Supporting information

Direct Oxidation of Methane to Methanol using $CuMoO_4$

Wenjian Wu[a], Wenzhi Li[a,b,*], Mingwei Wu[a], Hao Zhang[a], Chen Zhu[a], Yihang Jiang[a]

[a]Laboratory of Clean Low-Carbon Energy, University of Science and Technology of China, Hefei 230023, PR China;

[b]Institute of Energy, Hefei Comprehensive National Science Center, Hefei 230031, PR China.

* Corresponding author: Wenzhi Li

E-mail: liwenzhi@ustc.edu.cn;

Tel.: +86 0551 63600786;

Fax: +86 0551 63600786.

1. Characterization techniques

An Optima 7300 DV inductively coupled plasma-atomic emission spectrometer (ICP-AES, Perkin-Elmer, Co., USA) was used to determine the actual content of Cu element. Nitrogen physical adsorption and desorption experiments were carried out at ~77 K on a Micromeritics Tristar III 3020 instrument to obtain the BET data of the as-prepared catalysts. The transmission electron microscope (TEM), high-resolution transmission electron microscope (HRTEM) and scanning electron microscope (SEM) images of the catalysts were obtained under the Jeol JEM-2100F transmission electron microscope and field emission electron microscope (FEI XL-30 ESEM) at 200 kV. Elemental mapping images were collected by TEM. Power X-ray diffraction (XRD) patterns of the catalysts were obtained on a Rigaku TTR-III diffractor using Cu Kα radiation at 40 kV and 200 mA to verify the crystallinity. The spectra were collected in the 2θ range of 20°-80° and the speed was 10°/min. X-ray photoelectron spectroscopy (XPS) analysis was operated on a Thermo ESCALAB 250 spectrometer system with monochromatic Al Kα x-ray source (hv=1486.6 eV) at ultrahigh vacuum. Mo 3d and O 1s spectra of Cu/MoO_3 catalysts were recorded. The C 1s signal at 284.8 eV was adopted as internal standard for binding energy calibration. Transmission infrared spectroscopy (TS) was acquired by a Nicolet iS50 FT-IR spectrometer with a resolution of 4 cm^{-1} and an accumulation of 32 scans. IR beam directly passed through the pellets of catalyst (diluted within KBr) and the spectral detection interval is 400-4000 cm^{-1}. A chemstar TPX chemical adsorption instrument (Quantachrome, USA) was utilized for H_2-temperature program reduction (H2-TPR). First of all, 20 mg of catalyst was pretreated in flowing argon at 400℃ for 30 min. Second, the sample was exposed to 10 vol% H_2/Ar gas flow (30 mL/min). Finally, the sample temperature was heated from 30°C to 800°C at a heating rate of 10°C/min. A TCD detector was applied to detect H_2 consumption signals. UV-vis spectra were recorded by a SolidSpec-3700i/3700i DUV spectrometer at a scan rate of 200 ms per spectrum from 50 000 to 10 000 cm^{-1}. One thousand scans were averaged to produce a single spectrum. Raman measurements were implemented using a LabRamHR Evolution Raman microscope (JY, FRANCE) with a 532 nm laser power over a wavenumber range of 100-1500 cm^{-1}. Nuclear magnetic resonance hydrogen spectroscopy(^{1}H NMR) were tested by adding 700 μL collected liquid into the 200 μL D2O (deuterated water). And sodium,2,2,3,3-tetradeuterio-3-trimethylsilylpropanoate was used as internal standard. The ^{1}H spectrum peaks of CH_3OH, CH_3OOH and $OHCH_2OOH$ are at ~3.38, ~3.82 and ~5.04 ppm,

respectively.

