Supplementary Information

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Hydrogen production by steam reforming of methanol by Cu-Zn/$CeAlO_3$ perovskite

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1. *Characterization of materials*

Various physio-chemical techniques were used to characterize the catalysts. The crystallography data was obtained using a Rigaku-miniflex with CuK (1.54 Å). The BET surface area, pore volume and pore diameter were determined using nitrogen adsorption-desorption technique (Micromeritics ASAP2010). FESEM and EDX data were analysed with help of FEI Nova NanoSEM 450 and Bruker XFlash 6I30 spectrometer. HRTEM data was derived with Jeol JEM 2100 TEM instrument. The decomposition behaviour during calcination was simulated with TG-DSC in a Netzsch STA449F3 1293-M. H_2-Temperature programmed reduction (TPR) (Micromeritics AutoChem II) was performed to evaluate the metal-support interaction (MSI) of the catalyst. The XPS was carried out using Kratos Analytical (A Shimadzu Group company) Axis Supra having a PHI 5000 Versa Probe II equipped with a mono-chromatic Al Kα (1486.6 eV) X-ray source and a hemispherical analyser. Electrical compensation was applied during analysis.

2. *Experimental procedure*

Experiments were performed in a down-flow fixed bed reactor. In the beginning, reduction of the catalyst at a determined flow rate for 1 h was done in the reactor by flow of hydrogen. Then the solution containing water and methanol in a fixed proportion at pre-defined flow rate was fed using an HPLC pump. Nitrogen was chosen to be the carrier gas during the reaction. The water-methanol mixture was evaporated in a spider tube attached before the reactor and fed to the catalyst packed inside. The gaseous and liquid products were analysed by TCD and FID gas chromatography. To gauge the pressure within the system pressure transducer (range 0-10 MPa) (uncertainty ±0.01 MPa) was placed. Similarly, a temperature controller (West 6100, Germany) monitored the temperature throughout the process.

The methanol conversion was calculated using:

$$\text{Methanol conversion (\%)} = \frac{[\text{Methanol}]\text{in} - [\text{Methanol}]\text{out}}{[\text{Methanol}]\text{in}} \text{ x } 100 \qquad \text{(Eq. S1)}$$

where $[Methanol]_{in}$ and $[Methanol]_{out}$ denote the inlet and outlet molar flow rate (mol h^{-1}) of methanol.

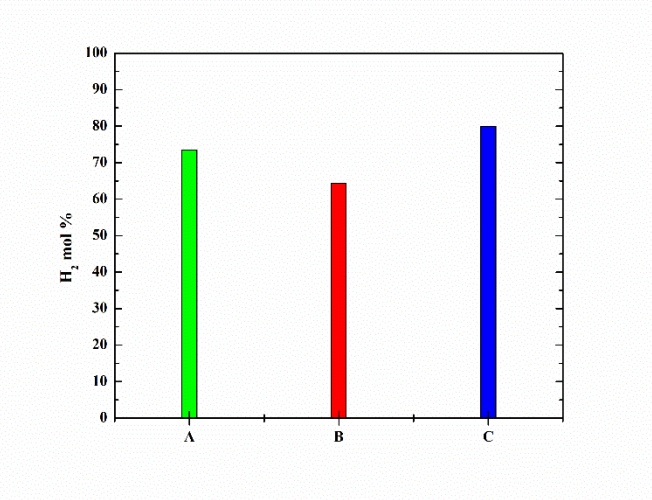
Yield of H_2 was calculated as:

$$H_2\ yield(\%) = \frac{[H_2]_{out}}{4\times[Methanol]_{in}} \times 100 \qquad \text{(Eq. S2)}$$

where $[H_2]out$ denotes the outlet molar flow rate (mol h^{-1}) of H_2.

Gas hourly space velocity (GHSV) was expressed as:

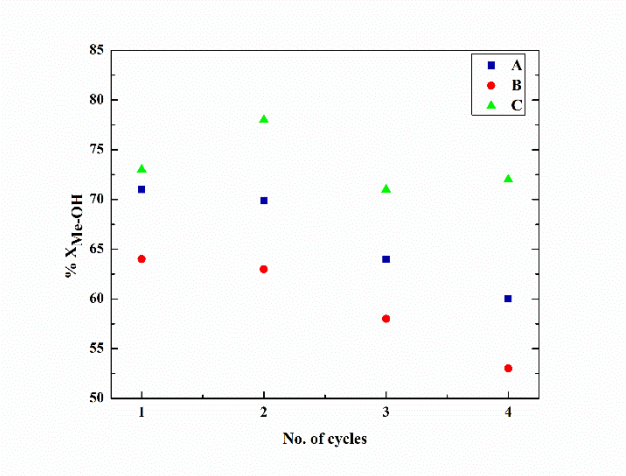
GHSV = Inlet gas flow (ml h^{-1}) / Weight of material (g) (Eq. S3)



[A – 5%Cu/$CeAlO_3$; B – 5%Zn/$CeAlO_3$; C – 5%Cu5%Zn/$CeAlO_3$]

Figure S1: H_2 product gas composition, Reaction conditions:

T - 593 K, S/C - 9, GHSV - 2700 $mLg^{-1}h^{-1}$.



