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Mechanism of methanol steam reforming with inverse ZrO_2/Cu catalyst

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Experimental section

Catalyst preparation

In the experiment, $Zr(NO_3)_4{\cdot}5H_2O$ (analytical grade, AR) was obtained from Macklin company (China), $Cu(NO_3)_2{\cdot}3H_2O$ (analytical grade, AR) and anhydrous oxalic acid (analytical grade, AR) were purchased from Aladdin company (China). Anhydrous ethanol (analytical grade, AR) was obtained from Shanghai Chemical Reagent Company (China).

The inverse ZrO_2-x/Cu (x is weight content of ZrO_2) catalyst was prepared using the oxalate sol-gel method. Take ZrO_2-0.25/Cu for example, 0.87 g of $Zr(NO_3)_4{\cdot}5H_2O$ and 2.85 g of $Cu(NO_3)_2{\cdot}3H_2O$ were dissolved in 50 mL of anhydrous ethanol. Subsequently, 1.35 g of anhydrous oxalic acid was dissolved in 30 mL of anhydrous ethanol. After that, the solutions were mixed and stirred vigorously at room temperature for 0.5 h and then aged for 2 h. The suspension was centrifuged three times at 5000 r/min, washed with anhydrous ethanol, and dried at 100 ^{o}C for 12 h. Finally, the dried material was calcined at 450 ^{o}C for 3 h to yield the ZrO_2-0.25/Cu catalyst.

Catalyst characterization

X-Ray Diffraction (XRD) pattern of the catalyst was performed on the Rigaku SmartLab SE diffractometer (Japan) at 35 kV and 25 mA at a scanning rate of 5^{o} min^{-1}. The surface structure was observed by Transmission Electron Microscope (TEM) on the JEOL JEM-F200 machine (Japan). Actual metal content of Zr and Cu was determined by the Inductively Coupled Plasma Optical Emission Spectrometry (ICP-

OES) on Thermo Fisher iCAP PRO (America) instrument. BET surface area was obtained on the Micromeritics ASAP 2460 machine (America).

Temperature-programmed desorption (TPD) experiment was performed on the TP-5850-α instrument (China) with a thermal conductivity detector (TCD). For the catalysts, three pre-treatment conditions were investigated. For the fresh ZrO_2-0.25/Cu without other pre-treatment condition, the sample was abbreviated as ZrO_2-0.25/Cu-dried. For the fresh ZrO_2-0.25/Cu under H_2O-bubbling atmosphere (H_2O bubbling in He flow (30 mL/min) for 30 min), the sample was labelled as ZrO_2-0.25/Cu-humidified. For the fresh ZrO_2-0.25/Cu after reduced (H_2/He mixed gas (5 vol% H_2)) for 30 min, 300 ^{o}C), the sample was named as ZrO_2-0.25/Cu-reduced. 50 mg catalyst (ZrO_2-0.25/Cu-dried, ZrO_2-0.25/Cu-humidified, or ZrO_2-0.25/Cu-reduced) was heated under He atmosphere (30 mL/min) to 800 ^{o}C at a ramping rate of 5 ^{o}C/min, and the signal was recorded by TCD.

In situ DRIFTS experiments were conducted on a Bruker INVENIO R spectrometer. Similarly, the catalysts were pre-treated under identical conditions in the TPD experiment mentioned above (ZrO_2-0.25/Cu-dried, ZrO_2-0.25/Cu-humidified, or ZrO_2-0.25/Cu-reduced). Firstly, the catalyst was loaded into the chamber with a diamond coated with ZnSe window and was flushed with He gas (30 mL/min) for 30 min, which was connected to a homemade device pumped down to $1*10^{-5}$ Pa by an SH-110 Dry Scroll Vacuum pump (Agilent technologies) at 25 ^{o}C to collect background. Secondly, the methanol was introduced into the system by the natural negative pressure until the pressure reaching $1.8*10^{-5}$ Pa. Thirdly, the system was evacuated to $1*10^{-5}$ Pa to remove physically adsorbed methanol. Finally, the system was heated from 25 ^{o}C to 250 ^{o}C at the interval of 25 ^{o}C to collect the corresponding spectrum.

