Supporting Information

Electrochemical Synthesized Cu-Mg Mesh Catalysts for Methanol Steam Reforming

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Experimental Methods

Materials and chemicals. The pieces of commercial customized 6 cm × 6 cm copper mesh (200 mesh, 0.05 mm wire diameter, 99.99% purity) were purchased from Anping County Chulin Metal Mesh Co., Ltd. Methanol (CH₃OH (MeOH), 99.99%) was purchased from Adamas-beta. Sodium nitrate (NaNO₃, AR) was purchased from Shanghai Titan Scientific Co., Ltd. Magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O, AR) was purchased from Sinopharm Chemical Reagent Co., Ltd. The Ar, N₂O, 10% H₂/90% N₂, and CO₂ gases were purchased from Shanghai Air Liquide Compressed Gas. All chemicals were used as received without further purification and ultrapure water (Millipore, 18.2 MΩ cm) used for all processes.

Materials synthesis. The pieces of commercial customized copper mesh were first cleaned by sonication in ethanol and ultrapure water for 10 min, respectively. Then, two copper pieces were chronopotentiometrically cycled in an electrolyte of metal nitrate solution by applying an alternating current of ± 240 mA (each segment for 30 s) for 200 segments on an electrochemical station (CORRTEST CS310X). Note that the area of the copper mesh immersed into the electrolyte is around 24 cm² (6 cm × 4 cm), therefore the current density is fixed at 10 mA/cm². *x*-CM was synthesized in the electrolyte of 0.02, 0.05 and 0.08 mol/L NaNO₃ solution, denoted as 0.02CM, 0.05CM and 0.08CM. *x*-CMM was synthesized in the electrolyte of 0.02, 0.05 and 0.08 mol/L Mg(NO₃)₂ solution, obtaining 0.02CMM, 0.05CMM and 0.08CMM. After the electrochemical synthesis process, the copper mesh catalysts were immersed into ultrapure water with 5 min sonication to remove blockage. Finally, the copper mesh catalysts were dried at 60 °C for 2 h and prepared for further treatments.

Characterizations. Scanning electron microscope (SEM) was performed on a Nova NanoSEM 450 field emission SEM, which was operated at the accelerating voltage of 15 kV and the detector current of 10 mA.

The content of Cu (W_{Cu}) was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (Agilent 725ES) for powder catalysts. Notably, for copper mesh catalysts, we first measure the mass of the catalyst as M1, and then subject the catalyst to acid etching to remove the deposition layers, obtaining the mass of the substrate (M_2). The Cu content in deposition layer (W_{Cu} , $_{deposit}$) was determined by ICP-OES. $W_{Cu} = W_{Cu, deposit} \times (M_1 - M_2)/M_1$, referring to the ratio of the mass of Cu in the deposition layer to the total mass of the copper mesh catalyst.

The exposed Cu surface area was determined by N_2O reactive frontal chromatography (N_2O -RFC) using a TP5000 (Tianjin Xianquan) instrument with a thermal conductivity detector (TCD). First, the fresh catalyst (50 mg) was pretreated in Ar atmosphere at 300 °C for 30 min. Then, the pretreated catalyst was treated by a temperature-programmed reduction (TPR) process in a 10%H₂/90%N₂ flow within the range of 30-300 °C at a heating rate of 10 °C/min to obtain the H₂-TPR curve. The corresponding hydrogen consumption was denoted as A₁. The reduced catalyst was then cooled to 50 °C in N₂, and the gas was switched to N₂O for 30 min to mildly oxidize surface Cu atoms to Cu₂O. Afterwards, the sample was flushed by Ar for 30 min, and measurement of TPR with hydrogen was performed by increasing the temperature from 50 to 300 °C at a rate of 10 °C/min. The corresponding hydrogen consumption was denoted as A₂. Next, the exposed Cu surface area (S_{Cu}) was calculated according to the equation S_{Cu} (m²/g) = $(2A_2 \times N_A \times W_{Cu})/(A_1 \times M_{Cu} \times 1.4 \times 10^{19})$, and the dispersion of Cu (D_{Cu}) was calculated according to the equation D_{Cu} (%) = $2A_2/A_1 \times 100\%$, where N_A is Avogadro's constant, W_{Cu} is the content of Cu, M_{Cu} is the molar mass of Cu, and 1.4×10^{19} means number of copper atoms per square meter on average. Note that the copper mesh catalyst was cut into 4 mm diameter discs to load into the quartz tube for the test.