[A – 5%Cu/$CeAlO_3$; B – 5%Zn/$CeAlO_3$; C – 5%Cu5%Zn/$CeAlO_3$]

Figure S2: Cyclic stability test, Reaction conditions:

T - 593 K, S/C - 9, GHSV - 2700 $mLg^{-1}h^{-1}$.

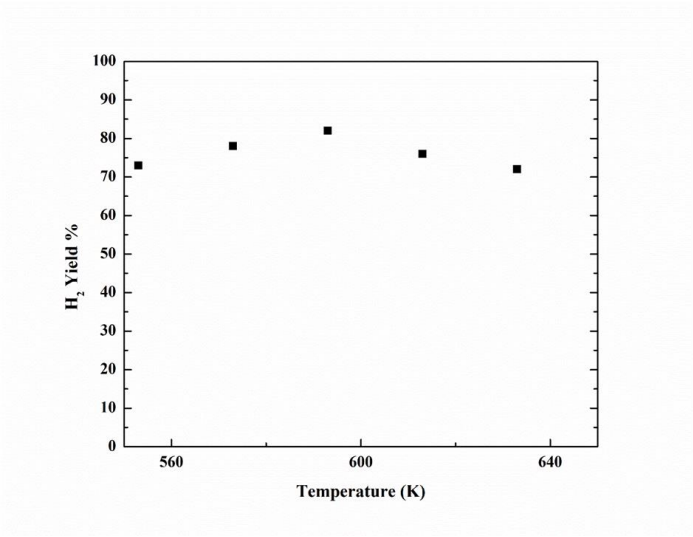


Figure S3: Effect of temperature on hydrogen yield using 5%Cu5%Zn/$CeAlO_3$, Reaction conditions: S/C - 9, GHSV - 2700 $mLg^{-1}h^{-1}$.

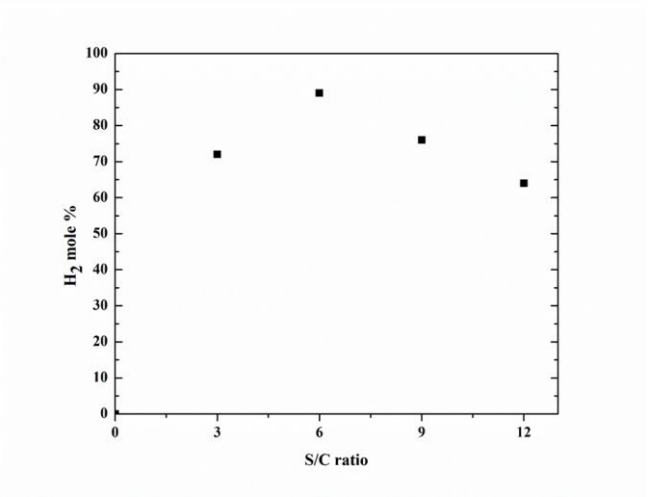


Figure S4: Effect of S/C ratio using 5%Cu5%Zn/$CeAlO_3$, Reaction conditions: temperature - 593 K, GHSV - 2700 $mLg^{-1}h^{-1}$.

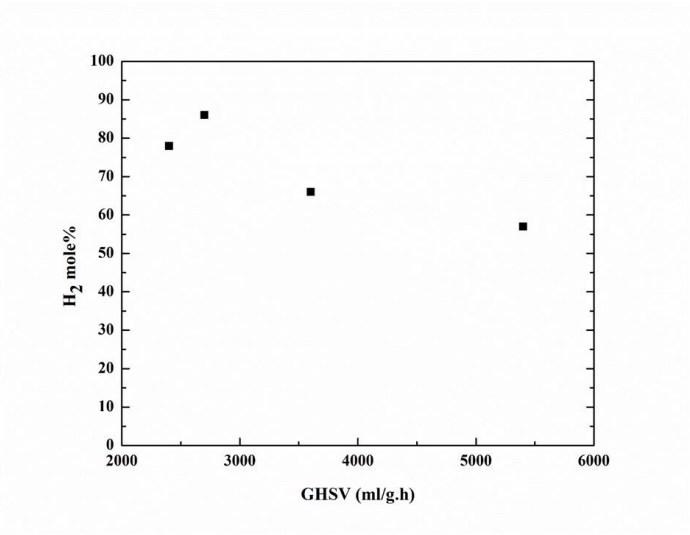


Figure S5: Effect of GHSV using 5%Cu5%Zn/$CeAlO_3$,
Reaction conditions: temperature - 593 K, S/C - 6.