Catalyst evaluation

The MSR reaction was carried out on a fixed-bed reactor (Fig. S1). 200 mg ZrO_{2-x}/Cu catalyst was placed into the reactor with an inner diameter of 9 mm and length of 450 mm. Initially, the catalyst was reduced with H_2/N_2 mixed gas (5 vol% H2, 30 mL/min) at 300 °C for 2 h. Subsequently, the atmosphere was switched to pure N_2 at a flow rate of 30 mL/min, and the temperature was adjusted to required temperature. Methanol and H2O mixed solution (molar ratio of 1:1) was introduced into the reactor by a peristaltic pump at a flow rate of 2 g/h. The effluent was analyzed by a gas chromatograph (GC9890B, Linghua Company).

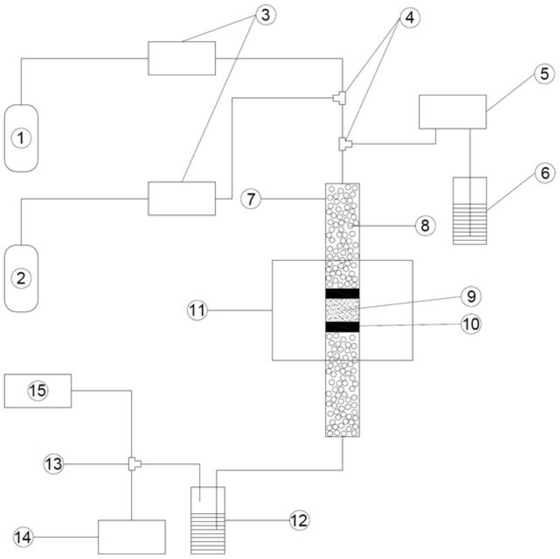

Fig. S1. Gas - solid phase catalyst evaluation reaction apparatus.

1. A 5% H_2/N_2 gas cylinder with an output pressure of 0.3 MPa.

2. A N_2 gas cylinder with an output pressure of 0.3 MPa.

3. Mass flow meters with an output pressure of 1 atmosphere and a measuring range of 100 mL/min each.

4. A three-way connector for connecting the gas circuit.

5. A metering pump (Oushisheng, DPS - 10).

6. A 50 wt.% methanol - water solution.

7. A quartz tube with an outer diameter of 25 mm and an inner diameter of 9 mm.

8. Quartz sand, with the mesh number gradually increasing from both ends to the center of the tube, varying from 16 mesh to 70 mesh.

9. Catalysts.

10 .Quartz wool, 4 - 6 μm.

11. A heating furnace with a constant - temperature zone of 200 mm.

12. A sealed 30 - mL sample bottle, sealed with a rubber stopper, containing deionized water for absorbing the reaction methanol.