The quantity or proportion of various basic sites on the samples was characterized by CO_2 temperature-programmed desorption (CO_2 -TPD) using the same chemisorption analyzer (TP5000). 50 mg sample was pretreated in Ar atmosphere at 300 °C for 30 min, and then cooled to 60 °C. Afterwards the gas was switched to CO_2 stream (50 mL/min) until CO_2 adsorption was saturated. The temperature was then raised from 60 to 700 °C at a linear rate of 10 °C/min and the TCD signals were recorded simultaneously.

In situ X-ray diffraction analysis was performed on a Bruker D8-Advance X-

ray diffractometer with a Cu K α ray source (wavelength, $\lambda = 0.154$ nm) at 40 kV and 40 mA. The copper mesh catalyst was cut into 6 mm diameter discs to load into a customized in situ cell appropriately, heated up to 250 °C with Ar. After heating 1 h, the reactants with a H₂O/MeOH molar ratio of 1.3:1 were introduced into the cell by bubbling Ar through a saturator filled with liquid H₂O/MeOH. The X-ray diffraction patterns were collected over a 20 (angle between transmitted X-ray beam and reflected beam) range of 30-80° with a resolution of 0.02°. The average particle size of each crystal phase (CuO, Cu) in these catalysts before and after the reaction was calculated via the Scherrer

$$D = \frac{K \times \lambda}{\beta \times c \ \rho \ s} \theta \quad \text{i} \quad D = \frac{K \times \lambda}{\beta \times c \ \rho \ s} \theta$$

equation: $\beta \times c \ o \ s \ \theta$ where D is the crystalline size (Å), K = 0.94 is applied here, λ is the X-ray wavelength (Å), β is the full width at half-maximum (fwhm) of the peak expressed in radians, and θ is the Bragg angle.

Scanning transmission electron microscopy (STEM) measurements were performed using a ThermoFisher Talos F200X. For High-angle annular darkfield STEM characterization, a half convergence angle of 11 mrad was used, and the internal and external collection angles were 59 and 200 mrad, respectively. Energy dispersive X-ray spectroscopy (EDS) was measured with 4 Super-X detectors in the column.

Quasi *in situ* X-ray photoelectron spectra were collected using a Thermo ESCALAB 250Xi spectrometer equipped with a monochromatic Al K α radiation source (1486.6 eV; pass energy, 20.0 eV). A pretreatment chamber was used for the catalyst heat or reaction treatments. Afterwards, the chamber

was evacuated, and the sample was directly transferred into the vacuum analysis chamber to avoid exposure to air. The binding energies were calibrated using the C1s peak at 284.8 eV as a reference.

An *in situ* Fourier transform infrared spectrometer (PerkinElmer, Spectrum 3) equipped with a diffuse reflection cell (Jiaxing Puxiang Tech. Ltd., RC-DRS-K01) was used for in situ DRIFTS analysis. Spectra were collected with a spectral resolution of 4 cm⁻¹, and each spectrum was the average of 64 scans. About 20 mg of the copper mesh catalyst was cut into 6 mm diameter discs to place into a customized reaction cell appropriately. For in situ temperature-programmed DRIFTS, the catalyst was first heated in Ar at 300 °C for 30 min and then cooled to 25 °C. Afterwards, reactants with a H₂O/MeOH molar ratio of 1.3:1 were introduced into the reactor by Ar for 30 min. The samples were then heated to 300 °C at a rate of 5 °C/min in flowing Ar, with the spectra collected every minute.

Catalytic activity evaluation. The MSR reaction measurements were conducted in a continuous plug flow fixed-bed reactor with a 4 mm inner diameter. Before the test, the copper mesh catalyst was cut into 4 mm diameter discs and then in situ pretreated under different conditions. An aqueous methanol solution with a specific H₂O/MeOH ratio of 1.3 was injected into the heated chamber by a syringe pump (0.02 mL/min) to evaporate the liquid. The steam was then mixed with the desired amount of Ar (30 mL/min) as the carrier

gas and introduced into the catalyst bed for reaction. The reactor effluent was separated in a phase separator and analyzed by online gas chromatography equipped with a methanizer and flame ionization detector and a thermal conductivity detector. H₂ yield and the selectivity of products were calculated according to equations (4) and (5). TOF of H₂ was calculated using equation (6) at 250 °C, with methanol conversions below 10%:

$$H_2 \text{ yield}=F(H_2, \text{out})/m_{cat}$$
 (4)

$$S_x$$
 selectivity = $F(x,out)/(F(CO,out)+F(CO_2,out)) \times 100\%$ (5)

Intrinsic activity=
$$H_2$$
 yield/ S_{cu} (6)

where F(x, out) represents the outlet molar flow rate of x (x = CO, CO₂), m_{cat} is the mass of loaded catalyst, and S_{Cu} is the exposed Cu surface area.



