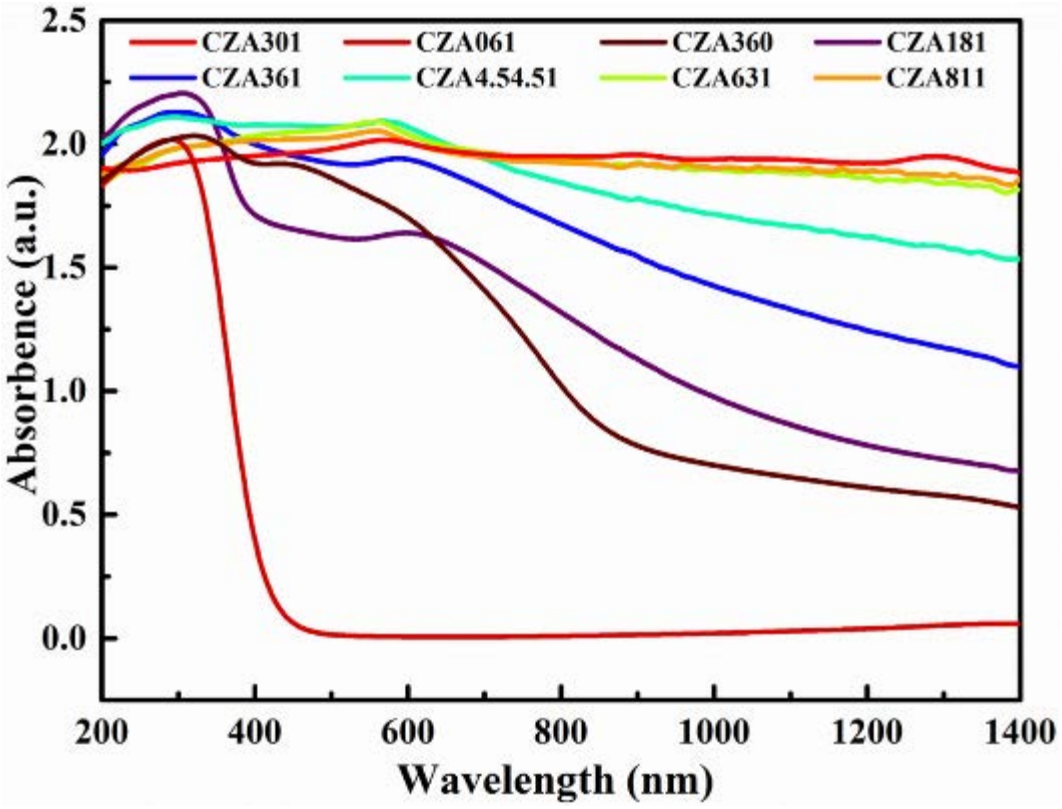

Figure S8. UV-visible spectra of hydrogen treated catalysts with different compositions

Comparative amount variation of Cu^{++} and Cu^{+} in TPC process (Figure S9.)

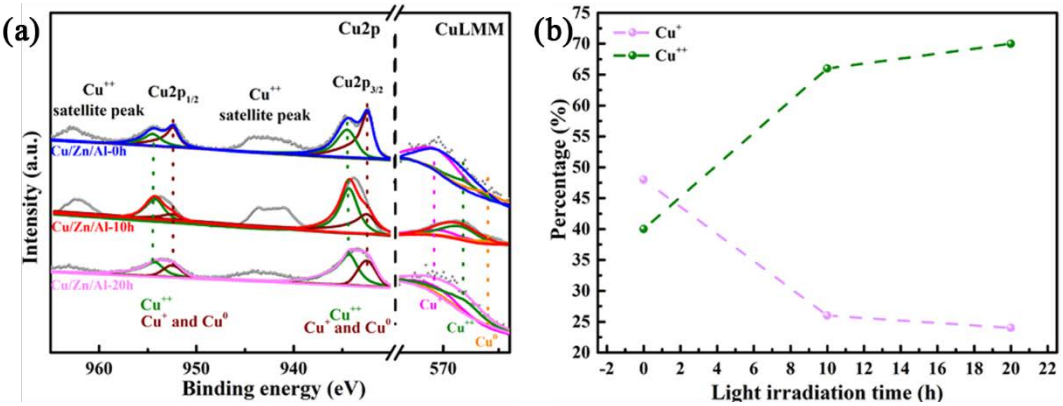

Figure S9. (a)XPS spectra of catalysts undergoing various thermo-photo catalytic periods (0h, 10h, 20h, denoted as Cu/Zn/Al-0h, Cu/Zn/Al-10h, Cu/Zn/Al-20h, respectively) and (b) variation in comparative amount of Cu^{++} and Cu^{+} in TPC process