13. A three - way ball valve for switching the gas circuit.

14. Atmospheric environment.

15. A soap - film flowmeter for analyzing gas flow rate.

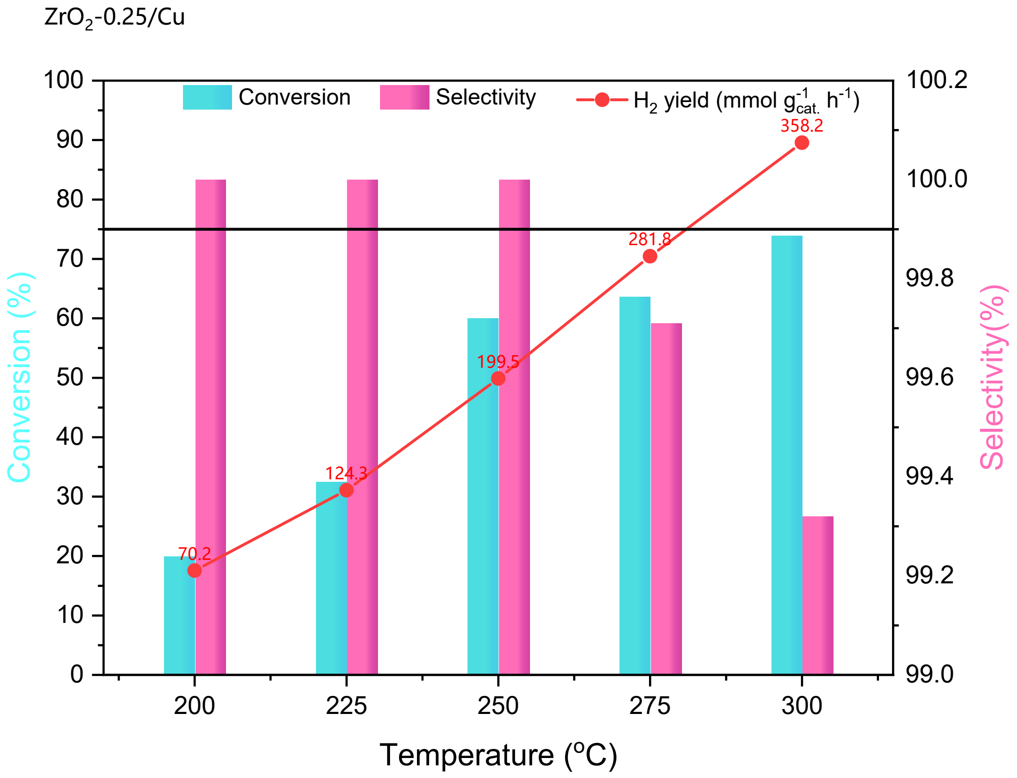

Fig. S2. Catalytic performance of ZrO$_2$-0.25/Cu.

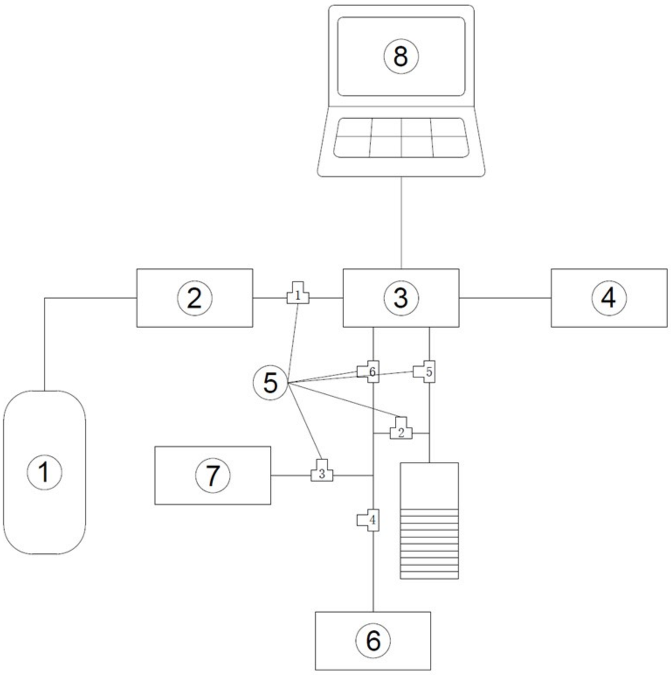

Fig. S3. Infrared Analysis Flowchart.

1.A 5% H_2/N_2 gas cylinder with an output pressure of 0.3 MPa.

2.Mass flow meters with an output pressure of 1 atmosphere and a measuring range of 100 mL/min.

3.In-situ reaction cell equipped with infrared spectroscopy.

4.Temperature control system.

5. The two-way ball valve, and the numerical values denote the valve identification number.

6.Vacuum pump, capable of pumping pressure down to 1 Pa.

7.Atmospheric environment.

8.OPUS software analysis system.