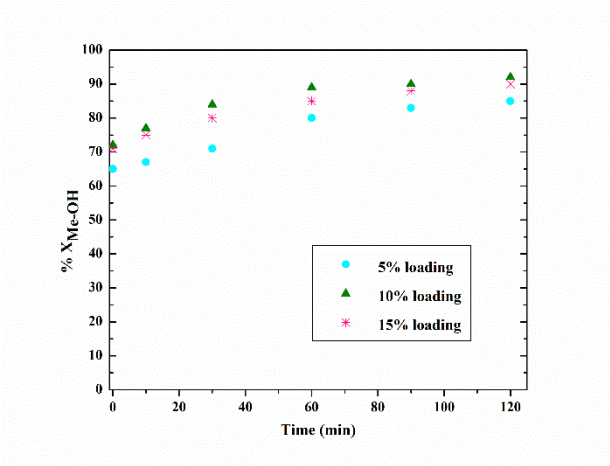


Figure S6: Effect of loading on conversion of methanol,
Reaction conditions: temperature - 593 K, S/C - 6, GHSV - 2700 $mLg^{-1}h^{-1}$.

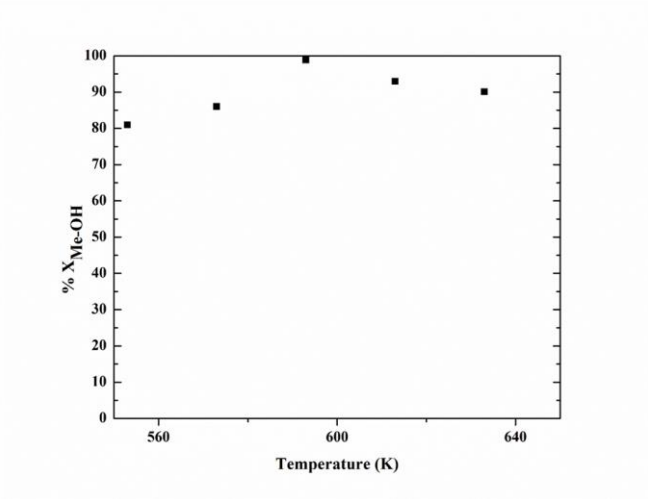


Figure S7: Conversion of methanol at different temperature using 10%Cu-10%Zn/$CeAlO_3$, Reaction conditions: S/C - 6, GHSV - 2700 $mLg^{-1}h^{-1}$.

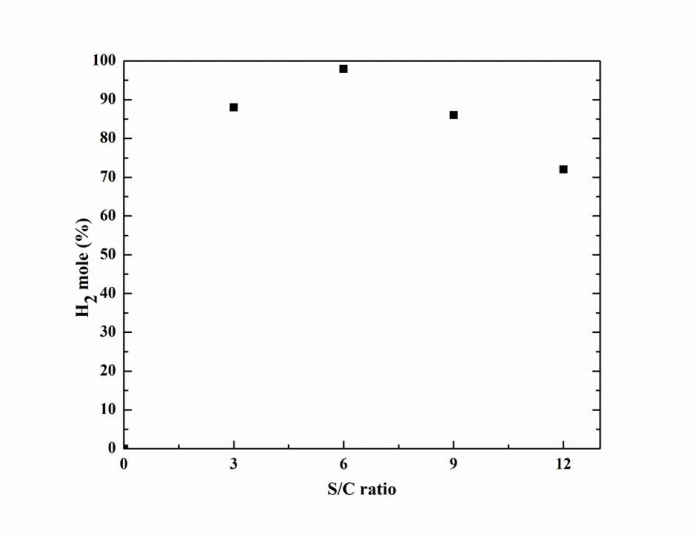


Figure S8: Effect of S/C ratio using 10%Cu-10%Zn/$CeAlO_3$, Reaction conditions: temperature - 593 K, GHSV – 2700 $mLg^{-1}h^{-1}$.

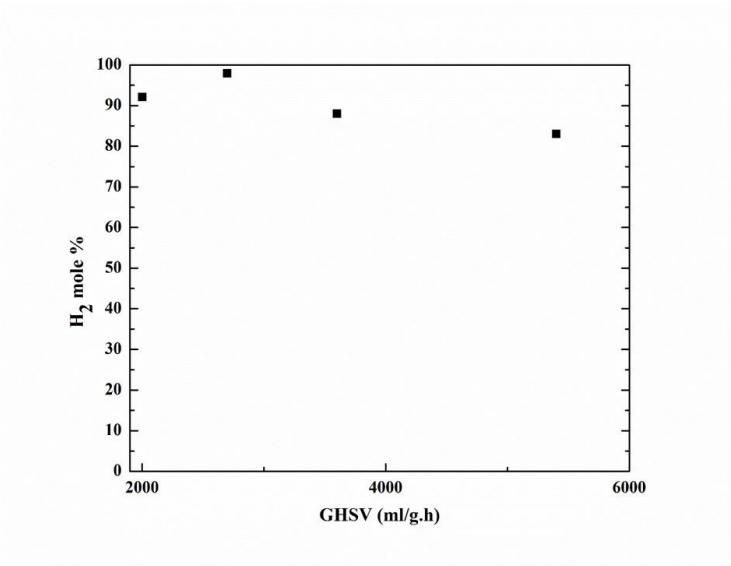


Figure S9: Effect of GHSV using 10%Cu-10%Zn/$CeAlO_3$, Reaction conditions: temperature - 593 K, S/C - 6.