TPC performance of Cu/Zn/Al catalysts with various composition

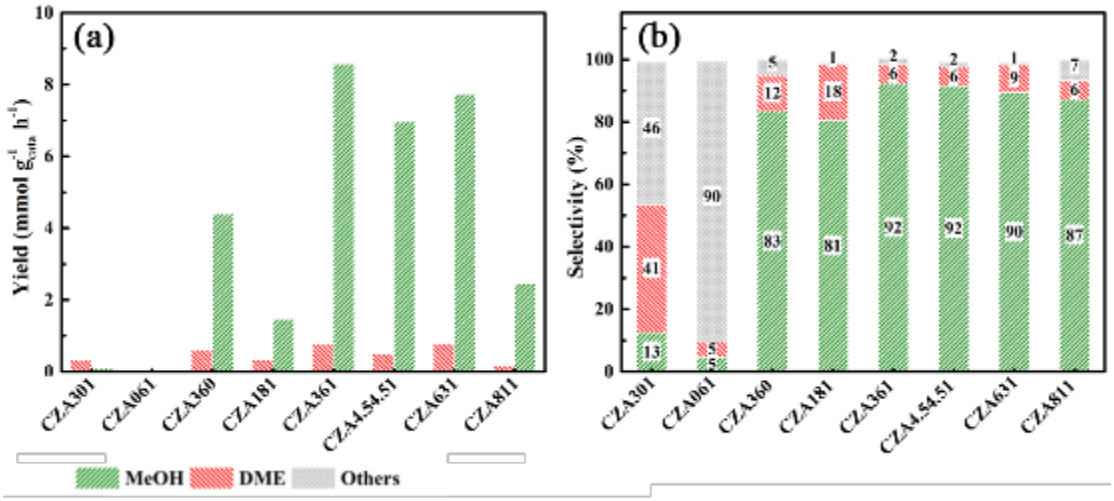

Figure S10. (a) Influence of catalysts composition on TPC methanol yield; (b) Impact of catalysts composition on TPC methanol selectivity (Temperature of catalyst surface: 350 ^{o}C, H_2:CO=2:1, P=3 MPa, GHSV=20 L $h^{-1}g^{-1}_{cata}$)

The increase in the molar ratio of Cu was favorable for the light absorption ability, which was due to the comparative lower energy band gap of CuO_x (Figure S4). The absence of copper or zinc led to negligible amount of oxygenated compounds; while the one without aluminum produced considerable amount of MeOH and DME. Therefore, the TPC performance mainly relied on Cu and Zn with Al acting as structural promoter.[2] In the meantime, redundant proportion of copper and zinc was detrimental for the TPC performance in terms of methanol yield and selectivity. The TPC performance of CZA catalyst seemed not to correlate with the BET specific surface area in Table S1, suggesting that the contribution of photocatalysis was also considerable.

Reference

(1) Baltes, C.; Vukojevic, S.; Schuth, F., Correlations between synthesis, precursor, and catalyst structure and activity of a large set of $CuO/ZnO/Al_2O_3$ catalysts for methanol synthesis. *J. Catal.* **2008,** *258,* 334-344.

(2) Behrens, M.; Studt, F.; Kasatkin, I.; Kühl, S.; Hävecker, M.; Abild-Pedersen, F.; Zander, S.; Girgsdies, F.; Kurr, P.; Kniep, B.-L.; Tovar, M.; Fischer, R. W.; Nørskov, J. K.; Schlögl, R., The Active Site of Methanol Synthesis over $Cu/ZnO/Al_2O_3$ Industrial Catalysts. *Science* **2012,** *336,* 893-897.