

Electronic Supplementary Information

Experimental section

Catalyst preparation

Preparation of Mo₂C-C: 2.0 g of sodium alginate (Adamas) and 2.0 g of Na₂MoO₄·2H₂O (Adamas) were dissolved into 180 mL of H₂O under continuous stirring 2 h. After the aqueous solution turned into transparent, it was freeze-dried and lyophilized to remove H₂O and form a 3D molybdate-organic precursor structure. The sample was heated to 900 °C at 5 °C min⁻¹ and held at this temperature for 3 h in Ar. Afterwards, the obtained black solid was ground into powder and washed with distilled water for several times to remove Na⁺ and residue of reactants, and finally dried in vacuum at 80 °C.

N-functional Mo₂C-C: 1 g of Mo₂C-C and urea (Adamas) with different weight ratio (Mo₂C/C:urea=1, 1.5, 2, and 3, respectively) were physically grinded, followed by adding a little ethanol as the wetting agent. The mixture was collected in a ceramic crucible and heated at 350 °C for 2 h under air atmosphere. The obtained product was washed with distilled water for removing unreacted urea. The as-synthesized N-functional Mo₂C-C catalysts, denoted as Mo₂C-N-C-1, Mo₂C-N-C-1.5, Mo₂C-N-C-2, and Mo₂C-N-C-3, were then collected and dried at 60 °C.

Preparation of Cu-Mo₂C-N-C-x: The Mo₂C-N-C-x with highly dispersed Cu were prepared by the solid grinding method using Mo₂C-N-C-x and Cu(NO₃)₂·3H₂O (Adamas) to obtain 5 wt% of Cu loading. The mixture was reduced at 400 °C for 2 h under 5% H₂/Ar atmosphere to obtain Cu-Mo₂C-N-C-1, Cu-Mo₂C-N-C-1.5, Cu-Mo₂C-N-C-2, and Cu-Mo₂C-N-C-3. The corresponding N content is 3.51, 4.27, 5.05, and 6.98 wt %, respectively. For comparison, 5 wt% Cu is also supported on pure C, N-functional C (N-C), and Mo₂C-C with the same procedure, respectively.

Catalyst characterization

The morphology and the microstructure of the catalysts were analyzed by field-emission scanning electron microscope (FE-SEM, JSM-7800, Japan), transmission electron microscope (TEM, Hitachi, Tokyo, Japan), X-ray diffraction (XRD-6000, Shimadzu), and X-ray photoelectron spectroscopy (XPS, PHI 550 ESCA/SAM), respectively. The Raman spectra were recorded on the Raman Scattering Spectroscopy (Renishaw 2000 system) with excitation by diode laser (514 nm, laser power of 25 mW) in backscattering geometry. The surface area of catalysts is measured from N₂ adsorption isotherms using Brunauer-Emmett-Teller (BET, Shimadzu, Micromeritics ASAP 2010 Instrument). Hydrogen temperature-programmed reduction (H₂-TPR) of the catalysts was carried out using a conventional apparatus equipped with a thermal conductivity detector.

Catalytic performance evaluation

The CO₂ hydrogenation reaction was carried out in a fixed-bed reactor at atmospheric pressure and the temperature range of 240 ~ 400 °C to investigate the catalytic performance of the catalysts. The reactor is a 6 mm i.d. quartz U-tube. Typically, 50 mg catalyst was pre-reduced at 400 °C for only 0.5 h at H₂ flow because these catalysts were reduced at 400 °C for 2 h under 5% H₂/Ar atmosphere during the preparation. When the catalyst cooled down to 200 °C under the H₂ flow, the feed gas (10 vol.% CO₂, 40 vol.% H₂ and 50 vol.% Ar) was introduced into the tube with the weight hourly space velocity (WHSV) of 60,000 mL⁻¹ g⁻¹ h⁻¹. The compositions of the feed gas and products were analyzed using a packed TDX-01 column with an on-line gas chromatograph (SC 200G) equipped with a thermal conductivity detector.