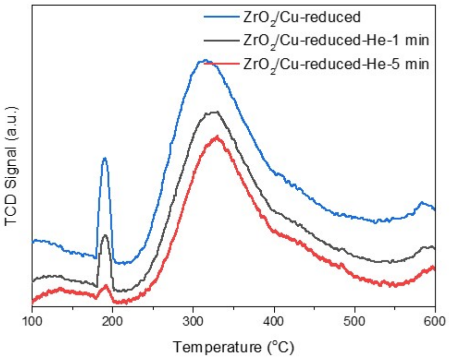

Fig. S4. H_2O-TPD spectra of ZrO_2/Cu-reduced, ZrO_2/Cu-reduced-He-1 min (ZrO_2/Cu-reduced treated under He flow for 1 min at 180 ^{o}C), and ZrO_2/Cu-reduced-He-5 min (ZrO_2/Cu-reduced treated under He flow for 5 min at 180 ^{o}C).

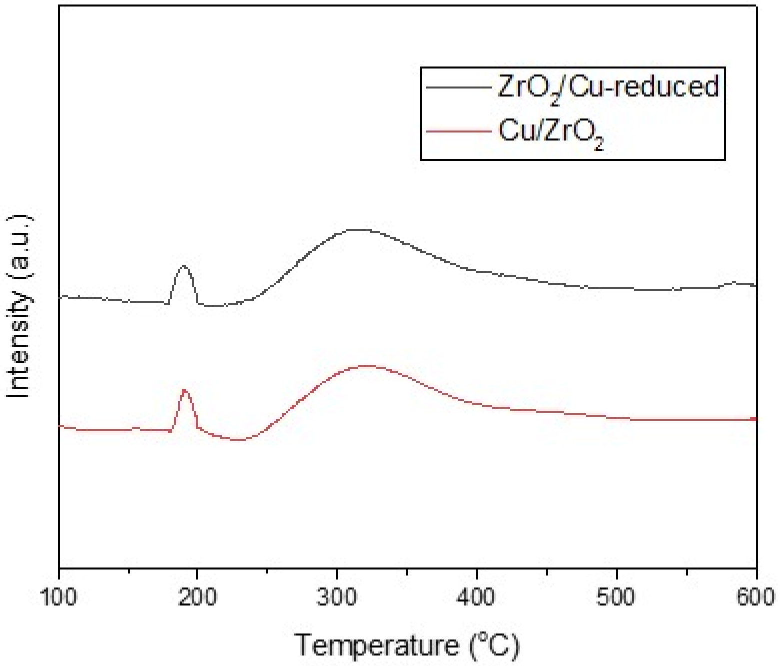

Fig. S5. H_2O-TPD spectra of ZrO_2/Cu-reduced, and traditional Cu/ZrO_2.

