Supplementary information

Hydrogen production via methanol steam reforming by using sepiolite-derived Cu-based spherical micro-mesoporous catalysts

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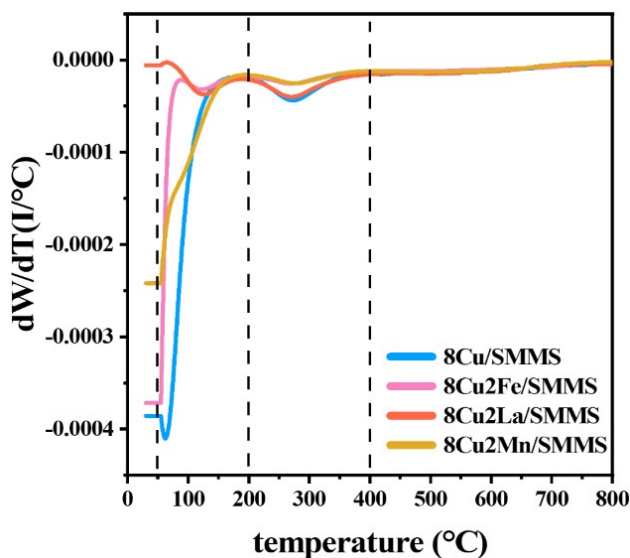
Fig.S1 **The DTG curves of spent 8Cu/SMMS, 8Cu2Fe/SMMS, 8Cu2La/SMMS and 8Cu2Mn/SMMS.**

Table S1: The element content in supports and as-prepared catalyst

Samples	element content (%)						
	Cu	Fe	La	Mn	Si	Al	Mg
SEP	/	/	/	/	38.97	15.19	0.22
SSS	/	/	/	/	34.12	14.92	0.35
SMMS	/	/	/	/	52.14	0.73	0.06
8Cu/SMMS	8.21	/	/	/	23.53	0.04	0.01
8Cu2Fe/SMMS	8.16	2.25	/	/	18.95	0.04	0.01
8Cu2La/SMMS	7.99	/	2.19	/	21.23	0.03	0.01
8Cu2Mn/SMMS	8.42	/	/	1.69	31.33	0.03	0.01

Table S2: Catalyst characterizations

Characterization	Instruments	Test conditions
ICP-OES	Agilent TCP-OES 5110 (US)	Each prepared sample was digested in an acidic solution
XRD	SmartLab SE (Cu Kα target, λ = 1.5406 Å) (Japan)	Scanning range: 5-85º; scanning step length rate: 2º/min; operating voltage: 40 kV; current: 40 mA.
SEM	ZEISS G5000 (Germany)	Operating voltage: 3.0 kV
HRTEM	Tecnai G2 F20 (USA)	Dispersing catalysts on carbon grids in ethanol under supersonic wave shaking.
N_2 adsorption-desorption	ASAP 2420 (USA)	Vacuum degassing: 250 ℃ for 4; the Calculated methods: Brunauer Emmett Teller and Barrett Joiner Halenda (BJH).

H$_2$-TPR	Auto Chem II 2920 (America)	Pretreatment: 50 mL/min Ar flow, 200 °C for 1 h; heated to 700 °C/min: 10 vol% H$_2$/Ar flow (50mL/min)
NH$_3$(CO$_2$)-TPD	Auto Chem II 2920 (America)	Pretreatment: 10mL/min He flow, 200 °C for 1 h; reaction: 5 % NH$_3$(CO$_2$)/He flow, 1 h; washing: 10mL/min He flow, 120 °C for 1 h; Record (TCD): 10 °C/min, 120 °C to 700 °C.
FT-IR	Nicolet 3800 (USA)	All catalysts were separately diluted with the spectral KBr powder; wavelength range: 4000-500 cm^{-1}; resolution: 2 cm^{-1}
XPS	ESCALAB 250Xi (monochrome Al Kα source: 1486.68 eV) (UK)	Beam spot onditions : 150 W and 500 μm; internal standard: C1s peak (284.8 eV)
EPR	Bruker A300 (GER)	Each test was performed with 50 mg of sample and evacuated to vacuum prior to measurement.
TGA	METTLER TGA2 (Switzerland)	During the test, the sample was raised from room temperature to 700 °C with the heating rate of 10°C/min under 50 mL/min air flow.

Table S3 Researchers in MSR and the corresponding catalytic activity

Catalyst	Temperature (°C)	S/C	Feed rate (h^{-1}) or space-time ration	H_2 productivity (mmol·$g_{cat.}^{-1}$·h^{-1}) or selectivity (%)	methanol Conversion (%)	CO selectivity (%)	References
Cu/MCM-41	350	3	2838 (GHSV)	99.5	82.3	17.7	[1]
Pd/Al$_2$O$_3$	300	2	8.5 (WHSV)	S_{H2}=99%	97	2.6	[2]
10La10Ni/Al$_2$O$_3$	400	3	1.3 (WHSV)	S_{H2}=78%	100	1	[3]
Cu-ZnO/MCM-41	300	3	1.62 (WHSV)	S_{H2}=93.3%	93.3	1.4	[4]
Cu-F/AZZ	450	3	9000 (GHSV)	S_{H2}=75%	/	0.3	[5]
5RuCe	400	2	3.47 (WHSV)	S_{H2}=28%	98	0.13	[6]
Cu/ZrO$_2$-SiO$_2$	260	1.3	3500 (GHSV)	370	73	0	[7]
1Cu1Zr/AZ	450	1.2	10.8 (WHSV)	S_{H2}=80%	75	3.2	[8]
8Cu/SMMS	400	1.5	3.7 (WHSV)	186.85	92.85	57.11	This work

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