Table. S1. Test results of ICP-AES and BET characterization techniques

Catalyst	actual value[a]	surface area[b] (m^2/g)	Pore volume[c] (cm^3/g)	Pore diameter[d] (nm)
Cu(0)/MoO_3	0	1.91	0.007	13.58
Cu(1)/MoO_3	0.98	2.11	0.010	38.62
Cu(2)/MoO_3	2.08	5.04	0.028	24.93
Cu(3)/MoO_3	3.05	7.07	0.038	22.21
Cu(5)/MoO_3	5.54	6.40	0.044	34.22
Cu(11)/MoO_3	11.79	12.40	0.099	29.86

[a]actual value, acquired by ICP-AES

[b]BET surface area, calculated by BET method

[c]Pore volume and [d]Pore diameter, calculated by Barrett–Joyner–Halenda (BJH) method

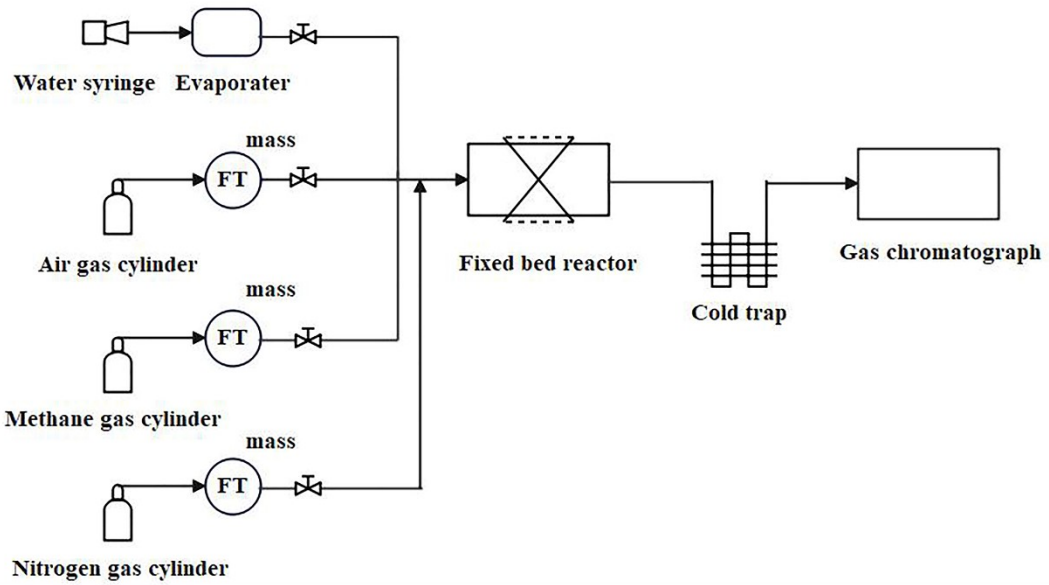

Fig. S1. Schematic diagram of the reaction device

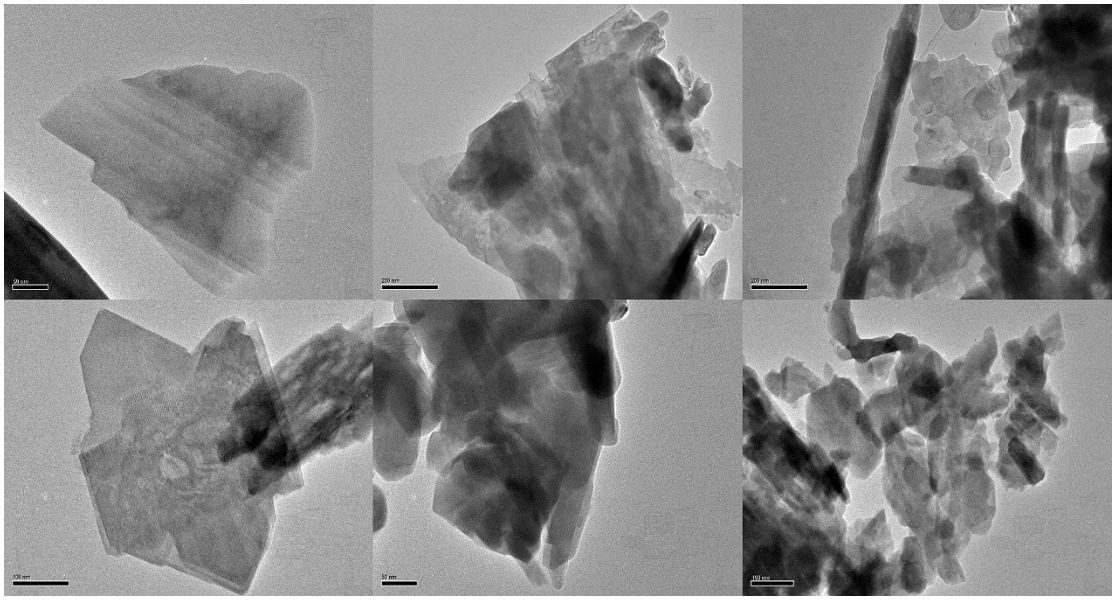

Fig. S2. TEM images of (a) Cu(0)/MoO_3, (b) Cu(1)/MoO_3, (c) Cu(2)/MoO_3, (d) Cu(3)/MoO_3, (e) Cu(5)/MoO_3, (f) Cu(11)/MoO_3.