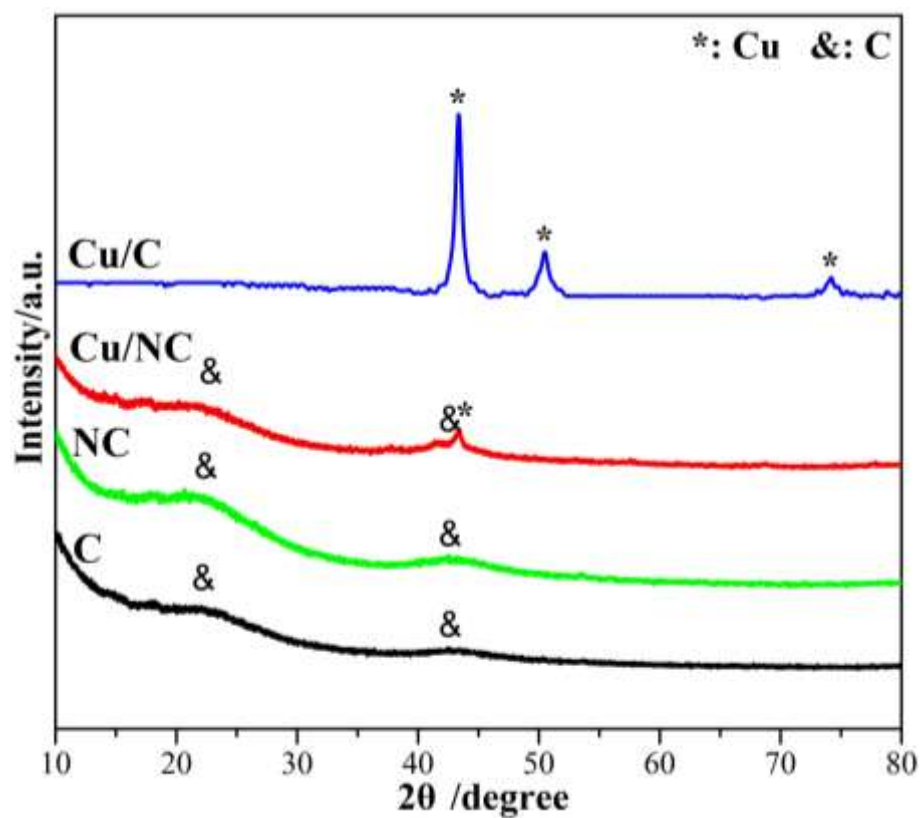


Fig. S1 XRD patterns of (a) C, (b) N-C, (c) Cu-N-C, and (d) Cu-C catalysts.

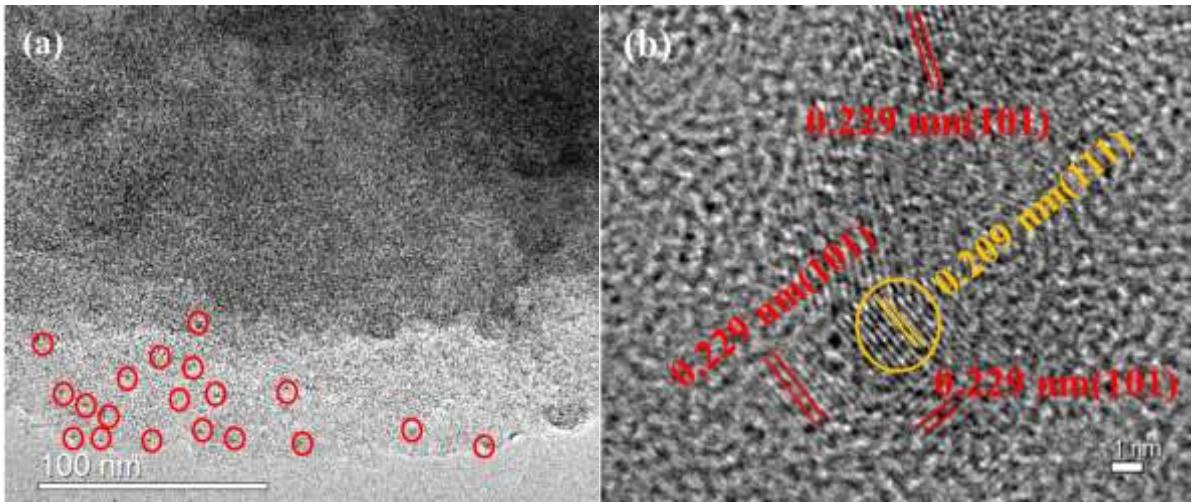


Fig. S2 TEM and HRTEM images of Cu-Mo₂C-N-C.