Semi-quantitative peak deconvolution of OH

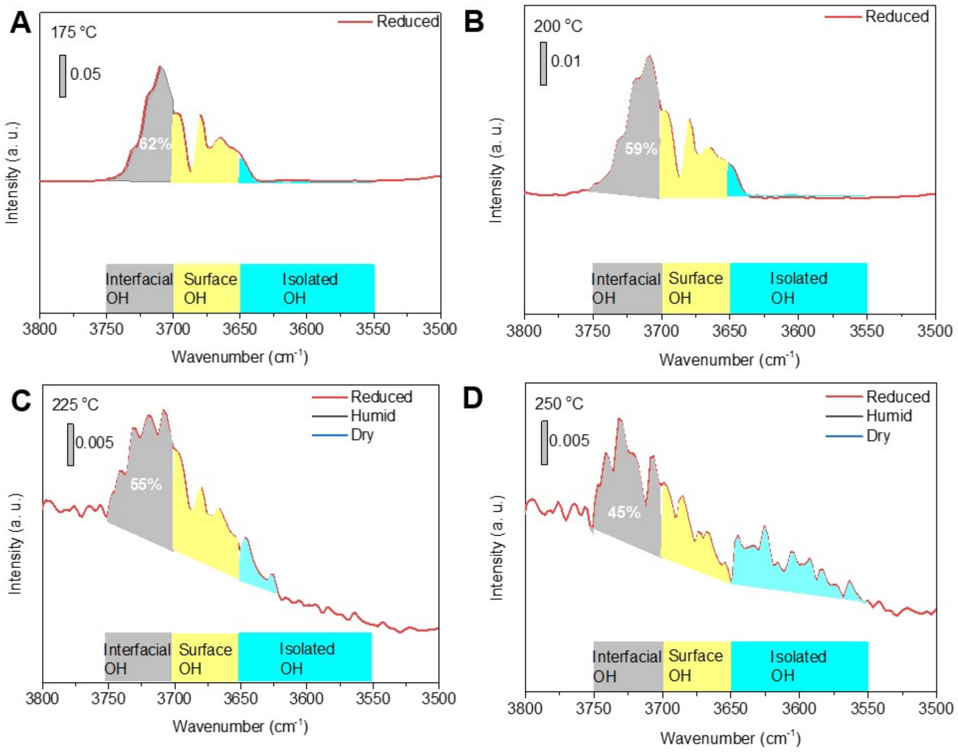

Fig. S6. Amplified *in situ* DRIFTS (3800-3500 cm^{-1}, to differentiate surface OH from interfacial OH) of ZrO_2/Cu-reduced, ZrO_2/Cu-humidified, and ZrO_2/Cu-dried after methanol reaction for 3 min at different temperatures.

To better understand the critical role of interfacial OH playing in the MSR reaction, we have deconvoluted the OH peaks. For the ZrO_2/Cu-humid and ZrO_2/Cu-dry, the OH contents are very low, so, we only calculate the interfacial OH content for ZrO_2/Cu-reduced for accuracy.

For ZrO_2/Cu-reduced with abundant OH, with the increase of reaction temperature (175-250 ^oC), we could find that the peak area of OH decreases obviously, which is caused by the depletion of OH. Moreover, with the increase of reaction temperature, the ratio of interfacial OH decreases (from 62% to 45%), corresponding with the reaction of interfacial OH with methanol and the transformation between interfacial OH and surface/isolated OH.

Table S1. Structure information of ZrO_2-0.25/Cu catalyst.

Catalyst	ZrO_2 loading[a] (wt.%)	Crystalline size (nm)[b]			
		Fresh		Reduced	
		CuO	t-ZrO_2	Cu	t-ZrO_2
ZrO_2-0.25/Cu	22.01	10-15	3-4	15-20	3-4

[a] Determined by ICP-OES.

[b] Derived from TEM.

Table S2. Catalytic performance of ZrO_2-x/Cu.

Catalyst	**Temperature (°C)**	**Conversion[*] (%)**	**Selectivity[*] (%)**	**H_2 yield[*] (mmol $g_{cat.}^{-1}$ h^{-1})**
	200	8.7	100	52.6
	225	24.8	100	105.2
ZrO_2-0.05/Cu	250	37.5	100	164.8
	275	50.0	99.6	264.1
	300	67.6	99.3	336.3
	200	19.9	100	70.2
	225	32.4	100	124.3
ZrO_2-0.25/Cu	250	60.0	100	199.5
	275	63.6	99.7	281.8
	300	73.8	99.3	358.2
	200	11.3	100	50.3
	225	23.7	100	155
ZrO_2-0.5/Cu	250	37.6	100	162.5
	275	48.2	99.7	241
	300	62.5	99.4	281.1

[*] Pretreatment was conducted at 300 °C utilizing a reducing atmosphere comprising 5% H_2 in N_2 at a constant flow rate of 30 mL/min over a duration of 2 hours. Thereafter, the catalytic activities of various catalysts were evaluated at distinct reaction temperatures, employing a space-time velocity of 10 h^{-1}, a catalyst mass of 200 mg, and an N_2 flow rate maintained at 30 mL/min.