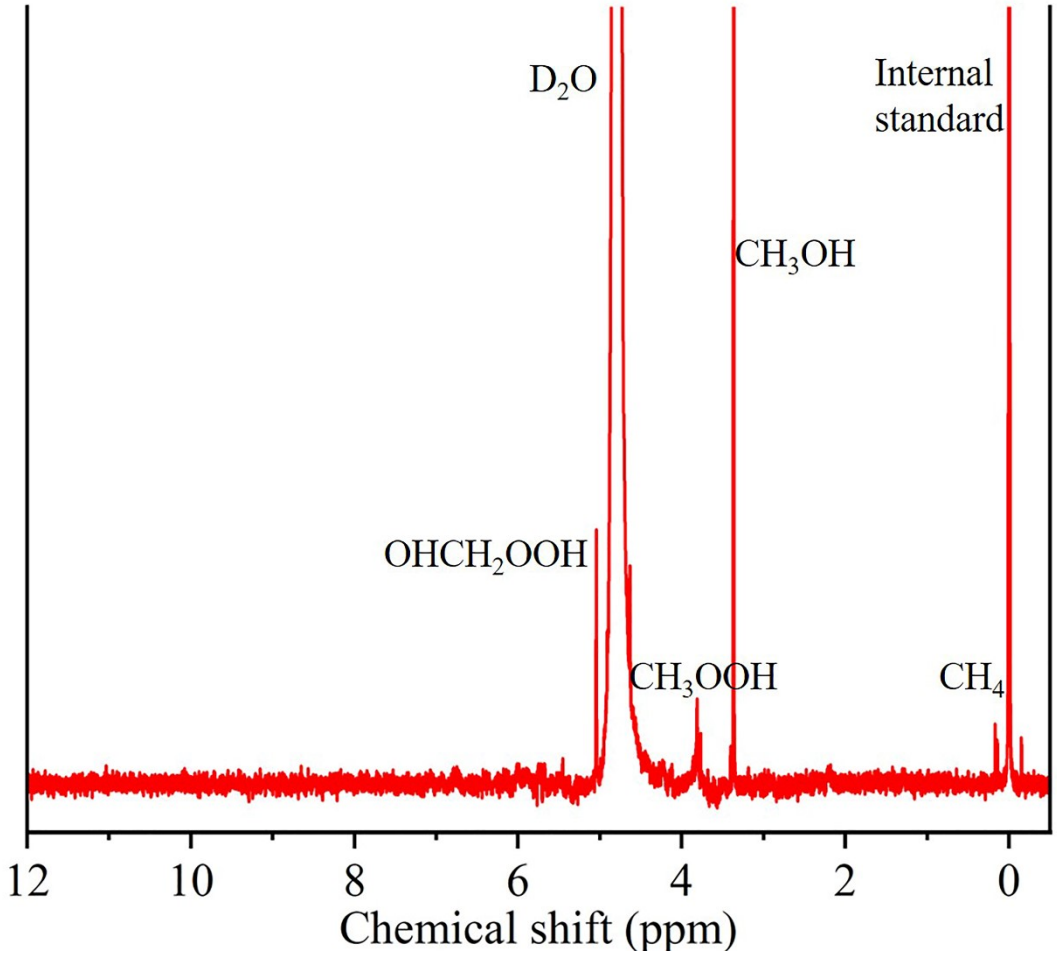

Fig. S3. ^{1}H NMR images of the liquid products obtained from the direct oxidation of methane over Cu(2)/MoO_3 at 600℃.

Table. S2. Conversion and selectivity of methane oxidation

Cu loading (wt. %)	Reaction temperature(℃)	STY_{CH3OH} (μmol/(g·h))	S_{CH3OH} (%)	S_{CH3OOH} (%)	$S_{OHCH2OOH}$ (%)
0	500	1.04	79.19	13.20	7.61
1	500	3.95	79.51	14.46	6.03
2	500	6.07	80.18	14.54	5.28
3	500	5.17	73.12	14.15	12.73
5	500	2.74	75.10	24.90	0
11	500	1.72	71.43	28.57	0
2	400	0.42	89.44	10.56	0
2	450	2.62	83.99	12.81	3.20
2	550	14.84	75.19	18.04	6.77
2	600	22.4	50	9.09	40.91