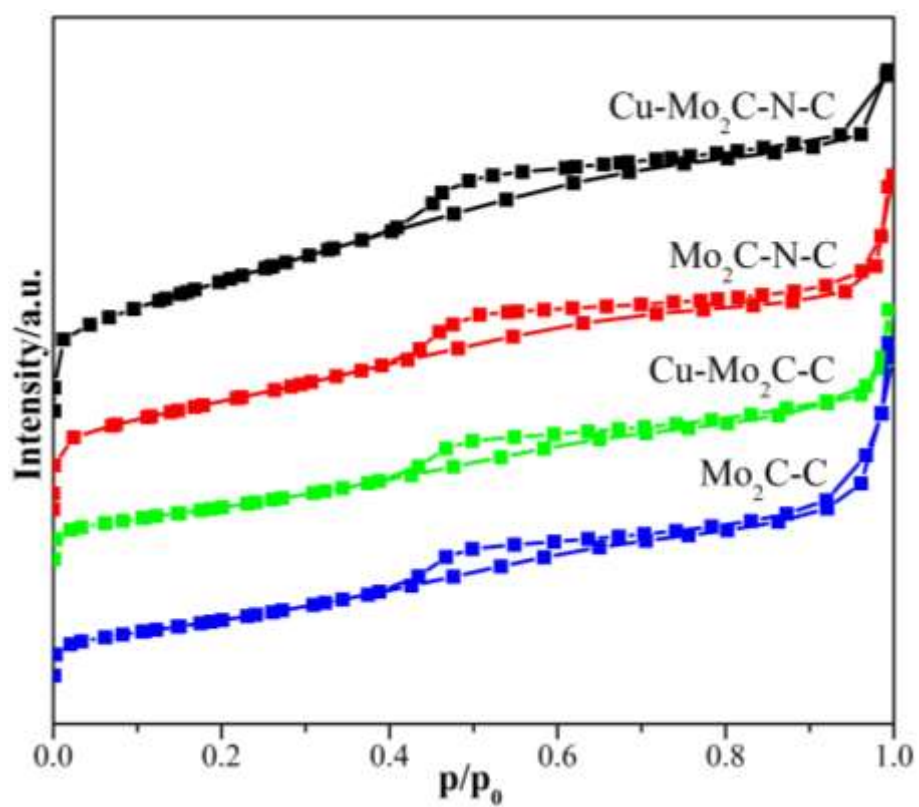


Fig. S3 N₂ adsorption-desorption isotherms of the catalysts.