Figure S1. H_2 yields of 0.05CMM catalysts prepared with different electrochemical parameters.



Figure S2. H_2 yields of 0.05CMM catalysts prepared with different pretreatment conditions.



Figure S3. H_2 -TPR curves (a) and 2nd- H_2 -TPR curves (b) of CM and CMM catalysts.



Figure S4. Cu dispersion (D_{Cu}) and transition frequency (TOF) of CMM.



Figure S5. Weight loss of 0.02CMM, 0.05CMM and 0.08CMM catalysts after an ultrasonic treatment in water for 1 h.



Figure S6. Mg 1s XPS spectrum of CMM after reaction.



Figure S7. In situ temperature-programmed DRIFTS spectra collected with an increasing temperature to 300 °C at a ramping rate of 5 °C min⁻¹ in Ar for 0.05CM.

Catalysts	Content of Mg (wt.%) ^{<i>a</i>}	Content of Cu (wt.%) ^{<i>a</i>}
0.02CMM	5.03 ± 0.15	36.18 ± 0.24
0.05CMM	9.46 ± 0.27	43.32 ± 0.21
0.08CMM	8.48 ± 0.21	47.83 ± 0.39

Table S1. Mg and Cu content on copper mesh catalysts.

^{*a*} Mg and Cu content in deposition layer is determined by ICP-OES. Note that the content of Mg and Cu in the copper mesh catalyst refers to the ratio of the mass of Mg and Cu in the deposition layer to the total mass of the catalyst.

Catalyst	Preparation method	T/∘C	WHSV/h ⁻¹	H ₂ O/MeOH	H_2 yield (mmol·g ⁻¹ ·h ⁻¹)	Ref.
0.05CMM	modified cycling chronopotentio metry method	250	12	1.3	205.8	This work
Cu-Mg-Zn/Al	Facile coprecipitation	200	3.8	1.0	172.1	[1]
CuO/CeO ₂ -R	Hydrothermal	260	800 ^a	1.2	54.7	[2]
CuO/ZnO/Al ₂ O ₃ - <i>x</i> Fe	coprecipitation	200	12	1.3	132.5	[3]
CuO/ZnO/ZrO ₂	coprecipitation	200	6	1.3	117.4	[4]
Cu_{25} - Fe_{12}/Al_{63}	Impregnation	220	800	1.2	364.3 ^b	[5]
Cu/CeO ₂ /ZnO	coprecipitation	200	6	1.3	94.6	[6]
Cu-Co-Al	solidification and casting	300	-	1.0	12.3 ^b	[7]

Table S2. Studies on the copper-based catalysts for MSR reactions.

Superscript: a: Gas hourly space velocity (cm³·g⁻¹·h⁻¹), b: H₂ yield (mL·kg⁻¹·s⁻¹).

Catalyst ^a	H_2 yield $(mmol/(g_{cat} \cdot h))^b$	CO selectivity(%) ^b	CO_2 selectivity(%) ^b
СМ	-	-	-
0.02CMM	111.63	0.29	99.71
0.05CMM	205.82	0.15	99.85
0.08CMM	144.26	0.17	99.83

 Table S3. MSR catalytic performance of copper mesh catalysts.

^{*a*} All represents the 30 min Ar pretreatment at 300 °C.

^{*b*} The H_2 yields and selectivities of CO were averaged over 3 h.

Sample	Mass before	Mass after	Mass loss
	treatment (g)	treatment (g)	(wt.%)
1	0.0186	0.0113	39.2
2	0.0228	0.0134	41.2
3	0.0118	0.0070	40.5
4	0.0108	0.0080	25.9
5	0.0336	0.0257	23.6
6	0.0142	0.0104	26.6

Table S4. Evaluation of the mass distribution of Ar treated sample via acidetching methods.

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