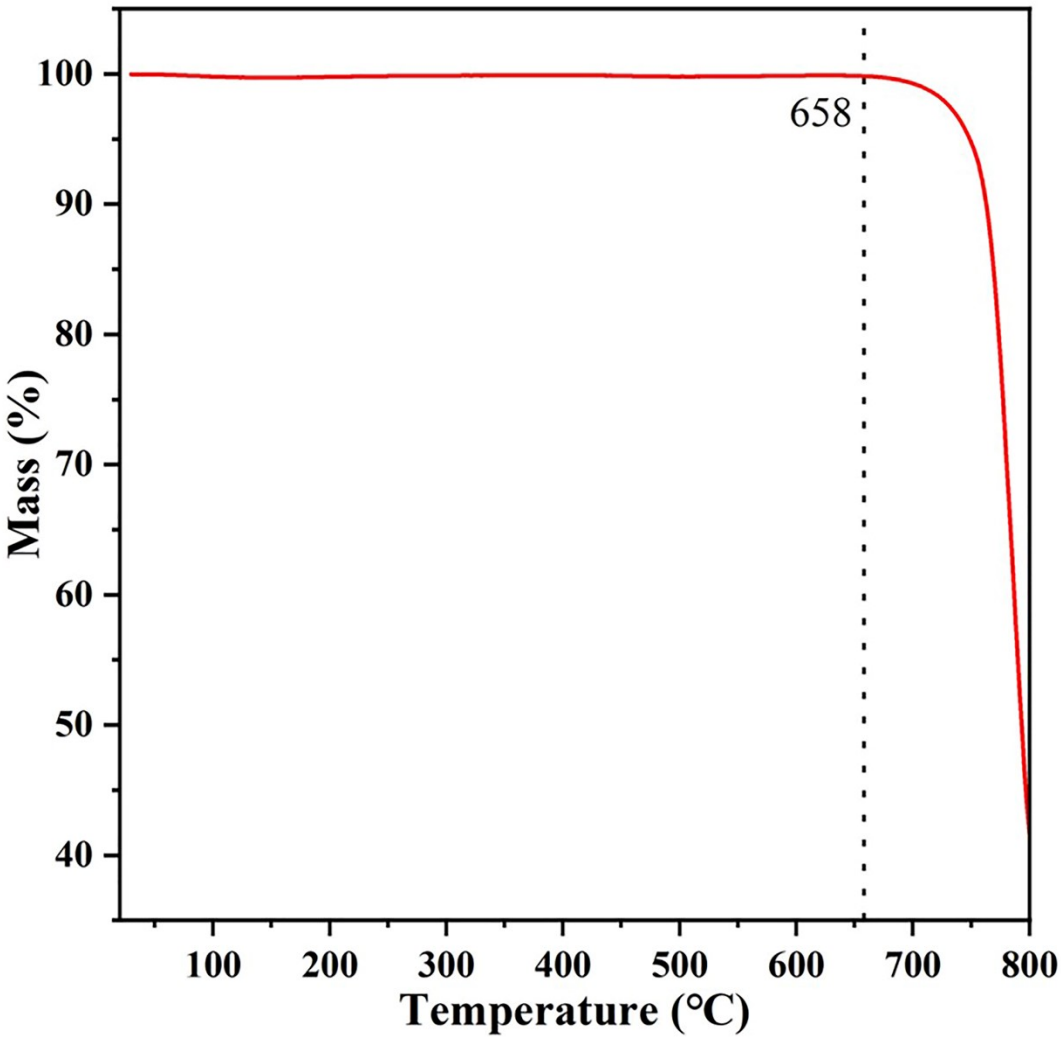

Fig. S4. Thermogravimetric analysis (TGA) of Cu(2)/MoO_3 catalyst.