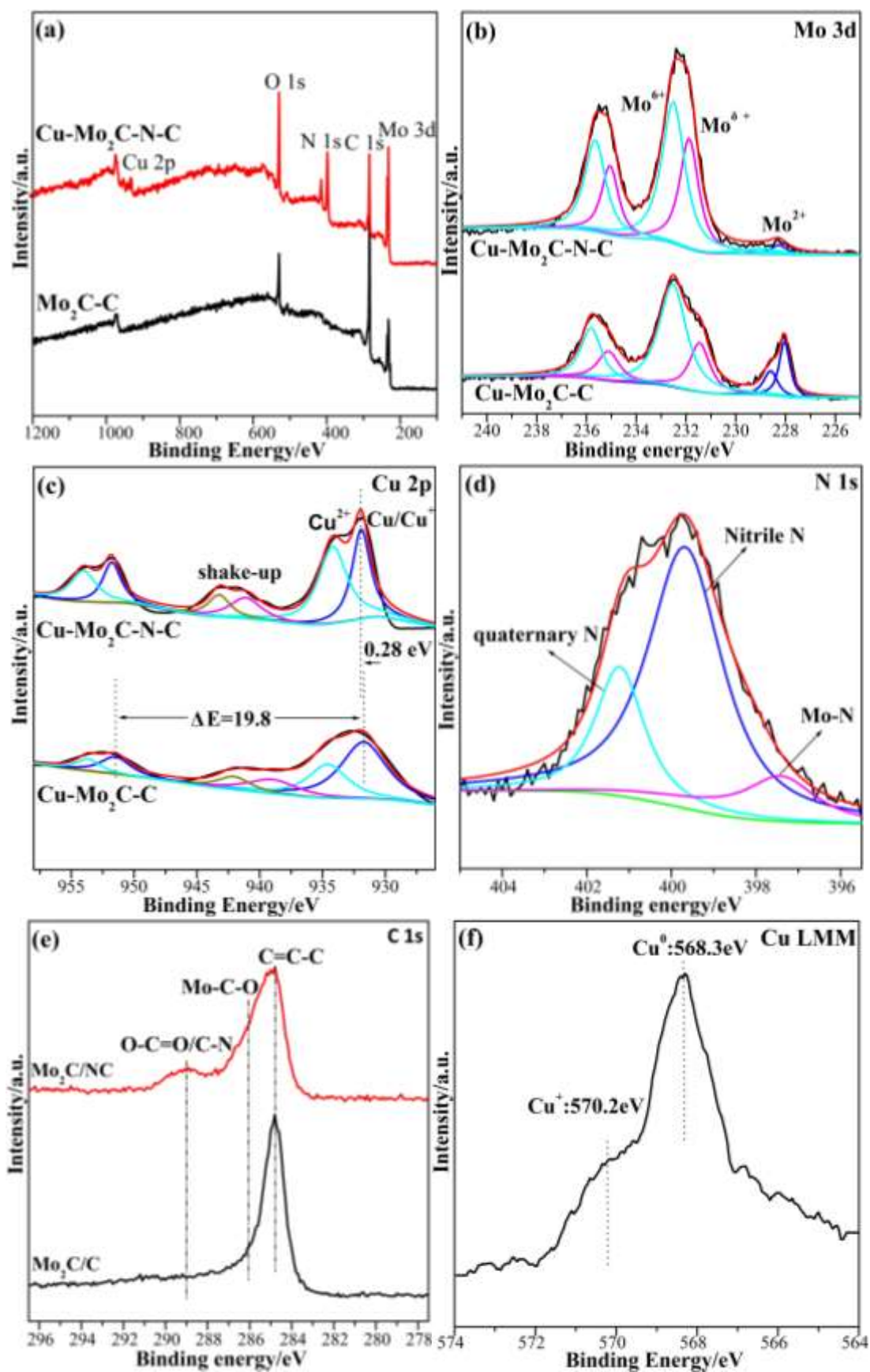


Fig. S4 XPS spectra of (a) survey, (b) Mo 3d, (c) Cu 2p; (d) N 1s; (e) C 1s and (f) Cu LMM

AES spectra.

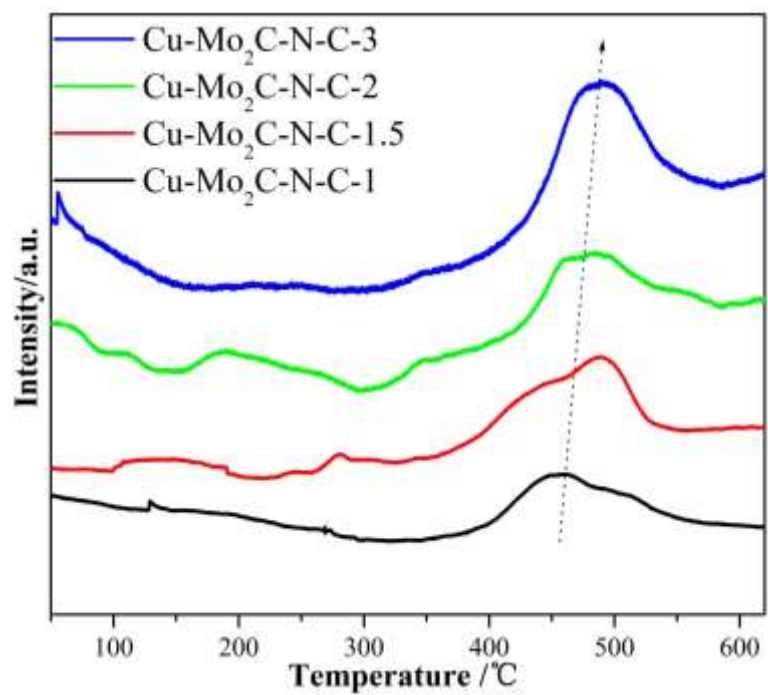


Fig. S5 CO₂-TPD profiles of the Cu-Mo₂C-N-C catalysts with different N content.

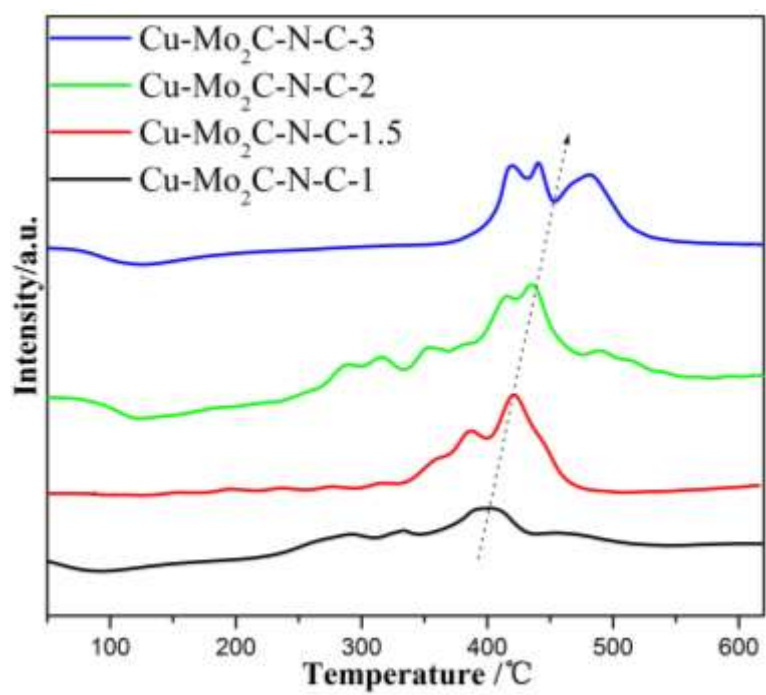


Fig. S6 H₂-TPR profiles of the Cu-Mo₂C-N-C catalysts with different N content.

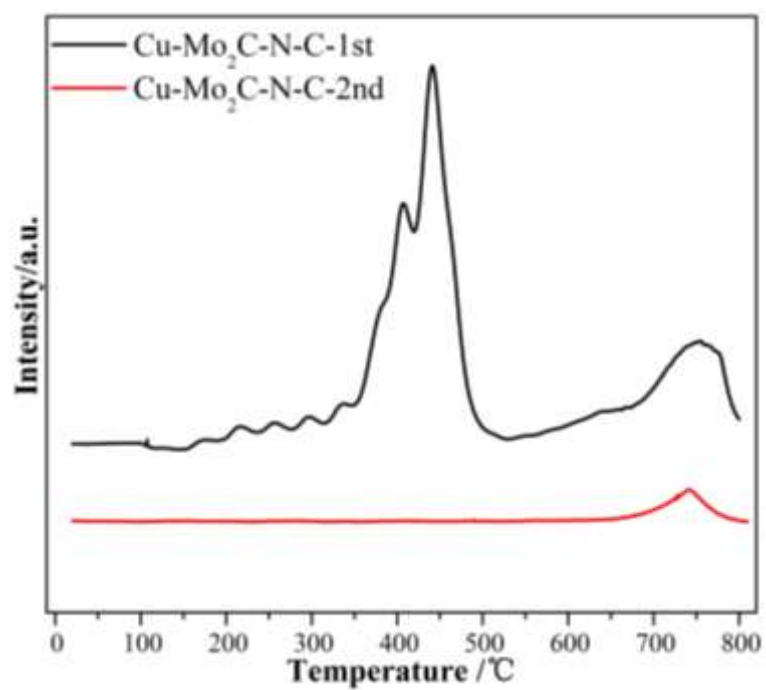


Fig. S7 H₂-TPR profiles of the representative Cu-Mo₂C-N-C-1.5 catalyst for continuously testing 2 times H₂-TPR experiment.