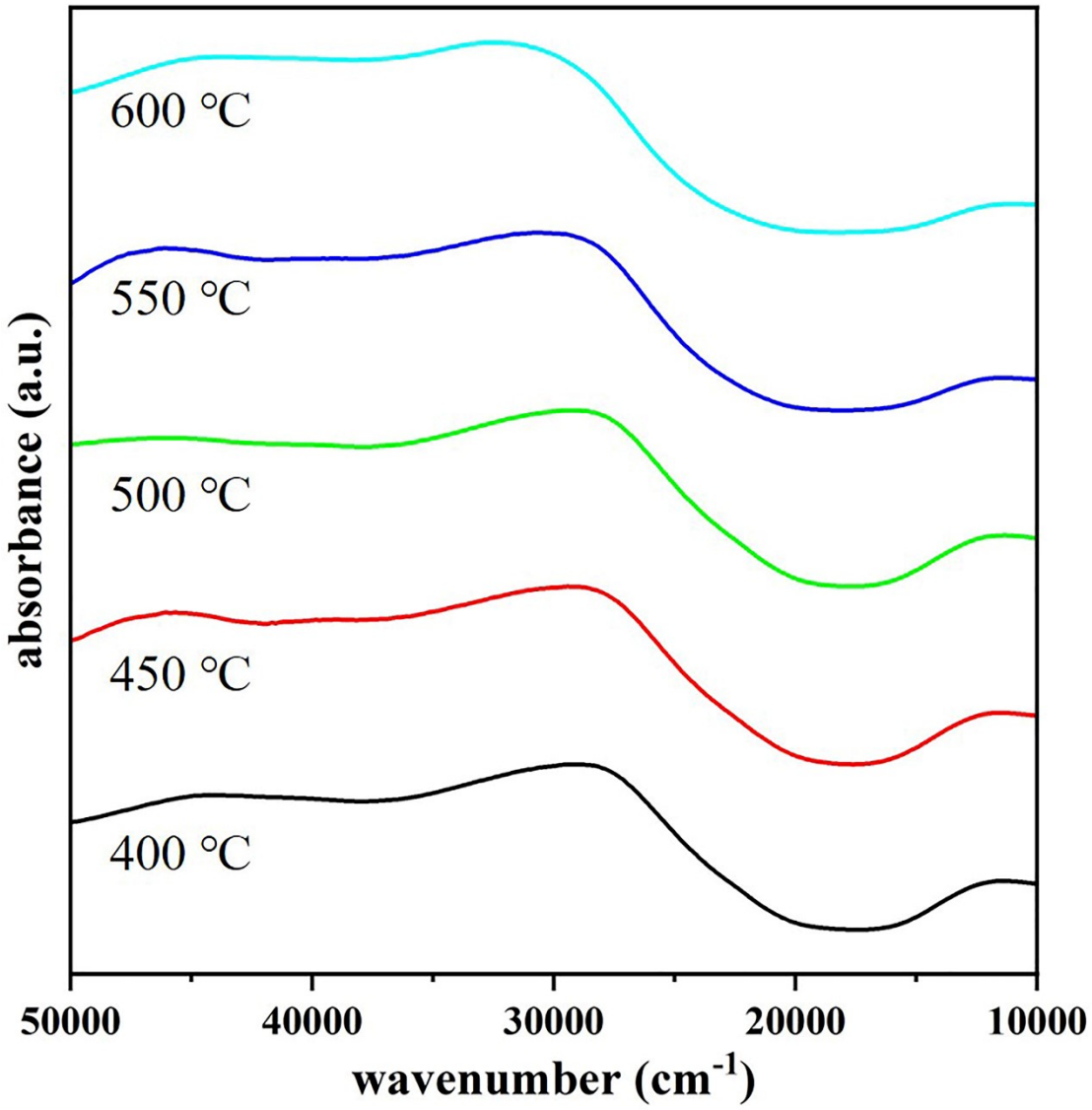

Fig. S5. UV-vis spectra of Cu(2)/MoO_3 catalyst at different temperature.

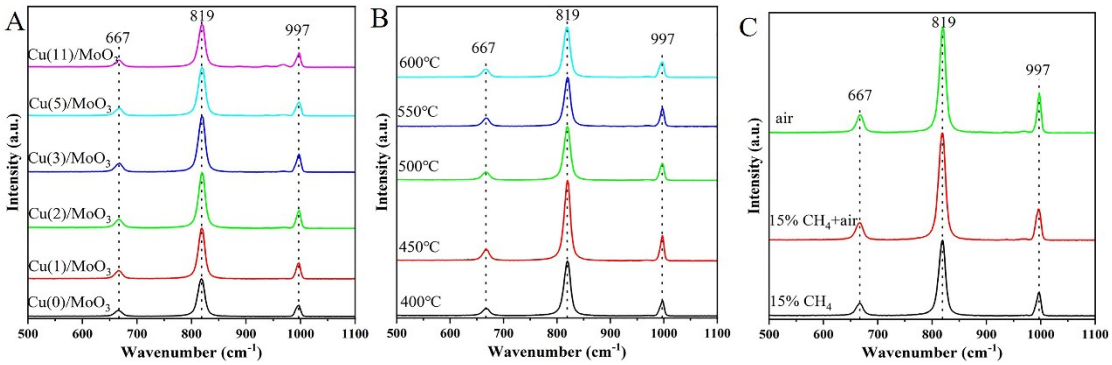

Fig. S6. A: Raman spectra of various Cu loading. B: Raman spectra of Cu(2)/MoO_3 at different temperature. C: Raman spectra of Cu(2)/MoO_3 at 600°C with different reaction gas.

Table. S3. XPS data of the four samples

Catalyst	O_{lat}	O_{ads}	O_{ads}/O_{lat}	Mo^{6+} $3d_{5/2}$	Mo^{6+} $3d_{3/2}$	Mo^{5+} $3d_{5/2}$	Mo^{5+} $3d_{3/2}$	Mo^{5+}/Mo^{6+}
(a) and (b)	530.9	531.8	0.21	233.09	236.19	231.99	234.99	0.052
(c) and (d)	530.8	531.7	0.17	233.00	236.10	231.90	234.90	0.037
(e) and (f)	530.9	531.8	0.29	233.13	236.23	232.03	235.03	0.073
(g) and (h)	531.0	531.9	0.19	233.14	236.26	232.04	235.04	0.046

(a) and (b): Cu(0)/MoO_3, (c) and (d): Cu(2)/MoO_3, (e) and (f): Cu(2)/MoO_3 before reaction at 600°C, (g) and (h): Cu(2)/MoO_3 after reaction at 600°C.