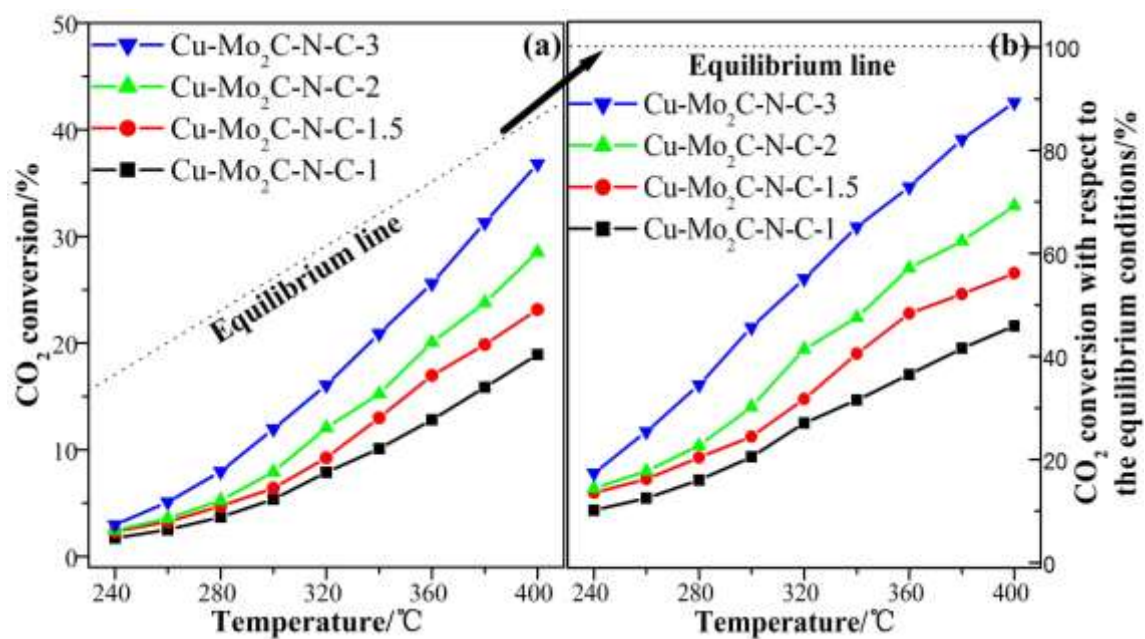


Fig. S8 (a) CO₂ conversion as a function of reaction temperature and (b) the corresponding CO₂ conversion with respect to the equilibrium conditions over the Cu-Mo₂C-N-C catalysts with different N content.

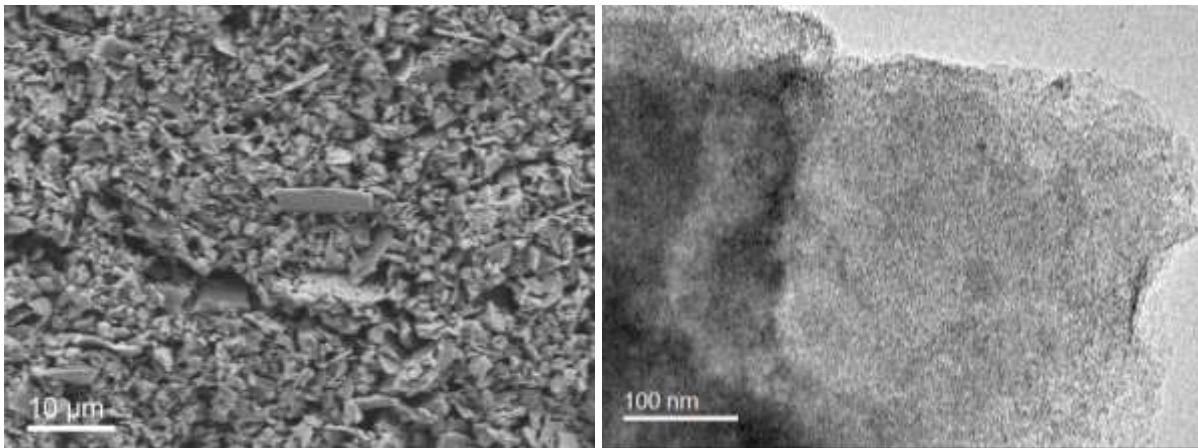


Fig. S9 FESEM and TEM images of used Cu-Mo₂C-N-C.

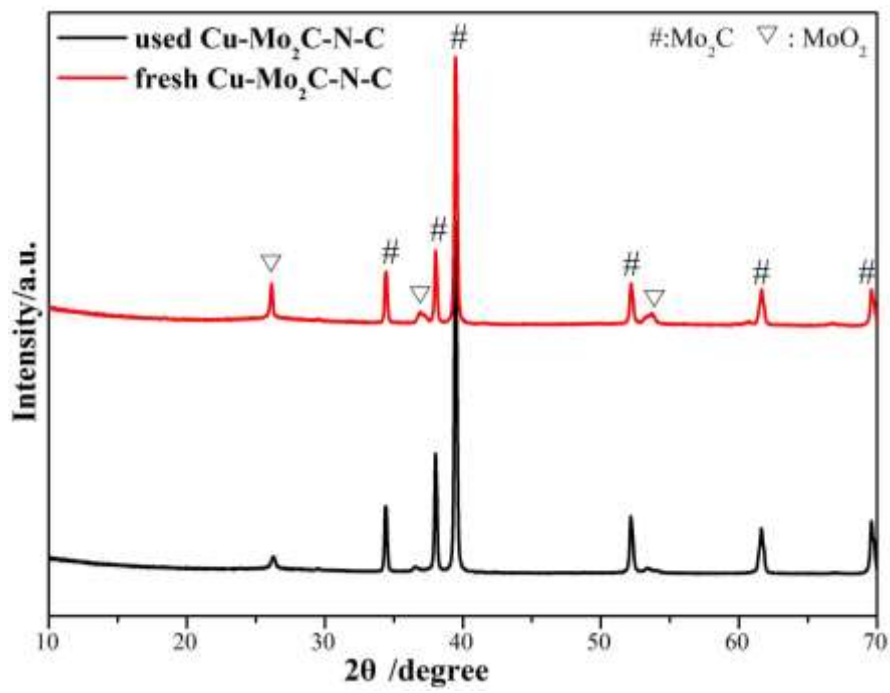


Fig. S10 XRD patterns of fresh and used Cu-Mo₂C-N-C catalyst.

Table S1. The surface area and porous characteristics of the catalysts.

Catalysts	Surface area ($\text{m}^2 \text{g}^{-1}$)	Pore diameter (nm)	Total pore volume ($\text{cm}^3 \text{g}^{-1}$)
Mo ₂ C-C	95.7	4.0	0.212
Cu-Mo ₂ C-C	78.9	4.0	0.155
Mo ₂ C-N-C	186.3	5.1	0.289
Cu-Mo ₂ C-N-C-1	180.6	5.1	0.263
Cu-Mo ₂ C-N-C-1.5	175.8	5.1	0.257
Cu-Mo ₂ C-N-C-2	183.4	5.1	0.274
Cu-Mo ₂ C-N-C-3	179.1	5.1	0.259

Table S2. Comparison of catalytic performance of Cu-Mo₂C-N-C-x from current work with similar catalysts from literature studies.

Catalysts	T (°C)	P (MPa)	CO ₂ :H ₂ ratio	WHSV (mL ⁻¹ g ⁻¹ h ⁻¹)	Conversion (%)	CO sel. (%)	Ref.
Cu-Mo ₂ C-N-C-1					18.92	100	
Cu-Mo ₂ C-N-C-1.5	400	0.1	1:4	60,000	23.15	100	This work
Cu-Mo ₂ C-N-C-2					27.53	95.6	
Cu-Mo ₂ C-N-C-3					37.41	89.3	
Mo ₂ C/γ-Al ₂ O ₃	300	2.1	1:3	3,024	19.9	73.5	<i>ChemSusChem</i> 2017 , 10, 2408
K-Mo ₂ C/γ-Al ₂ O ₃					18.1	95.9	
β-Mo ₂ C	400	0.1	1:2	300,000	~2	100	<i>ACS Catal.</i> 2017 , 7, 912
Cu/β-Mo ₂ C					~16	97.6	
α-MoC _{1-x} nanowires	400	0.1	1:4	36,000	~20	>99	<i>Catal. Commun.</i> 2016 , 84, 147
β-Mo ₂ C nanowires					~30	>98	
Polycrystalline α-Mo ₂ C	400	0.1	1:1	3000	16	>99	<i>ACS Catal.</i> 2017 , 7, 4323
Cu-Mo ₂ C					19	38	
Ni-Mo ₂ C	300	2	1:5	9,000	29	22	<i>Catal. Lett.</i> 2015 , 145, 1365
Co-Mo ₂ C					31	19	
Mo ₂ C					8.7	93.5	<i>Angew. Chem. Int.</i> <i>Ed.</i> 2014 , 53, 6705
Co-Mo ₂ C	300	0.1	1:2	36,000	9.5	98.1	
PtCo/TiO ₂					8.2	98.8	<i>Angew. Chem. Int.</i> <i>Ed.</i> 2016 , 55, 7968
PtCo/CeO ₂	300	0.1	1:2	36,000	9.1	92.3	
PtCo/ZrO ₂					7.8	89.5	